CHEMICAL SIGNATURES OF MAGMAS AT TIMES OF FRONTAL ARC MIGRATION: EXAMPLES FROM THE CENTRAL ANDES AND SOUTHERN CENTRAL AMERICA

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CHEMICAL SIGNATURES OF MAGMAS AT TIMES OF FRONTAL ARC MIGRATION: EXAMPLES FROM THE CENTRAL ANDES AND SOUTHERN

CENTRAL AMERICA

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Within the Central Andes (27°-28.5° S) and in southeastern Central America (7°-11° N), discrete episodes of late Miocene-Pliocene frontal arc migration were accompanied by backarc slab shallowing and increased rates of forearc subduction erosion. Arc lavas erupting during and following these short-lived periods exhibit adakitic geochemical signatures indicative of high-pressure melting of mafic crust (i.e., steep REE patterns and elevated Sr concentrations). Geochemical and petrologic data from these lavas are used to address fundamental questions regarding the genesis of adakitic magmas spatially and temporally associated with arc migration.

Along both margins, enrichment in radiogenic isotopic ratios in late Miocene-Pliocene adakitic lavas compared to early-mid Miocene and Quaternary arc lavas cannot be attributed to melting of subducted oceanic crust or pelagic sediments. Instead, these trends are better explained by partial melting of mafic forearc crust transported to mantle depths during times of accelerated forearc subduction erosion. Mass balance calculations and isotopic modeling results agree with compositional estimates of the Central American and Chilean forearc and indicate that mantle contamination by eroded forearc crust is an inevitable and observable process. In arcs with thick crust such as the central Andes (> 60 km), partial melting of garnet-bearing lower crust contributes to the adakitic signature of lavas erupting during frontal arc migration. Strong HFSE-depletion characteristic of the Central Andean adakites is attributed to HFSE-bearing residual phases in equilibrium with the melt. Geochemical trends and near-chondritic Nb/Ta ratios support a change from a rutile-bearing eclogite to a garnet-bearing amphibolite residue consistent with cooler more-hydrous conditions that evolved over the shallowing slab during the late Miocene.

As magmatism diminished along the arc, rising adakitic magmas unreplenished by mantle-derived or lower crustal melts stalled within the Andean upper crust. Here, crustal assimilation and fractional crystallization subdued the primary adakitic signature and enriched the isotopic composition of the perched magma. After a 3-1 Ma period of effusive dome eruptions, rapid magma mixing caused the stalled system to explode at ~ 0.51 Ma. The resultant Incapillo Caldera and Ignimbrite mark the youngest volcanic event within the currently amagmatic flatslab segment of the Central Andes.

BIOGRAPHICAL SKETCH

Adam Robert Goss was born on January 2, 1979 in Milford, Massachusetts, the first son of Robert Myles Goss Jr. and Deborah Joan Goss. Since he was a child, Adam has been in awe of the ageless functions of the Earth, its slow tectonic processes that formed the metamorphic and igneous rocks in his backyard. Weekend trips to the Milford granite quarries and Purgatory Chasm lit a spark in his mind as to the origin of these and other crustal features of Central New England. How did this happen? The first time he tried to answer this question was a third grade elementary science fair. The title of his presentation: Pangaea and Plate Tectonics.

After graduating from Hopedale Jr./Sr. High School in Hopedale, Massachusetts, Adam attended Wesleyan University in Middletown, Connecticut graduating in 2001 with University and High Honors and as a member of Phi Beta Kappa with a B.A. in Earth and Environmental Science. A Watson Fellowship to study the socio-cultural relationship between volcanic hazards and society allowed for a one year independent journey to Europe, Asia, Central and South America, and the Caribbean after college. Upon returning home in the summer of 2002, Adam returned to academic life and matriculated at Cornell University to begin graduate school in geochemistry/volcanology under the direction of Dr. Suzanne Kay.

During graduate school, Adam experienced the daily toils of academic research and the joys that accompany scientific discovery. The frustration with mass spectrometers and the excitement of examining fresh new data define the simultaneous highs and lows of graduate work in geochemistry. In his second year, Adam was awarded a NASA Earth System Science Graduate Research Fellowship to fund his doctoral research that took him to a remote corner of the Central Andes to study the chemical evolution of the highest caldera on Earth. Another high moment was that earlier that year, Adam met the woman he would eventual marry, Janice CruzCardona, a young and enthusiastic veterinary student from the island of Puerto Rico.

With the presentation of this thesis, Adam begins a new chapter in his life as he begins post-doctoral work at the University of Florida on the geochemical interactions between hydrothermal fluids and active mid-ocean ridges. On July 21, 2007 Adam and Janice were married amongst the karst in the bride's hometown of Isabela, Puerto Rico. To Mom , Dad, and Janice

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LIST OF ABBREVIATIONS

Ma	<i>megaannum</i> , or a unit of measurement of geological time equal to one million years (10^6) before present
Ga	<i>gigaannum</i> , or a unit of measurement of geological time equal to one billion years (10^9) before present
m.y.	one million years, a period of geological time
opx	orthopyroxene (Mg,Fe) ₂ Si ₂ O ₆
срх	clinopyroxene (Ca,Mg,Fe) ₂ Si ₂ O ₆
mt	magnetite (Fe ₃ O ₄)
ilm	ilmenite (FeTiO ₃)
Fo ₀₋₁₀₀	molar component of forsterite (Mg ₂ SiO ₄) in olivine
Fa ₀₋₁₀₀	molar component of fayalite (Fe ₂ SiO ₄) in olivine
En ₀₋₁₀₀	molar component of enstatite (MgSiO ₃) in orthopyroxene
Fs ₀₋₁₀₀	molar component of ferrosilite (FeSiO ₃) in orthopyroxene
Wo ₀₋₁₀₀	molar component of wollastonite (CaSiO ₃) in clinopyroxene
An ₀₋₁₀₀	molar component of anorthite ($CaAl_2Si_2O_8$) in plagioclase feldspar
HFSE	high field strength elements (Nb, Ta, Hf, Zr)
REE	rare earth elements (La to Lu)
LREE	light rare earth elements (La to Sm)
MREE	middle rare earth elements (Sm to Dy)
HREE	heavy rare earth elements (Ho to Lu)
LILE	large ionic lithophile elements (e.g., Rb, Cs, Sr, Ba)
INAA	Instrumental Neutron Activation Analysis
Mg #	molar ratio $[Mg/(Mg + Fe^{2+}_{total Fe})]$

Eu/Eu*	deviation of measured Eu concentration from predicted Eu concentration assuming similar compatibility to the other REE
Kd	Elemental partition (distribution) coefficient (for element <i>i</i> ; Kd = C_{A}^{i}/C_{B}^{i} between phases A and B)
MORB	mid-ocean ridge basalt
OIB	ocean island basalt
HIMU	Mantle isotopic domain (high- μ where μ = ²³⁸ U/ ²⁰⁴ Pb) characterized by radiogenic ²⁰⁶ Pb/ ²⁰⁴ Pb
CLIP	Caribbean Large Igneous Province
DSDP	Deep Sea Drilling Project
CVZ	Andean Central Volcanic Zone spanning from Volcán Coropuna in Peru (14° S) to Ojos del Salado (27° S) in northern Chile
SVZ	Andean Southern Volcanic Zone spanning from Volcán Tupungatito in central Argentina/Chile (33° S) to Cerro Hudson (46° S) in southern Chile
CHARGE	CHile ARgentina Geophysical Experiment
pmP	Teleseismically-recorded earthquake depth phase precursors
NUVEL-1	Geophysical Plate Kinematic Model (DeMets et al., 1990)
CHUR	Composition of chondritic meteorites

LIST OF SYMBOLS

εNd	$\left[\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}_{\text{initial}}} \right)^{143}\text{Nd}^{144}\text{Nd}_{\text{CHUR, t}} \right) - 1 \right] \times 10^{4}$
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- $\delta^{18}O$ (‰) [($^{18}O/^{16}O_{sample}/^{18}O/^{16}O_{standard}$) -1] x 1000
- δ^{7} Li (‰) [(⁷Li/⁶Li_{sample}/⁷Li/⁶Li_{standard}) -1] x 1000
- f_{O2} Oxygen fugacity
- σ Standard deviation
- μ $^{238}U/^{204}Pb$

INTRODUCTION

CHEMICAL GEODYNAMICS IN UNSTABLE ARC SETTINGS

I. INTRODUCTION

Chemical geodynamics involves understanding margin-wide tectonic processes using temporal and spatial variations in geochemical signatures (e.g., Allégre, 1982; Zindler and Hart, 1986). Specific to convergent margins, the only way to trace crustal material once exposed at the Earth's surface completely through the plate tectonic cycle is to identify and quantify its chemical components in magmas and/or hydrothermal systems. A multidisciplinary systems approach is key to interpreting these signatures, as chemical variability in arc magmas is the result of complex interactions between tectonic and surficial processes. Geochemistry and petrology record information about tectonomagmatic processes, source compositions, and physical conditions at sub-arc depths. Field observations combined with remote sensing techniques provide important spatial and time-dependant constraints on petrologic and geochemical data. Geophysical imaging yields critical information regarding arc structure including convergence rates, the shape of the Wadati-Benioff zone, and magma chamber depths and gives basic information on the composition of potential sources to arc magmas including upper and lower crust, forearc units, and subducted sediments. Chemical geodynamics provides the compositional link between tectonic, magmatic, and surficial processes in order to generate whole system models of arc petrogenesis.

The main objective of this work is to use the chemical and petrologic variability measured in arc lavas from two non-accreting convergent margins to examine large-scale processes affecting the crust and mantle over changing tectonic conditions. The spatial and temporal focus of the four included studies is confined to ephemeral

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periods of tectonic disturbance in unstable arc systems. This research is directed towards the eastern Pacific margin, specifically southern Central America and the central Andes of Argentina and Chile between 27°-28.5° S latitude. At unsystematic times and locations along these margins, short-lived periods (~ 5 Ma) of shallow subduction, ridge collision, and increased forearc subduction erosion have disrupted the once stable arc system causing not only a landward migration of the volcanic front, but also an observable change in the chemical and petrologic character of mafic, intermediate, and evolved lavas.

Chemical data presented in this work include over 100 new major element, ~ 90 trace element, and ~ 50 isotopic analyses on mafic and felsic lavas from the central Andes. Additionally, over 200 *in situ* major element microprobe analyses on mineral phenocrysts from intermediate lavas are reported and are used to calculate magma equilibration temperatures. New geochronological data, both K-Ar and 40 Ar/³⁹Ar, are presented and interpreted with existing age data to understand the temporal evolution of the magmatic systems. Finally, petrogenetic models for Andean and Central American arc magmas, constrained by new and previously published data, explain the observed spatial and temporal geochemical trends.

II. CONVERGENT MARGIN GEOCHEMISTRY

Convergent margins occur at subduction zones where one lithospheric plate sinks below another (Isacks et al., 1968) and fluid mass is transferred from the downgoing oceanic plate to the overlying mantle wedge (Figure 0.1). Partial melting of the mantle, caused by the depression of the mantle solidus brought on by the flux of these hydrous slab-derived fluids (e.g., Ringwood, 1972; Nicholls and Ringwood, 1973; Tatsumi et al., 1986; Peacock, 1990; Poli and Schmidt, 1995), results in the formation of an arcuate chain of steep-sided stratovolcanoes known as a volcanic arc.



Figure 0.1 Schematic cartoon of a continental subduction zone showing the subduction channel composed of subducted sediments and eroded forearc crust, the zone of slab dehydration in response to metamorphic reactions, and the region of flux melting within the asthenospheric mantle wedge (modified after Wyllie, 1984). LILE are fluid mobile and carried with the slab-derived fluids. Non-mobile elements such as the HFSE, REE, and U and Th are retained within the slab giving arc lavas their characteristic geochemical signature.

Incompatible trace element compositions of arc-derived lavas provide strong evidence for fluid transport from the subducting slab to the mantle wedge (e.g., Kay, 1980; Pearce et al., 1995; Elliott et al., 1997; Pearce, 2003). Figure 0.1 shows that the sub-arc mantle is enriched in large ionic lithophile elements (LILE) including Ba, Rb, K, and Pb carried by slab-derived fluids released during dehydration metamorphic reactions within the subducted slab (Figure 0.1; Tatsumi et al., 1986; Hawkesworth et al., 1991). These elements may also be transferred to the overlying mantle wedge through leaching of and/or flux melting of pelagic and terrigeneous sediments subducted to sub-arc depths (e.g., White and Dupré, 1986; Ben Othman et al., 1989; White, 1989; Plank and Langmuir, 1993; Plank and Langmuir, 1998). Other elements, particularly the high field strength elements (HFSE: Nb, Ta, Hf, and Zr), Th, and the rare earth elements (REE), are far less soluble in fluid phases and are therefore less easily transported from slab to mantle (Figure 0.1; Brenan et al., 1995b; Pearce et al., 2002). The HFSE are also compatible in oxide phases, such as rutile and sphene, that are stable in the hydrous eclogitic crust of the subducting slab (Ryerson and Watson, 1987; Stalder et al., 1998; Foley et al., 2000; Walker et al., 2001; Schmidt et al., 2004; Audetat and Keppler, 2005). Arc magmas are uniformly depleted in these elements with respect to the mobile LILE and it is this principle difference in compatibility that gives arc magmas their distinctive geochemical signature.

In continental convergent margins, where oceanic crust subducts below continental crust, such as in the Andes or Cascadia (Figure 0.1), the arc geochemical signature is complicated by the assimilation of lower and upper crustal components into primary arc magmas (e.g., Kay et al., 1987; Hildreth and Moorbath, 1988). Deciphering purely mantle-source versus *in situ* crustal contamination in continental arc magmas relies heavily on radiogenic and stable isotopic trends in the most-mafic of all erupted lavas (Magaritz et al., 1978; James, 1981; Stern, 1991; Harmon and Hoefs,

1995; Davidson, 1996; Kay et al., 2005). Moreover, in arc settings with exceptionally thick crust (> 45 km), anatexis of mafic amphibolitic or eclogitic lower crust by underplating of mantle-derived melts generates andesitic to dacitic melts in equilibrium with a plagioclase-poor garnet-bearing residue (Kay et al., 1991; Rapp et al., 1991; Atherton and Petford, 1993). These melts exhibit an "adakitic" geochemical signature characterized by strong HREE depletion (Yb \leq 1.9 ppm; Y \leq 18 ppm; La/Yb > 20) and high Sr concentrations (> 400 ppm; Sr/Y >20-40) that are similar to magmas derived from melting of young (< 5 Ma) eclogitized oceanic crust (Defant and Drummond, 1990; Kay et al., 1993).

III ACCRETING VS. NON-ACCRETING MARGINS

Fluxes of crustal material transported to mantle source regions of subduction zones depend largely on the structural geometry of the margin. Various authors have classified convergent margins into two types, accretionary (non-erosive) and non-accretionary (erosive), based on the geology of forearc units and the net rates of crustal growth or erosion along the forearc (Figure 0.2; von Huene and Scholl, 1991; 1993; Clift and Vannucchi, 2004). The main process that adds crustal mass to a forearc margin is subduction accretion, or the tectonic scraping of lower plate sediments (pelagic and terrigeneous) and slivers of oceanic crust into an accretionary prism (Figure 0.1). Subduction erosion, which is defined as the tectonic removal of upper plate crust and mantle, and sediment subduction are the dominant crustal recycling processes operating along convergent margins. Subducted crustal material is transported to the mantle as a viscous non-Newtonian fluid via a thin shear zone known as a subduction channel between the two plates (Figure 0.1; Cloos and Shreve, 1988).

At accretionary margins, such as Cascadia in the northwestern United States, the rate of sediment accretion is greater than the combined rates of sediment subduction and subduction erosion. A net addition of crustal material results in the formation of an accretionary prism that progressively thickens, widens, and migrates seaward over time. In contrast, non-accretionary margins, such as the Central Andes and southern Central America, are characterized by a net crustal loss governed by faster rates of sediment subduction and subduction erosion. These margins generally lack an accretionary prism and exhibit a landward migration of the trench axis as forearc material is eroded away from below. The forearc of non-accreting margins is often composed of dense crystalline crustal basement of the overriding plate (von Huene and Scholl, 1991; 1993; Clift and Vannucchi, 2004).



Figure 0.2 Map of the 15 major tectonic plates of the Earth's lithosphere (modified from USGS public domain image Tectonic_Plates.png). Black lines show divergent and transform plate boundaries. Thick colored lines show convergent plate boundaries presently characterized by net accretion (blue lines) and net erosion (yellow lines) (von Huene and Scholl, 1993).

IV TECTONIC DISTURBANCE AND ARC INSTABILITY

The subduction factory concept compares the net fluxes into and out of a convergent margin to a well-managed factory (Tatsumi and Kogiso, 2002; Hacker et al., 2003a; 2003b; Stern et al., 2006). The factory recycles raw materials from the sea floor and mantle to generate final products on the surface of the Earth in the form of arc magmas, hydrothermal fluids, and volcanic gases. Approximately 20 million years after "opening for business", the factory generally runs under equilibrium conditions with its crustal and mantle inputs more or less balancing its magmatic outputs (Cloos and Shreve, 1988). During these stable periods, fluid transfer causes mantle flux melting and arc lavas erupt onto the surface. These stable arc lavas are not the prime focus of these papers, though they provide a geochemical baseline to which all other lavas can be compared. Regardless of their accretionary or non-accretionary status, most arc segments worldwide operate under quasi-equilibrium conditions. Along-arc geochemical discrepancies are typically time-independent and explained by spatial variations in mantle and crustal sources. For example, the north to south along-arc enrichment in radiogenic Pb isotopes from Lesser Antilles arc lavas neatly corresponds to a spatially-variant sediment source from dominantly pelagic sediment in the north to terrigeneous Guiana Highlands-derived sediment to the south (White and Dupré, 1986). Similarly, the sharp increase towards more radiogenic Sr and Nd isotope ratios in Guatemalan arc lavas, compared to the rest of the Central American arc, is explained by the unique presence of older granitic and metamorphic crustal basement below northwestern Central America (Feigenson and Carr, 1986; Feigenson et al., 2004). Chemical heterogeneity in these arc systems is due to spatial differences in source composition and not to source changes brought on by a sudden or localized shift in tectonic setting.

At the subduction factory, various problems can have a short-term effect on the quality and composition of the final product. These temporally and spatially restricted episodes of tectonic disturbance result in instability within the arc system. The driving forces controlling arc instability are largely unknown, but their effects on non-accretionary margins are often evidenced by shallowing of the subducted slab, thinning of the asthenospheric wedge, landward migration of the frontal volcanic arc, and an increase in the rate of forearc subduction erosion. The papers included in this thesis address the ephemeral geochemical response to transient periods of arc instability associated with these tectonic processes.

Slab shallowing

The stable dip angle of oceanic lithosphere subducting below either oceanic or continental lithosphere is largely governed by the transferal of stress to the lower plate by upper plate processes. Lallemand et al. (2005) showed that for 159 transects across both accreting and non-accreting subduction zones not perturbed by recent collisions of aseismic ridges or oceanic plateaus, slab dip best corresponds to the net stress regime (extensional vs. compressional) and tectonic setting (oceanic vs. continental). Steeply-dipping slabs are found in oceanic arcs characterized by active back-arc spreading and a net extensional stress regime in the overriding plate. Shallower slab dips correspond to continental arcs characterized by back-arc shortening and a net compressional stress regime. Previous models relied on the inverse correlation between slab age and thermal buoyancy, such that hotter more-buoyant young lithosphere should exhibit a shallower dip than colder old lithosphere (Stevenson and Turner, 1977; Tovish et al., 1978; Wortel and Vlaar, 1978; Sacks, 1983; Cloos, 1993). However, recent studies show that worldwide there is no evident correlation between slab dip angle and the age of subducting lithosphere (Cruciani et al., 2005; Lallemand et al., 2005).

The subduction of a bathymetric ridge or oceanic plateau can alter the equilibrium stress regime between upper and lower plates and can incite a *transient* period of slab shallowing (Gutscher et al., 2000b; Yañez et al., 2001; Gutscher, 2002). In the case of the Andean margin between 0°-10° S (Peruvian flatslab) and 28°-33° S (Chilean-Pampean flatslab), geophysical imaging of the Benioff zone indicates horizontal Nazca plate slab geometries extending eastward from the arc front into the backarc (Barazangi and Isacks, 1976; Cahill and Isacks, 1992; Pardo et al., 2002). Both of these Andean flatslab segments spatially and temporally correspond to the subduction of aseismic ridges (Nazca Ridge-Peru flatslab and Juan Fernandez Ridge-Chile flatslab). Geophysical contouring of the subducting Nazca plate has revealed the seismic outline of these subducted ridges (Gutscher et al., 2000b; Pardo et al., 2003). Further north, the collision of the Cocos ridge with the Central American margin at \sim 5 Ma (Kolarsky et al., 1995; Protti et al., 1995) likely caused the shallowing of the Cocos plate and simultaneous uplift of the Cordillera de Talamanca, the highest mountain range in Central America. In fact, of the 10 largest flatslab regions worldwide, 9 are related to the collision of a ridge or accreted terrane (Gutscher et al., 2000b and references therein).

The geochemical response in arc lavas along shallowing subduction zones is a theme carried throughout these papers. Both locations examined in this work are situated at the transitional edges of currently amagmatic arc segments characterized by shallow (southern Costa Rica to central Panama) or flat (central Andes) subduction. Adakitic lavas occur in most flatslab locations worldwide, suggesting a causal link between ridge collision, slab shallowing, arc migration, and adakitic magmatism (Gutscher et al., 2000a). In southern Central America and the Central Andes however, *extreme* adakitic signatures (La/Yb \leq 80; Sr \leq 1400 ppm) in lavas erupting during a late Miocene period of arc instability strongly contrast with non- or mildly-adakitic lavas

(La/Yb \leq 25; Sr < 500 ppm) erupting before and after the period of instability. The transient appearance of these extreme signatures is assessed with respect to temporal and spatial changes in tectonic setting.

Increased rate of forearc subduction erosion

Subduction erosion, including both frontal and basal subduction erosion, is the dominant process of crustal recycling worldwide (von Huene and Scholl, 1991; 1993; Clift and Vannucchi, 2004; von Huene et al., 2004). Frontal erosion involves destruction of crustal material at the toe of the forearc trench slope, whereas basal erosion constitutes removal of the underside of upper plate forearc (von Huene and Lallemand, 1990). Of the 1.6 km³/year total flux of crustal and pelagic detritus subducted globally, only ~ 0.7 km^3 /year was derived from subducted sediments and the rest, ~ 0.9 km^3 /year, from subduction erosion (von Huene and Scholl, 1991; Rea and Ruff, 1996; Plank and Langmuir, 1998). Under stable conditions at non-accreting margins, subduction erosion rates approximate ~ 30 km^3 /m.y. per kilometer along the margin (von Huene and Scholl, 1991; 1993).

The removal and transport of overriding plate forearc crust and mantle is heightened during periods of arc instability at non-accreting margins as evidenced by micropaleontologic, bathymetric, and geophysical studies of the Central American and Andean forearcs. At sediment-starved trenches, such as along the coast of northern Chile (Schweller et al., 1981), lower-plate extensional horst and graben structures abrade upper plate forearc crust weakened by hydrothermal fluid penetration. These grabens are subsequently filled with collapsing eroded forearc material transported to depth within the subduction channel (von Huene and Ranero, 2003; von Huene et al., 2004). Geophysically-imaged scars and grabens in outer forearc units are evidence for the erosive forces of colliding aseismic seamounts, ridges, and plateaus (von Huene et al., 1997; Ranero and von Huene, 2000; Laursen et al., 2002). Vannucchi et al. (2003) estimated faster short-term rates of subduction erosion over the last 6 m.y. along the Central American margin (107-123 km³/m.y./km). For northern Chile, a similar short-term subduction erosion rate (72 to 94 km³/m.y./km) is calculated for the last 10 m.y. (von Huene et al., 1999). Figure 0.3 shows that during these short-lived periods, eroded forearc material constituted 86-91 % of the total subducted volume along these two convergent margins (Clift and Vannucchi, 2004).



Figure 0.3 Schematic representation of subducted volumes of eroded forearc vs. sediment (including pelagic and terrigeneous) for the non-accretionary North Chile and Costa Rica convergent margins (Clift and Vannucchi, 2004). Rates calculated by these authors are based on subducted sediment volume and trench retreat rates over the last 10 m.y. (Vannucchi et al., 2001; Laursen et al., 2002).

Along the eastern Pacific, transient periods of accelerated forearc subduction erosion are contemporaneous with episodes of arc instability and the simultaneous arrival of anomalous trace element and isotopic signatures in erupted arc lavas. Despite the understanding of subduction erosion as a primary crustal recycling process, eroded forearc crust has largely been ignored by the arc geochemical community. Of the hundreds of geochemical papers written regarding the involvement of subducted sediment in arc lava petrogenesis, only a handful consider tectonically-eroded crust as a potential source contaminant (e.g., Stern, 1991; Kay et al., 2005). For both southern Central America and the northern flatslab transition zone of the central Andes (27°-28.5° S), the sudden increase in eroded forearc material delivered to the sub-arc mantle wedge during a late Miocene period of tectonic instability is apparent in the geochemical signatures of temporally-coincident erupted arc lavas. In this thesis, the geochemical consequence of this subducted forearc material is considered through isotopic mixing models and elemental mass balance.

Arc migration

An active volcanic arc along a convergent margin marks the surficial expression of magmatic processes operating at mantle depths. The equilibrium distance of the arc-trench gap depends largely on the subduction angle and the net crustal growth rate along the margin. In the same way that the position of a barrier island responds to changes in sea-level rise, the position of the active volcanic arc front can migrate trench-ward or landward from its stable position in response to changing tectonic parameters. In this sense, arc migration is the most observable response to tectonic disturbance and arc instability.

In non-accreting margins near the edges of shallowing slabs, deciphering the underlying forces that drive arc migration is enigmatic and requires synthesis of geophysical and volcanological data. Within the northern and southern margins of the Chilean flatslab region, abrupt \sim 30-50 km landward translations of the arc front over short time scales (1-2 Ma) are difficult to attribute to the gradual shallowing of the subducted Nazca slab. Moreover, the dip of the Nazca plate below the Andean forearc and the arc-trench gap (\sim 300 km) are relatively uniform along the entire length of the Andean margin (Cahill and Isacks, 1992) with virtually all of the shallowing occurring

behind the volcanic front in the backarc. As shown in Figure 0.4 and applied to the southern Andes by Kay et al. (2005), a retreating trench and forearc caused by a pulse of rapid forearc subduction erosion generates a corresponding jump in the position of the active magmatic arc. In this way, the subduction zone *dynamically* responds to tectonically-driven changes in its structural geometry in order to re-establish tectonic equilibrium.



Figure 0.4 Schematic cartoon from Lallemand (1995) showing arc geometries before (dashed outlines) and after (solid lines) frontal arc migration and subduction erosion. Upper plate is fixed so that lateral slab migration controls trench and arc retreat. The three ubiquitous signs of an actively eroding margin are shown: volcanic arc retreat, trench retreat, and forearc margin subsidence.

One of the principle aims of this work is to understand the anomalous geochemical changes in intermediate and evolved lavas erupting within migrating volcanic arcs and to link these changes to processes operating within the sub-arc crust and mantle. For the margins considered in these studies, the transient arrival of an adakitic geochemical signature coupled with discrete changes in the isotopic character of the erupted lavas occurs contemporaneous with episodic landward migration of the frontal arc. New geochronological data presented in this thesis show that the composition of arc lavas evolve with respect to *space* and *time* in response to varying tectonic forces.

V SUBMITTED MANUSCRIPTS

The following outlines the objectives for the four manuscripts included in this thesis regarding arc instability and petrogenesis along the eastern Pacific margin.

Chapter 1 Steep REE patterns and enriched Pb isotopes in southern Central American arc magmas: Evidence for forearc subduction erosion?

Authors: A. R. Goss and S. M. Kay

The main objective of this paper is to examine published trace element and isotopic data from Central American arc lavas in order to evaluate the sources and fluxes involved in magma genesis within a spatial and temporal context. The heterogeneous along-arc Pb isotopic signal of exposed Cretaceous-Paleogene forearc ophiolites is traced through the subduction zone and into the mantle source of the erupted arc lavas. Through isotopic mixing models and mass balance calculations, the ~ 5 Ma arrival of an enriched Pb isotopic signal in southern Central American arc lavas coincident with the appearance of adakitic geochemical signatures is explained by an increased flux of mafic forearc delivered to the sub-arc mantle. This study, which was published in Geochemistry, Geophysics, and Geosystems (G³) in May 2006, provides direct isotopic evidence of subduction erosion processes influencing the geochemical composition of Central American arc lavas (Goss and Kay, 2006a).

Chapter 2 Central Andean adakites from the northern edge of the Chilean flatslab (27-28.5° S) associated with arc migration and forearc subduction erosion

Authors: A. R. Goss, S. M. Kay, and C. Mpodozis

The sources and magmatic evolution of high-Mg andesites from the northern margin of the Chilean flatslab (27-28.5° S) constitutes the focus of this paper in which over 50 new major and trace element analyses are presented. These glassy amphiboledominated andesites, known as the Pircas Negras, track the broadening of the Andean arc at this latitude during a 7-3 Ma period of arc migration and tectonic disturbance. Transient adakitic geochemical signatures in these lavas combined with a shift toward more radiogenic Sr and Nd isotopic ratios contrast with neighboring arc lavas that erupted both before and after the period of instability. Mineral chemistry data support hypotheses from major and trace elements that these magmas were anomalously hot and record involvement of mantle sources in precursor melts. Through trace element and isotopic modeling, the petrogenesis of the Pircas Negras high-Mg andesites is considered with respect to experimental data and known models for adakitic magmatism. These results show that Pircas Negras magmatism records evidence for high-pressure melting in equilibrium with garnet-bearing *in situ* lower crust as well as a transient mantle-source contaminant derived from eroded mafic forearc. Considering a constant arc-trench gap during the late Miocene, the mass flux of eroded forearc crust is estimated. Lastly, a regional model for Andean petrogenesis during the late Miocene period of tectonic instability is presented. This manuscript will be submitted to the Journal of Petrology.

Chapter 3 Extreme High Field Strength element (HFSE) depletion and nearchondritic Nb/Ta ratios in Central Andean adakite-like lavas (~ 28° S, ~ 68° W)

Authors: A. R. Goss and S. M. Kay

This paper examines new ICP-MS high-field strength element data for the late Miocene Pircas Negras lavas in order to explain exceptionally strong HFSE-depletion evident in these lavas. The main motivation for this project was to identify the fluid or crystal phase stable in the high-pressure source of the Pircas Negras high-Mg andesites responsible for the strong HFSE anomalies. These new data indicate a range of chondritic Nb/Ta ratios in 8-6 Ma Pircas Negras lavas that contrast with subchondritic ratios in younger 6-2 Ma Pircas Negras lavas. Chondritic and superchondritic Nb/Ta ratios are exceptionally rare in arc lavas worldwide and in crustal rocks in general. Examining these results with respect to experimentally determined HFSE partitioning behavior and existing eclogite melting models suggest a change from rutile-controlled to amphibole-controlled HFSE compositions in the highpressure mineral residues in equilibrium with Pircas Negras adakitic magma. This change in residual mineral assemblage is temporally consistent with the inception of arc migration and slab shallowing along the northern flatslab transition zone and is best explained by a cooler and more-hydrated lower crust and mantle within an unstable arc setting. This manuscript will be submitted to Earth and Planetary Science Letters.

Chapter 4 The Incapillo Caldera (~ 28° S): A stranded magma chamber over a dying Andean arc

Authors: A. R. Goss, S. M. Kay, C. Mpodozis, and B. S. Singer

The effect of arc instability on evolved magmas, with regard to eruptive style, size, and geochemistry is the main focus of this paper. Through field mapping and geochronology on erupted ignimbrites and domes, an eruptive model for the Incapillo Caldera and Dome Complex is presented. Based on new ⁴⁰Ar/³⁹Ar ages as young as 0.51 Ma, the Incapillo ignimbrite marks the youngest eruptive event for \sim 700 km along the presently amagmatic flatslab section of the Andean cordillera. These lavas represent the final melts to reach the surface as magma production in the volcanic arc waned in response to backarc slab shallowing. Using high-resolution digital topography, the erupted volumes of Incapillo dome and ignimbritic material are calculated. Over 30 major and trace element analyses combined with ~ 20 Sr, Nd, and Pb isotopic ratios shed new light on the sources involved in Incapillo magma genesis. Based on the subdued adakitic signatures in Incapillo melts, precursor magmas were likely similar to the Pircas Negras andesites and originated as partial melts of eclogitic or garnet amphibolitic lower crust. Energy-constrained assimilation-fractional crystallization (AFC) modeling reveals that upper crustal processes altered the composition of these precursor melts as they lost contact with the mantle and stalled at shallow crustal depths. In contrast to the large explosive caldera complexes of the Puna and Altiplano that erupted over a steepening slab between 11 and 4 Ma, Incapillo defines the model of a dominantly effusive siliceous system evolving over a shallowing slab and cooling mantle.

CHAPTER 1

STEEP REE PATTERNS AND ENRICHED PB ISOTOPES IN SOUTHERN CENTRAL AMERICAN ARC MAGMAS: EVIDENCE FOR SUBDUCTION EROSION?

ABSTRACT

The appearance of adakitic magmas with steep REE patterns in southern Costa Rica and Panama at ca. 4 Ma coincides with the collision of the Cocos Ridge and the inception of slab shallowing along the margin. Distinctly higher ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios in these adakitic lavas than in older Miocene lavas suggest that components enriched in radiogenic Pb also entered the mantle magma source at ca. 4 Ma. Published Pb-isotopic data for Central American arc lavas show that a similar radiogenic component is not present in lavas further north, and that maxima in post-Miocene ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios occur in central Costa Rica and western Panama. Cretaceous and early Tertiary ophiolites in the forearc, whose origins have been linked to the Galápagos hotspot, show a similar spatial pattern in Pb isotopic ratios. The incorporation of ophiolitic forearc crust into the mantle wedge by forearc subduction erosion can explain the along-arc spatial and temporal pattern of Pbisotopic ratios in southern Central American arc lavas. Partial melting of crust removed from the base of the forearc and subjected to high pressure metamorphism in the subduction channel provides an explanation for the steep adakitic REE patterns in some Costa Rican and Panamanian lavas.

I INTRODUCTION

Identifying chemical evidence for forearc subduction erosion in arc magmas requires tracing missing forearc continental lithosphere down the subduction channel
and into the melt zone of arc magmas. Recognizing the effects of forearc crust is usually problematic as subducted sediment, mantle heterogeneities, and contaminants incorporated into melts ascending through the crust can severely dilute chemical signals from tectonically-eroded forearc crust introduced into the mantle source.

Radiogenic isotopic ratios can be particularly useful tracers of magma sources as they are not fractionated by magmatic processes. High Pb concentrations in the crust, the relative mobility of Pb in slab-derived fluids, and large isotopic differences between possible sources make Pb isotopes the best potential tracer for forearc material removed by subduction erosion. Parallels in along-arc differences in Pb isotopic ratios in southern Central American frontal arc lavas and Cretaceous/Tertiary forearc ophiolites make this part of the Central American arc an ideal region to investigate and test the role of subducted forearc crust in arc magma genesis.

Adakites, or andesites with steep REE patterns (SiO₂ > 56 wt %, Al₂O₃ > 15 wt %, La/Yb > 20) and elevated Sr contents (> 400 ppm, Sr/Y > 20), are sensitive indicators of high pressure crustal melting of mafic protoliths (e.g., Defant and Drummond, 1990). When adakites erupt along arcs where the subducting slab is too old to melt and crustal thicknesses are insufficient to permit garnet-bearing lower crustal residues, subducted forearc crust must be considered as a possible contaminant in the mantle source (Stern, 1991; Kay and Mpodozis, 2002; Kay et al., 2005). The spatial and temporal distribution of Costa Rican and Panamanian adakites provides yet another constraint in elucidating the role of subduction erosion along the southern Central American margin.

II TECTONIC SETTING

Miocene to Holocene calc-alkaline arc volcanism along the Central American margin (Figure 1.1) is attributed to the subduction of the Cocos and Nazca plates

beneath the Caribbean plate (Carr, 1984; de Boer et al., 1991). This volcanism began after the breakup of the Farallon plate (Hey, 1977) with initiation of the Costa Rican volcanic arc at 23 Ma (Seyfried et al., 1991). The NW-SE trending active volcanic arc stretches 1200 km from western Guatemala to central Panama. Sub-arc crustal thicknesses decrease from 48 km in western Guatemala to 32 km in Nicaragua and increase again to 32-40 km in Costa Rica (Carr et al., 1990; Sallarès et al., 1999). Gravity data suggest a Moho depth of < 30 km under Panama (Mickus, 2003). Along the margin, fast nearly-orthogonal subduction of the Cocos plate under Costa Rica (Figure 1.1; 8.8 cm/yr at 032°) contrasts with slower oblique convergence of the Nazca plate (3.7 cm/yr at 070°) under western Panama (DeMets, 2001).

Earthquake hypocenter depths that define the Wadati-Benioff zone show a progressive change in subduction angle from 60° beneath Guatemala to less than 30° under central Costa Rica (Protti et al., 1995). Below the Cordillera de Talamanca and into central Panama, the Wadati-Benioff zone is unconstrained by intraplate seismicity and can only be traced 100 km east of the trench where the depth is less than 50 km. The lack of deep earthquakes in this region has been explained by Protti et al. (1995) as younger hotter crust (< 15 Ma) subducting below southern Costa Rica and Panama reaches the brittle-ductile transition at shallower depths than older crust subducting to the north. Protti et al. (1995) argue that the slab shallows and follows a sub-horizontal $(\sim 10^{\circ})$ path under the base of the Caribbean plate below Panama. Uplift of the Cordillera de Talamanca and progressive slab shallowing have been attributed to the subduction of the aseismic Cocos Ridge that collided with southern Costa Rica at < 5 Ma (Kolarsky et al., 1995). Contemporaneous with ridge collision, the onset of low-angle subduction is thought to have caused 40 to 50 kms of northeastward arc migration in central Costa Rica (Alvarado et al., 1993; Marshall et al., 2003). Alternatively, the opening of an asthenospheric slab window below western Panama

between 10-6 Ma, formed by the subduction of an extinct arm of the Cocos-Nazca spreading ridge and Panama Fracture Zone, has been proposed to explain the lack of intraplate seismicity and the appearance of late Miocene backarc alkalic volcanism (Johnston and Thorkelson, 1997).



Figure 1.1 Map of Central America showing major tectonic features. Black triangles show positions of frontal arc volcanoes with open triangles marking locations of adakitic magmatism (de Boer et al., 1991; Defant et al., 1991a; 1991b; Feigenson et al., 2004). Gray circles show sites of pre-Quaternary backarc lavas (Abratis and Wörner, 2001; Feigenson et al., 2004). Volcanic centers mentioned in the text are: Nejapa (NE), Arenal (AR), Platanar (PL), Laguna del Pato Frontal Cone (LP), La Yeguada (LY), El Valle (EL), Providencia back arc lavas (PROV), Bribri back arc lavas (BR). Deep Sea Drilling Program sites (DSDP) are marked with +'s (495, Cocos Plate sediments; 158, Cocos Ridge; 084, Cocos Plate. 155, Coiba Ridge). Shaded colored regions identify outcrop locations of Cretaceous/Tertiary forearc igneous complexes. Stippled region shows the regional extent of the Cordillera de Talamanca. PFZ = Panama Fracture Zone. Convergence rates and directions from DeMets (2001)



Figure 1.2 Map of southeastern Costa Rica and western Panama revised from Defant et al. (1991a). Geographic exposures of forearc ophiolite complexes (Osa, Burica, Golfito, Coiba Island, Soná, and Azuero) are shown by solid red fields. Shaded grey fields represent major volcanic centers of the Quaternary volcanic arc of Panama and Cordillera de Talamanca. Smaller cones and domes are shown in white. Locations of adakitic lavas (open triangles) are grouped in blue rectangles (Defant et al., 1991a; 1991b; 1992; de Boer et al., 1995; Abratis and Wörner, 2001). In general, the adakitic magmas erupted behind large exposures of forearc ophiolite.

The Costa Rican forearc is dominantly composed of the late Cretaceous (60-100 Ma) Nicoya Complex ophiolite belt (*sensu lato*) that extends from the northernmost Santa Elena Peninsula to the Burica Peninsula in the south (Figure 1.1). Hauff et al. (2000b) have shown that the obducted basalts and gabbros in the forearc have chemical characteristics similar to the Caribbean Large Igneous Province (CLIP) that forms the basement of the southern Caribbean Sea and interpret them as accreted segments of Caribbean crust. As shown in Figure 1.2, obducted ophiolite further south is exposed on the peninsulas along the southwestern Panamanian coast, with the

most voluminous outcrops on the Azuero and Soná Peninsulas. As in the Costa Rican forearc, ⁴⁰Ar/³⁹Ar ages and isotopic ratios indicate that Panamanian forearc ophiolites are accreted segments of the Caribbean igneous province (Hoernle et al., 2002). Though the ophiolite is not exposed in the forearc north of the Santa Elena Peninsula, basic and ultrabasic Cretaceous basement rocks were recovered in DSDP Leg 84 cores from the forearc offshore Guatemala/El Salvador (von Huene et al., 1985).

III GEOCHEMICAL TRENDS

The along-arc trace element and Pb isotopic variations in Miocene to Holocene Central American lavas (Defant et al., 1991a; 1991b; Abratis and Wörner, 2001; Feigenson et al., 2004) and variations in Pb isotopic ratios in Cretaceous and Tertiary Nicoya Complex forearc ophiolites (Hauff et al., 2000b; Hoernle et al., 2002) are outlined below. Spatial and temporal relationships in these data are used to examine the role of tectonically-eroded forearc crust in the evolution of Central American arc magmas.

Central American Arc and Backarc Magmas

Arc magmas erupting along the Central American volcanic front have been interpreted to contain components from several types of mantle sources. Isotopic and trace element signatures in frontal arc lavas from Guatemala to El Salvador have been associated with a depleted mantle source that has been modified by slab-related mobile element-enriched fluids (Feigenson and Carr, 1986; Carr et al., 1990). Comparatively higher Ba/La (80-120) and lower La/Yb (2-4) ratios in western Nicaraguan lavas have been attributed to an increased slab-derived fluid flux resulting in higher degrees of melting (Carr et al., 1990). In contrast, arc rocks in Costa Rica with high La/Yb (20-35) and low Ba/La (15-50) ratios have been associated with low degrees of melting of an enriched mantle source (Carr et al., 1990). Alkaline backarc centers in Costa Rica with a subdued arc signature (Bribri lavas, Ba/La=13-19, La/Ta =24-29) and elevated Nb/Zr (0.17-0.24) ratios have been associated with an enriched OIB source that entered the backarc mantle after 6 Ma (Abratis and Wörner, 2001).

Arc volcanic rocks in the Cordillera de Talamanca and in west-central Panama with ages of < 4 Ma are chemically distinct from lavas to the north in having steeper REE patterns (Figure 1.3; La/Yb = 20-90, Sm/Yb = 2-10) and Sr/Yb ratios > 700. These adakitic signatures became dominant after 2.5 Ma and are absent in the older Miocene volcanic rocks from the same region (Defant et al., 1991a; 1991b; de Boer et al., 1995). Panamanian adakites have higher La/Yb than lavas classified as adakites in the Aleutians (La/Yb = 30-57; Kay, 1978; Yogodzinski et al., 1994), Japan (La/Yb = 15-23; Shimoda et al., 1998), the Cascades (La/Yb = 8-13; Grove et al., 2002), the Austral Andes (La/Yb = 30-35; Kay et al., 1993; Stern and Killian, 1996) and Kamchatka (La/Yb = 4-7; Kepezhinskas et al., 1997). Their high ratios are like those in the Central Andes that have been related to thickened crust and forearc subduction erosion (Kay and Mpodozis, 2002; Kay et al., 2005; Goss and Kay, 2006b).

Pb-isotopic data for lavas along the entire arc (Figure 1.4a) show that an enriched mantle source component with HIMU-like tendencies (high- μ where $\mu = {}^{238}\text{U}/{}^{204}\text{Pb}$) is present in arc lavas from central Costa Rica and Panama (Abratis and Wörner, 2001; Feigenson et al., 2004). These lavas have ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ and ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ ratios greater than 18.7 and 38.3 respectively, whereas volcanic front lavas north of central Costa Rica have ${}^{206}\text{Pb}/{}^{204}\text{Pb} < 18.7$ and ${}^{208}\text{Pb}/{}^{204}\text{Pb} < 38.3$ (Feigenson et al., 2004). A distinct temporal change to a similar enriched source is seen in the Cordillera de Talamanca where older Miocene volcanic rocks have lower ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ and ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ ratios (< 18.7 and < 38.6) than < 4 Ma adakitic lavas (> 19.0 and > 38.7) (Abratis and Wörner, 2001). As discussed by Feigenson et al. (2004), an

exception to this is the 14 Ma frontal cone lava from Laguna del Pato in Panama (Figure 1.2) with a ²⁰⁶Pb/²⁰⁴Pb ratio of 19.15. These authors further note that pre-Quaternary backarc lavas (Figure 1.1) in eastern Costa Rica have a greater involvement of a radiogenic Pb component than those to the north in Nicaragua and Honduras.



Figure 1.3 Graphs showing (A) La/Yb ratio vs. SiO₂ concentration and (B) La/Sm vs. Sm/Yb ratios for lavas from southern Costa Rica (Cordillera de Talamanca) and west-central Panama (El Valle and La Yeguada). Data are from Defant et al. (1991a; 1991b) and de Boer et al. (1995). Shaded symbols are > 4 Ma lavas. Open symbols are < 4 Ma adakitic lavas.



Figure 1.4 Graphs of ²⁰⁶Pb/²⁰⁴Pb vs. ²⁰⁸Pb/²⁰⁴Pb for (A) Central American volcanic front lavas and (B) Cretaceous/Tertiary forearc complexes. Data for volcanic arc lavas from Feigenson et al. (2004) and Abratis and Wörner (2001). Shaded triangles mark > 4 Ma Talamancan lavas while open triangles show data from < 4 Ma Talamancan adakites. Data for forearc complexes from Hauff et al. (2000b) and Hoernle et al., (2002). Isotopic data for DSDP site 495 sediments and granitic basement are from Feigenson et al. (2004). Fields for Cocos Ridge, Coiba Ridge, Cocos Plate, and Costa Rican seamounts from Hauff et al. (2000b), Werner et al. (2003), Hoernle et al. (2000), and Harpp et al. (2005). Plotted values have not been age corrected and therefore reflect measured ratios. NHRL refers to Northern Hemisphere Reference Line (Zindler and Hart, 1986).

Cretaceous/Tertiary Nicoya Complex basement

A study of the ophiolitic Nicova Complex terrane in Costa Rica by Hauff et al. (2000b) shows along-margin isotopic differences exist within the forearc rocks. As shown in Figure 1.4b, the lowest Pb isotopic ratios occur in the 120 Ma layered gabbros and pillow basalts from the northernmost ophiolite complex on the Santa Elena Peninsula. Based on depletions in high field strength elements (Nb and Ta) and high degrees of serpentinization, Hauff et al. (2000b) interpreted Santa Elena Units II, III, and IV as uplifted segments of an allochthonous subduction zone mantle wedge. The volumetrically minor Santa Elena Unit I has OIB-type trace element characteristics and more radiogenic Pb isotopes and thus is interpreted as an accreted off-axis seamount (Frisch et al., 1992; Hauff et al., 2000b). Pb isotopic ratios in 95-75 Ma ophiolites from the Nicoya, Herradura, Golfito, and Burica complexes are isotopically similar to Caribbean plate lavas and are interpreted as early magmas erupted from the Galápagos hotspot (Hauff et al., 2000b). The distinctive Sr, Nd, and Pb initial isotopic ratios in the 89 Ma Tortugal alkaline tholeiites suggest they formed from another source within the CLIP. Among younger (65-59 Ma) ophiolites, those from the Quepos Peninsula are more radiogenic than those from the Osa Peninsula. These ophiolites are interpreted as originating from an ocean-island volcano and/or bathymetric ridge formed over the paleo-Galápagos hotspot (Hauff et al., 2000b). Further south, the 51-29 Ma Azuero and 71 Ma Soná complexes are among the most radiogenic forearc ophiolites in Central America (Hoernle et al., 2002).

Potential Slab and Crustal Sources

Other potential source components in Central American arc lavas are subducting Cocos and Nazca plate basalts, pelagic and hemipelagic sediments, the Cocos and other bathymetric ridges, alkaline seamounts, granitic and metamorphic basement, and mafic lower crust. As seen in Figure 1.4a, all of these sources have distinctive isotopic signatures.

(1) MORB-like tholeiitic lavas dredged from the Cocos and Nazca plates have significantly less radiogenic Pb isotopic ratios (206 Pb/ 204 Pb=18.52-18.59; 208 Pb/ 204 Pb=38.07-38.13) than Central American arc lavas and forearc ophiolites (Hauff et al., 2000b; Werner et al., 2003).

(2) Pelagic and hemipelagic sediments from DSDP drill site 495 on the Cocos plate offshore Guatemala have low 206 Pb/ 204 Pb (18.47-18.78) and high 87 Sr/ 86 Sr (0.7076-0.7086) ratios (Feigenson et al., 2004).

(3) Tholeiitic lavas from the bathymetric Cocos and Coiba Ridges (Hauff et al., 2000b; Hoernle et al., 2000; Werner et al., 2003; Harpp et al., 2005) as well from Cocos Island (Castillo et al., 1988) have low 87 Sr/ 86 Sr (0.7029-0.7035), high ϵ Nd (+6 to +8), and radiogenic Pb isotopic ratios (206 Pb/ 204 Pb = 18.85-19.66; 208 Pb/ 204 Pb = 38.33-39.38). Their isotopic ratios are similar to those of lavas erupted within the central and southern Galápagos hotspot domains (White et al., 1993; Hoernle et al., 2002).

(4) Seamounts and conical cones northwest of the Cocos Ridge are dominantly alkaline lavas (hawaiites to trachytes) with slightly more radiogenic Sr and Pb isotopic ratios (87 Sr/ 86 Sr = 0.7032-0.7045; 206 Pb/ 204 Pb = 19.03-19.91; 208 Pb/ 204 Pb = 38.89-39.60) and lower ϵ Nd (+2.3 to +6.6) values than lavas from the Cocos and Coiba ridges. They are distinctly enriched in incompatible trace elements (Ba = 440-620 ppm, Sr = 474-675 ppm, Th = 3.77-6.20 ppm) and have steeper REE patterns (La/Yb = 6-21) than Cocos/Nazca oceanic crust (Ba = 3-25 ppm, Sr = 45-118, Th = 0.08-0.29; La/Yb < 1) or Cocos/Coiba ridge lavas (Ba = 30-50 ppm, Sr = 142-222, Th = 0.52-1.72; La/Yb < 6) (Hauff et al., 2000b; Hoernle et al., 2000; Werner et al., 2003; Harpp et al., 2005).

(5) Guatemalan granitic and metamorphic basement rocks have ²⁰⁶Pb/²⁰⁴Pb values of 18.69-18.78 and 19.13-19.32 respectively (Feigenson et al., 2004).

(6) Noritic and gabbroic crustal xenoliths from Volcán El Valle in Panama and Volcán Arenal in Costa Rica (Cigolini et al., 1991; Defant et al., 1991a; Cigolini, 1998) have trace element characteristics generally like those of the Nicoya Complex ophiolites. Their significantly higher Sr (350-700 ppm) and Ba (~ 140 ppm for Arenal; 380-400 ppm for El Valle) concentrations could be due to excess plagioclase. No Pb-isotopic data exist for Costa Rican mafic crustal xenoliths.

IV EVIDENCE FOR FOREARC SUBDUCTION EROSION

Subduction erosion, or the removal and transport to depth of forearc crustal and mantle lithosphere, has been argued to be a major process in shaping the nonaccretionary Central American margin (von Huene and Scholl, 1991; Ranero and von Huene, 2000). Based on the 3-5 km subsidence of outer forearc basinal sediments and the presence of a margin-wide seismic reflector marking the base of slope sediment along the Nicova shelf (Meschede et al., 1999a), Vannucchi et al. (2001) estimated a loss of \sim 560-600 km³km⁻¹ of the Costa Rican margin via subduction erosion over the last 17 Ma. The equivalent erosion rate of 34-36 km³m.y.⁻¹km⁻¹ is similar to rates estimated for the Chilean margin by von Huene and Scholl (1991). Accelerated subduction erosion along the Costa Rican margin during the last 5-6 Ma is supported by sediment drilling records that indicate a dramatic landward shift in the coastline coincident with a 40 to 50 km NE-migration of the arc volcanic front (Alvarado et al., 1993; Meschede et al., 1999a). Vannucchi et al. (2003) used these data to argue for a subduction erosion rate of 107-123 km³m.y.⁻¹km⁻¹ over the last 5-6 Ma. The observed uplift of innermost Costa Rican forearc units (Gardner et al., 1992; Marshall and Anderson, 1995; Fisher et al., 1998) is consistent with models of margins affected by

subduction erosion and likely reflects the topographic effects of subducted seamounts, serpentinization, and/or sediment underplating (Lallemand, 1995; Meschede et al., 1999a). Clift and Vannucchi (2004) estimated the total proportions of eroded forearc and incoming sediments subducted below Costa Rica in the last 6 Ma. Over this period, they calculated that eroded forearc composed c.a. 86 % of this subducted material. In Central Panama, c.a. 120 km of apparent arc migration (~ 2.7 mm/yr) since the Eocene has been attributed to subduction erosion (Lissinna et al., 2002). To the north, progressive subsidence of the Guatemalan forearc began at 19 Ma with an average subduction erosion rate of 11.3-13.1 km³m.y.⁻¹km⁻¹; approximately 1/3 the long-term rate estimated for Costa Rica (Vannucchi et al., 2004).

Other support for subduction erosion along the Central American margin comes from seismic reflection images presented by Ranero and von Huene (2000). Evidence includes forearc normal faulting, subduction of 10-15 km long by 1.5-2.0 km wide "mega-lenses" from the upper plate, and 0.5-0.7 km wide scars in the continental slope where seamounts were subducted. Though seamount subduction along convergent margins accelerates removal of upper-plate material, high-resolution bathymetric studies have shown that subduction erosion also occurs when normal "unperturbed" oceanic crust is subducted (Meschede et al., 1999a; Ranero and von Huene, 2000).

Geophysical studies (von Huene and Flueh, 1994; Ye et al., 1996; Christeson et al., 1999) combined with ODP/DSDP drilling (Aubouin et al., 1985; von Huene et al., 1985; Vannucchi et al., 2001) reveal that the Central American forearc basement is likely composed of the seaward extension of the Nicoya complex and that collapsing forearc basement dominates the subducted material (Meschede et al., 1999a). Mélange exposed on the Osa Peninsula in southern Costa Rica contains tectonized blocks of late Cretaceous to early Tertiary basalt that have been to depths of 10-15 km and temperatures near 200 °C (Meschede et al., 1999b). These authors interpret this low-grade metamorphic sequence as an exhumed Miocene-Pliocene subduction channel that transported upper plate ophiolitic material into the subduction zone. In their model, the collision of the Cocos Ridge with the Middle American trench at ~ 4 Ma could have increased the amount of forearc material eroded from the overriding plate and led to thickening of the mélange in the subduction channel.

Chemical data provide additional evidence for subduction erosion along the southern Central American margin. Morris et al. (2002) argued that much lower concentrations of ¹⁰Be (a cosmogenic isotope prevalent in young pelagic sediments; 1.5 m.y. half-life) in Costa Rican compared to Nicaraguan lavas required either sediment underplating or dilution of the subducted sediment component in the mantle wedge by eroded forearc basement. Clift et al. (2005) used spikes in Li/Y and B/Be ratios in analyses of < 2.5 Ma airfall tephra from ODP Legs 170 and 205 offshore Costa Rica to identify periods of enhanced subduction flux along the margin. High ϵ Nd, δ^7 Li, and La/Yb ratios during some of these periods were thought to reflect subduction erosion and assimilation of Nicoya Complex basement into the source of central Costa Rican arc magmas. Elsewhere, Kay and Mpodozis (2002) and Kay et al. (2005) have suggested that spikes in La/Yb and La/Ta ratios in Central Andean Neogene lavas reflect episodic crustal contamination of the sub-arc mantle by subduction erosion during periods of heightened arc migration.

V DISCUSSION

Evidence for the incorporation of forearc crust into the mantle wedge by subduction erosion comes from Pb isotopic and trace element characteristics of magmas erupted along the Central American arc. Multi-component Pb-isotopic modeling combined with Pb mass balance calculations presented below support the hypothesis that tectonically-eroded forearc crust is a potential source in Central American arc magma genesis. Furthermore, the spatial and temporal pattern of erupted adakites with enriched Pb-isotopes substantiates a model of subduction erosion and high-pressure melting of forearc ophiolitic crust.

Previous Models for Enriched Pb Isotopic Signatures in Central American Lavas

The correlation between enriched Pb isotopic ratios and adakitic magmatism in southeastern Costa Rica was first addressed by Abratis and Wörner (2001). These authors showed that the ²⁰⁶Pb/²⁰⁴Pb ratios of adakitic lavas within the Cordillera de Talamanca are too high to be explained by melting of subducted MORB crust of the Cocos plate as initially proposed by de Boer et al. (1995). Using thermal considerations, they argued that the bulk of the colliding Galápagos-derived Cocos Ridge was too old (15 Ma) and subducting at too fast a rate (7-9 cm/yr) to melt. As an alternative, they proposed that Talamancan adakitic magmas formed when the slab window proposed by Johnston and Thorkelson (1997) opened from 10 to 6 Ma below western Panama allowing upwelling asthenosphere to melt the leading edges of the Cocos Ridge. The model however fails to explain why: (1) lavas with similarly high ²⁰⁶Pb/²⁰⁴Pb ratios erupted far from the proposed slab window in north-central Costa Rica (ex. Volcán Platanar), (2) lavas with high ²⁰⁶Pb/²⁰⁴Pb ratios (19.15) erupted at the Laguna del Pato center in Panama at 14 Ma before the slab window opened (Figure 1.2) (Defant et al., 1992; Feigenson et al., 2004), and (3) pre-slab window (> 10 Ma) calc-alkaline and tholeiitic Talamancan lavas have elevated $^{206}\text{Pb}/^{204}\text{Pb}$ and ²⁰⁸Pb/²⁰⁴Pb ratios with respect Central American arc lavas north of central Costa Rica.

Recently, Feigenson et al. (2004) used Sr, Nd, and Pb isotopic data to show that the majority of Central American volcanic front lavas, including those with elevated ²⁰⁶Pb/²⁰⁴Pb ratios, show little contamination from passage through the crust.

Based on the non-radiogenic character of the Pb in pelagic sediments, they ruled out subducted sediment as the source of the high ²⁰⁶Pb/²⁰⁴Pb ratios in the arc lavas. They further argued that backarc magmas with the elevated ²⁰⁶Pb/²⁰⁴Pb ratios required the enriched Galápagos-like source to be a primary feature of the ambient mantle. In their model, they used granitic and metamorphic Guatemalan crust to represent the average crust below Central America. Alternatively, mafic CLIP crust could extend below southern Central America and be the source of the enriched Pb.

Pb Isotopic Evidence for Subduction Erosion in Central American Arc Magmas

A source with enriched Pb isotopes not thoroughly considered in previous models is the Cretaceous/Tertiary Nicoya Complex ophiolites in the forearc. Figure 1.5 shows that the measured ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios in recently erupted lavas along the Central American arc have a striking similarity to those of the Costa Rican and Panamanian forearc ophiolites. A way to explain this similarity is that the Pb signatures in the arc front lavas reflect assimilation of mafic forearc crust into the mantle wedge by subduction erosion (Goss et al., 2003; Nichols et al., 2003). In detail, central Costa Rican arc lavas generally have elevated Pb isotopic ratios that fall within the range of those for the Nicoya, Tortugal, and Herradura ophiolites.

The slightly lower Pb isotopic ratios in the Talamancan lavas can be explained by contamination of their mantle source by Osa/Burica/Golfito-type ophiolitic basement. Lavas with higher ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb from western Panama could reflect assimilation of the Burica and Golfito forearc complexes. In central Panama, Tertiary mafic lavas from the Azuero Peninsula have Pb isotopic ratios similar to the adakites (El Valle and La Yeguada) that erupted directly behind this large exposure of forearc ophiolite. Though the Soná Peninsula ophiolite has more radiogenic Pb than the central Panamanian adakites, dilution of this enriched forearc material within the sub-arc mantle could produce Pb isotopic ratios similar to the adakites.



Figure 1.5 Graphs of (A) ²⁰⁶Pb/²⁰⁴Pb ratios and (B) ²⁰⁸Pb/²⁰⁴Pb ratios vs. latitude for Central American frontal arc lavas (data points) and Cretaceous/Tertiary forearc ophiolites (shaded fields). Data are from the same sources as in Figure 1.4 and reflect measured isotopic ratios. Latitudes for the Costa Rican and Panamanian forearc complexes have been projected under the active volcanic arc using convergence azimuths of 032° and 070° respectively.



Figure 1.6 Graphs of measured 206 Pb/ 204 Pb ratios vs. (A) Th/U and (B) Nd/Pb ratios for Costa Rican (blue diamonds) and Panamanian (open squares) forearc ophiolites showing the negligible geochemical effects of hydrothermal alteration. Data are from Hauff et al. (2000b). Value for MORB (24 ± 5) from (Rehkaemper and Hofmann, 1997).

The effects of U^{6+} and Pb mobility during Miocene to Recent subductionrelated hydrothermal alteration of the Nicoya Complex ophiolites was investigated by Hauff et al. (2000a). They showed that most Cretaceous ophiolitic lavas had Th/U ratios near 3.05 (R²=0.99) and that the lavas with the *lowest* Th/U ratio (indicative of U-enrichment) generally have the lowest 206 Pb/ 204 Pb ratios (Santa Elena) (Figure 1.6a). Hauff et al. (2000a) further demonstrated that most Nicoya ophiolites have Nd/Pb ratios similar to MORB (24 ± 5). By assuming both Nd and Pb are relatively incompatible in the dry mantle and that Pb is more mobile than Nd in hydrothermal fluids, they reasoned that only the few Nicoya lavas with extreme Pb isotopic ratios reflect Pb-loss or U-enrichment related to hydrothermal alteration. However, these authors note that initial Pb-isotopic ratios indicate that the majority of this alteration occurred immediately after eruption and that the effects of post-Miocene subduction-related alteration are negligible.

Chemical and Isotopic Modeling

A 3-component Pb isotopic model in Figure 1.7 shows that the source of Costa Rican arc lavas with enriched Pb isotopes (i.e., Platanar, Arenal, Barva, and Irazú) must involve a component with high ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios like the Nicoya complex forearc lavas. The trace element and isotopic compositions of the three components considered in the model are shown in Table 1.1 and discussed below.

The first modeled component is the ambient enriched mantle below central Costa Rica. The Pb isotopic ratios ($^{206}Pb/^{204}Pb = 19.05$; $^{208}Pb/^{204}Pb = 38.58$) used for this component are from the most radiogenic backarc lava found at La Providencia island (Feigenson et al., 2004). The isotopic ratios of this lava are likely to be close to the pristine enriched mantle based on its location far from the trench and eruption through purely oceanic crust (Figure 1.1). As Pb and Th concentrations in the enriched mantle (EM) are poorly constrained, the modeled concentrations of these elements are calculated from the Pb and Th concentrations in MORB (Hofmann, 1988), depleted mantle (DM; Salters and Stracke, 2004), and average Galápagos tholeiitic basalts (Pb = 3.00; Th = 1.88; Geist et al., 2002). Assuming similar degrees of mantle partial melting for MORB and Galápagos basalts, Pb and Th concentrations in the enriched Galápagos-like mantle below Costa Rica are estimated to be 0.15 ppm

and 0.14 ppm respectively. Calculated Pb values are consistent with Pb concentrations reported by McDonough and Sun (1995) for pyrolitic mantle $(Pb_{py} = 0.15 \text{ ppm})$, whereas Th concentrations are somewhat higher $(Th_{py} = 0.079)$.

The second modeled component is subducted pelagic and hemipelagic sediments. The trace element and isotopic composition of this component is based on analyses of sediments drilled at DSDP Site 495 (shown in Figure 1.1) (Pb = 7.36 ppm; Th = 0.93 ppm; 206 Pb/ 204 Pb = 18.58; 208 Pb/ 204 Pb = 38.37; Plank and Langmuir, 1998; Feigenson et al., 2004).

The third modeled component is the forearc ophiolites removed via subduction erosion. An average of trace element and Pb isotopic values from the Nicoya ophiolites (Pb = 0.27 ppm; Th = 0.30 ppm; 206 Pb/ 204 Pb = 19.28; 208 Pb/ 204 Pb = 38.95) are used for this component as this is the largest forearc ophiolite complex and is situated directly outboard of the enriched Costa Rican arc lavas.

The resultant mixing model shown in Figure 1.7 illustrates that the enriched Pb isotopes in the Costa Rican lavas cannot be explained by mixing of enriched mantle and sediments alone. A source enriched in both ²⁰⁶Pb and ²⁰⁸Pb like the forearc ophiolites and/or mafic Galápagos-derived CLIP basement that likely underlies the volcanic arc is needed. The calculations show that subducted sediments can contribute no more than ~ 1-2 % of the mass of Pb in the Costa Rican arc lavas and that the lavas with the most enriched isotopic signature could be dominated (95 %) by forearc Pb. If the most radiogenic Nicoya samples are used in Figure 1.7 as the forearc component (²⁰⁶Pb/²⁰⁴Pb = 19.85 and ²⁰⁸Pb/²⁰⁴Pb = 39.85) rather than the averaged value, the entire range of Pb values in Costa Rican lavas can be modeled by variable mixtures of ~ 1-2 % sediments, 0-60 % forearc material, and 0-99 % ambient mantle.



Figure 1.7 Graph of ²⁰⁶Pb/²⁰⁴Pb vs. ²⁰⁸Pb/²⁰⁴Pb ratios showing results of 3component Pb isotope mixing model of enriched Costa Rican arc lavas. Chemical and isotopic values for various sources include: (1) enriched mantle (blue square) represented by the most enriched La Providencia backarc basalts (Feigenson et al., 2004), (2) subduction erosion component (red circle) estimated by the average of Nicoya complex forearc ophiolites (Hauff et al., 2000b), and (3) subducted sediments (yellow triangle) from DSDP Site 495 sediments (Plank and Langmuir, 1998; Feigenson et al., 2004). Costa Rican arc lavas with enriched Pbisotopic signatures (Platanar, Arenal, Barva, and Irazú) are shown with black crosses and grouped within the grey field. Calculated mixing lines are for 1 %, 3 %, and 5 % mixing of DSDP 495 sediments. Numbers and ticks show mixing between enriched mantle and forearc components.

Table 1.1

Table 1.1							
Input parameters for the Pb-isotope mixing model of enriched Costa Rican Arc lavas							
	X _{total}	Pb (ppm)	Th (ppm)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb		
Eroded Forearc ^a	0-1.0	0.27	0.31	19.28	38.95		
Ambient Mantle ^b	0-1.0	0.15	0.14	19.05	38.58		
Pelagic Sediments ^c	< 0.05	7.36	0.93	18.58	38.37		
Total	1.0						

^aForearc ophiolite (average of Nicoya ophiolitic complex samples (Hauff et al., 2000b)) ^bAmbient mantle represented by the most radiogenic of analyzed La Providencia backarc lavas (Feigenson et al., 2004)

^cDSDP 495 sediment (Plank and Langmuir, 1998; Feigenson et al., 2004)

Subducted alkaline seamounts like those of the Costa Rican seamount province west of the Cocos Ridge are another potential source with elevated $^{206}Pb/^{204}Pb$ ratios (Figure 1.1). Whereas this province has enriched Pb isotopes (Hoernle et al., 2000; Werner et al., 2003), it is unlikely that flux melting of spatiallylimited bathymetric features is the source of radiogenic Pb in central Costa Rican lavas (e.g., Volcán Platanar). A hydrous melting model (10 % H₂0, 1200 °C, 3 GPa, cpx/garnet at 50/50 modal composition, partition coefficients from Green et al. (2000)) of the Costa Rican seamounts generates highly alkaline melts with extremely steep REE patterns (La/Yb = ~ 330 and ~ 52 for 10 % and 50 % melt respectively) and super-enrichment in incompatible element concentrations (Ba and Sr = ~ 1100 ppm for 50 % melt). These modeled melts are unlike the arc lavas from central Costa Rica (La/Yb < 35, Sr = 300-900 ppm; Carr et al., 1990; Cigolini, 1998) and therefore cannot be the source of these magmas.

Forward Mass Balance

The relatively low concentrations of Pb (typically < 1 ppm) in forearc ophiolites raises the question as to if there is enough Pb transported into the mantle via forearc subduction erosion to control the Pb isotopic ratio of the erupted arc lavas. The forward mass balance model for the Costa Rican arc shown in Table 1.2 and discussed below demonstrates that the total amount of forearc Pb subducted approaches the total mass of Pb erupted.

The calculation of the input flux illustrates that over half (61-65 %) of the mass of crustal Pb delivered to the arc wedge could be from forearc subduction erosion. Using the subduction erosion flux of 107-123 km³my⁻¹km⁻¹ for the last 6 Ma from Vannucchi et al. (2003), an average forearc ophiolite Pb concentration of 0.50 ppm (Hauff et al., 2000b), and a crustal density of 2.95 g/cm³; the amount of forearc Pb

subducted into the sub-arc mantle in the last 6 Ma ranges from 9.5×10^{11} to 11.1×10^{11} g/km. In comparison, using a sediment delivery rate of 16.9 km³m.y.⁻¹km⁻¹ (Clift and Vannucchi, 2004), an average Pb concentration of 7.36 ppm in hemipelagic mud and pelagic carbonates from DSDP Site 495, an average sediment density of 1.62 g/cm³, and an average pore water content of 48.69 wt % (Plank and Langmuir, 1998), the amount of sediment-derived Pb is estimated to be 5.9 $\times 10^{11}$ g/km. It is important to note that the isotopic mixing model discussed above (Figure 1.7) clearly shows that the proportion of sediment-derived Pb in the Pb budget is negligible. The total Pb input in the last 6 Ma along the Costa Rican margin is then approximately 15.0-17.0 $\times 10^{11}$ g/km.

The calculation of the outgoing Pb flux assumes an average Costa Rican arc magma production rate of 108 km³m.y.⁻¹km⁻¹ (Clift and Vannucchi, 2004) for the same 6 Ma period and a basalt density of 2.90 g/cm³. Given a Pb concentration of 1 ppm for an undifferentiated magma in equilibrium with enriched Central American mantle, the Pb output flux would be 18.8 x10¹¹ g/km. The Pb concentration of the undifferentiated magma is slightly less than that reported for a suite of mafic arc basalts from Nejapa Volcano in Nicaragua (Pb = 1.23-1.34 ppm; SiO₂ < 48 %; MgO 9-11 %; FeO 11.28-11.53 %; Cr > 300 ppm, Ni > 140 ppm; Walker, 1984; Walker et al., 2001). Only 10-18 % of the calculated output Pb is unaccounted for by sediment subduction and forearc subduction erosion processes. When compared to the input fluxes, over half (~ 50-55 %) of the Pb recycled to the Costa Rican crust via subduction zone volcanism during the last 6 Ma can be explained by Pb added to the mantle wedge from subducted forearc ophiolite.

Compared to the isotopic model, the forward mass balance appears to overestimate the proportions of sediment mixed into the Costa Rican magma source (30 % of total output Pb). The mass of sediment calculated from the forward model

reflects a maximum of sediment delivered to the trench as constrained by erosion rates and subduction fluxes. This value is limited by the Pb isotopic model that shows no more than 1-2 % sediment is mixed into the source of the Costa Rican arc lavas. Therefore, the bulk of these sediments must be underplated beneath the lower slope of the Costa Rican forearc and are ultimately not delivered to the mantle source. Morris et al. (2002) arrived at the same conclusion in explaining the lower ¹⁰Be concentration in Costa Rican lavas than in Nicaraguan lavas to the north. Additional evidence for sediment underplating below Costa Rica comes from seismic reflection data showing thrust ramps and changes in stratigraphic level of the basal detachment (Shipley et al., 1992). Alternatively, sediments subducting below Costa Rica could contain more radiogenic Pb than those subducting below Guatemala, though no isotopic data yet exists for these sediments.

Considering that subduction erosion may transport hydrothermally-altered segments of the lower forearc wedge into the subduction zone, average Pb concentrations of fresh Nicoya complex lavas (Hauff et al., 2000b) may not accurately reflect the Pb concentration of tectonically-transported Nicoya complex chloritized basalts and serpentines. To explore this potential problem, a Th mass balance is shown in Table 1.2 in addition to the Pb balance. Since Th is virtually immobile in aqueous fluids, the average Th concentration in altered Nicoya basalts should reflect that of the unaltered Nicoya parent (0.36 ppm; Hauff et al., 2000b). Using the same boundary conditions as in the Pb mass balance, the total Th input is 8.61 x 10^{11} g/km (7.9 x 10^{11} g/km from subduction erosion and 0.74 x 10^{11} g/km from subducted sediments) and the total magmatic output is 5.4 x 10^{11} g/km. As with Pb, mass balance shows that Th in the mantle is dominated by Th delivered to the wedge via subduction erosion.

To und Th for ward mass out	lunee model for	eosta relean are la	T CLO						
INPUT FLUXES	Element ^a	Erosion Flux ^d	Period ^e	Erosion Flux	Density ^f	Erosion Flux	Element Flux		
Subduction Erosion	ppm	km ³ /my km	m.y.	km ³ /km	g/cm ³	g/km	g/km	% of Input	% of Output
Pb	0.5	123	6	738	2.95	2.18E+18	1.11E+12	65	59
Th	0.36	123	6	738	2.95	2.18E+18	7.86E+11	91	140
	Element ^b	Sediment Flux ^d	Period ^e	Sediment Flux	Density ^f	Sediment Flux	Element Flux		
Sediment	ppm (wet)	km ³ /my km	m.y.	km ³ /km	g/cm ³	g/km	g/km	% of Input	% of Output
Pb	3.58	16.9	6	101.4	1.62	1.64E+17	5.89E+11	35	31
Th	0.45	16.9	6	101.4	1.62	1.64E+17	7.40E+10	9	13
						Total input	g/km		
						Pb	1.68E+12		
						Th	8.61E+11		
		Magma		Magma					
OUTPUT FLUXES	Element ^c	Productivity ^d	Period ^e	Productivity	Density ^f	Magma Flux	Element Flux		
Mantle-derived basalt	ppm	km ³ /m.y./km	m.y.	km ³ /km	g/cm ³	g/km	g/km		
Pb	1.0	108	6	648	2.9	1.88E+18	1.88E+12		
Th	0.3	108	6	648	2.9	1.88E+18	5.64E+11		

Table 1.2

Ph and Th forward mass balance model for Costa Rican arc layas

^aTrace element concentrations for forearc ophiolites are averages of concentrations reported by Hauff et al. (2000b).

^bDry sediment trace element concentrations are from DSDP Site 495 (Carr et al., 1990; Plank and Langmuir, 1998) and wet sediment concentrations are calculated using 48.69 % H₂O (Plank and Langmuir, 1998).

^cMantle-derived melt elemental concentrations are similar to average of Nejapa (Nicaragua) basalts (Walker, 1984).

^dEstimates for subduction erosion flux from Vannucchi et al. (2003). Sediment flux and magmatic productivity are from Clift and Vannucchi (2004).

^eVannucchi et al. (2003) report an enhanced subduction erosion rate over the last 6 Ma.

^fDensities for subducted sediments from Plank and Langmuir (1998). Slightly higher densities in forearc lavas compared to basalt (2.90 g/cm³) reflect the presence of ultramafic lavas within the Nicoya complex.

The Pb and Th balance above is consistent with the proportions of Nicoya complex basement (30 to 80 %) relative to subducted sediment mixed into the parental melt of Costa Rican arc lavas estimated by Clift et al. (2005). During transient periods of heightened subduction erosion, Clift et al. (2005) estimate that over 80 % of the downgoing material above the subducted plate comes from forearc basement. At these times, the flux of forearc Pb and Th into the melt zone would potentially dominate the Pb and Th budget within the mantle wedge. The output Pb not accounted for by subduction of mafic forearc material or pelagic sediments (10-18 %) could be from the ambient mantle and/or the *in situ* crust. In sum, despite low Pb and Th concentrations in forearc ophiolites, a continual flux of forearc basement into the sub-arc mantle is a possible mechanism for changing the Pb-isotopic signature of the southern Central American mantle source.

Adakite Genesis and Subduction Erosion

The adakitic trace element signatures in some southern Costa Rica/Panama arc volcanic rocks can be also be explained by introduction of mafic forearc crust into the mantle wedge by subduction erosion. To generate the characteristic steep REE patterns of adakitic lavas, heavy REE need to preferentially partition into garnet in a high-pressure feldspar-poor residual mineral assemblage, leaving the magma depleted in these elements and enriched in Sr. Some adakites, like those in the southernmost Andes are possible slab melts (Kay et al., 1993; Stern and Killian, 1996), but most adakites are unlikely to originate in this way. In the central Andes and regions with a thickened crust, the adakitic signature can be explained as garnet becomes stable in mafic compositions at crustal depths >50 km (e.g., Kay et al., 1987; Hildreth and Moorbath, 1988). In the absence of a thick crust, such as in southern Central America, transport of forearc crust into the mantle wedge during periods of increased

subduction erosion can explain the transient existence of adakites as argued for the south central Andes by Kay and Mpodozis (2002) and Kay et al. (2005).

All previous models for Central American adakites are in some way related to slab melting. Most recently, Bindeman et al. (2005) used oxygen isotopic data to argue against a slab melting model that relies on top-down conductive heating of the subducting Cocos and Nazca slabs. They show that the Panamanian adakites $(\delta^{18}O_{olivine} = 5.08-5.88 \%; \delta^{18}O_{parental melts} = 6.36-6.95 \%)$ cannot solely be derived from melting of the upper 1-2 km of subducting slab and sediments ($\delta^{18}O = 7-15 \%$) or the hydrothermally-altered lower oceanic crust and peridotite of the slab interior ($\delta^{18}O = 0.6 \%$). As an alternative, they propose melting of a mixture of upper oceanic crust with high $\delta^{18}O$ and the slab interior with low $\delta^{18}O$ slab to produce a final value slightly greater than MORB. They recognize that this is only possible if the slab is delaminated or torn. Earlier, Abratis (1998) proposed slab-window induced melting at various depths within the altered Cocos Ridge edge to explain slightly higher $\delta^{18}O$ values in the Talamancan adakites ($\delta^{18}O_{parental melts} = 6.77-7.23 \%$).

The oxygen isotope data from < 4 Ma adakites can also be explained in terms of forearc subduction erosion. As no oxygen isotope data exists for the Nicoya complex and its equivalents in Costa Rica and Panama, the argument below comes from whole rock oxygen isotope data from a 7000 m thick profile of Samail ophiolite in Oman (Gregory and Taylor, 1981; Bosch et al., 2004). These values range from δ^{18} O values of 7.5-12 ‰ for the top 1 km of hydrothermally-altered upper crust to as low as 4 ‰ for the gabbroic lower crustal section yielding a depth-integrated average similar to MORB (δ^{18} O = 5.7 ± 0.2). If the obducted Panamanian forearc complexes have an oxygen isotope profile like the Samail ophiolite, then melting of eroded upper and lower segments of forearc mafic complexes could explain the MORB-like δ^{18} O character of the Panamanian adakites. The higher δ^{18} O in the Talamancan adakites

could reflect melting of a more altered segment of oceanic forearc crust related to underthrusting of the Cocos Ridge. A similar argument can be used to explain MORB-like δ^7 Li (+1.4 to +4.2) values in the Panamanian adakites that are inconsistent with melting of the upper 1 km of ocean crust that has substantially interacted with seawater (δ^7 Li = +32) (Tomascak et al., 2000).

Recent support for slab melting in Central America has come from new thermal modeling of the Costa Rican subduction zone by Peacock et al. (2005). Using an olivine-mantle wedge rheology at 3 GPa, these authors calculate slab-mantle interface temperatures of 805 °C for Nicaragua, 791 °C for NW Costa Rica, 804 °C for Central Costa Rica, and 818 °C for SE Costa Rica. These temperatures are 150-180 °C higher than slab-mantle interface temperatures they calculated using an isoviscous mantle rheology. On the basis of the higher temperatures, Peacock et al. (2005) argue that the uppermost 500 m of the subducting slab in central to southeastern Costa Rica could undergo substantial anhydrous partial melting at depths of ~ 100 km. Such a slab melting model leaves a number of observations from the Central American arc unexplained. These include: 1) a lack of lavas from central Costa Rica with adakitic geochemical signatures, 2) the sudden appearance of adakitic volcanism at < 4 Ma in southeastern Costa Rican and south central Panama, and 3) isotopic evidence [²⁰⁶Pb/²⁰⁴Pb (Abratis and Wörner, 2001); δ^{18} O; (Bindeman et al., 2005), and δ^7 Li (Tomascak et al., 2000)] at odds with a conductive top-down slab heating model for the adakites.

The alternative to a slab melting model to explain the Central American adakites is that the source region of these magmas includes forearc material that has been removed by subduction erosion and subjected to eclogite facies metamorphism. Modeling of the enriched Pb isotopic signatures in the Talamancan adakites (Figure 1.4) supports this model. Using the same modeling technique as for the enriched Costa Rican arc lavas, a mixing model for the Talamancan adakites is shown in Table 1.3. A mixture of Pb derived from 95 % forearc ophiolite, 4.5 % ambient mantle, and 0.5 % DSDP sediment generates Pb-isotopic ratios that match those of the Talamancan adakites.

Table	1.3
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Multi-component Pb-isotope mixing model of Talamancan adakites								
	X _{total}	Pb (ppm)	Th (ppm)	% Pb of Total	% Th of Total	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	
Eroded Forearc ^a	0.95	0.50	0.36	0.916	1.287	19.20	38.85	
Ambient Mantle ^b	0.045	0.15	0.14	0.013	0.024	19.31	38.73	
Pelagic Sediments ^c Total	0.005 1.00	7.36	0.93	0.071	0.017	18.58	38.37	
						²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	
Modeled output						19.16	38.81	
Average of Talamancan adakites ^d						19.16	38.83	

^aForearc ophiolite (average of Burica, Golfito, Osa, and Quepos ophiolitic complexes (Hauff et al., 2000b))

^bAmbient mantle represented by Bribri backarc lavas (Abratis and Wörner, 2001)

^cDSDP 495 sediment (Plank and Langmuir, 1998; Feigenson et al., 2004)

^d Average of Pb isotopic ratios from Talamancan adakites (Abratis and Wörner, 2001)

Subduction Erosion Model

The general model for incorporating forearc crust from subduction erosion into the mantle source of Central America is shown in Figure 1.8a. The model, which is based on that of von Huene et al. (2004), invokes collapse and accommodation of upper plate material into trench-parallel grabens formed by plate bending stresses and subsequent normal faulting. This smoothes the slab-mantle interface and creates a subduction channel décollement approximately 1 km above the grabens. Eroded forearc crust transported to mantle depths in the channel would stabilize garnet as the **Figure 1.8** (A) Schematic illustration showing the general model of subduction erosion adapted from von Huene et al. (2004) for the southeastern Costa Rican forearc. The active thrust interface progressively migrates upwards as hydro-fracturing disaggregates and transports collapsing forearc basement down into the subduction channel. Ultimately, forearc material moves into the melt zone of the asthenospheric mantle wedge within the subduction channel décollement.

(B) Cartoon showing a transect across the Central American arc through the Osa Peninsula and Cordillera de Talamanca during the Pliocene (~ 4 Ma). Cocos plate subduction geometry is based on seismic imaging of Wadati-Benioff zone (Protti et al., 1995) and forearc (< 50 km depth) (Sallarès et al., 2001). Subduction velocity from DeMets (2001) and Cocos plate lithospheric thickness (35 km depth at 1300 °C isotherm) obtained from half-space cooling of 10 Ma slab. Slab-surface temperatures given from Peacock et al. (2005) using an isoviscous mantle wedge rheology model. Subduction channel model adapted from Cloos and Shreve (1988). The hatched forearc area represents the calculated amount of forearc eroded in the last 6 Ma (~ 50 km arc retreat) (Alvarado et al., 1993; Meschede et al., 1999a; Vannucchi et al., 2003). Crustal geology adapted from Kolarsky et al. (1995). Inset schematic of forearc material transported into hotter overriding asthenospheric mantle wedge modified from von Huene et al. (2004).





crust is subjected to eclogite-facies metamorphism. Forearc material will partially melt as it enters the sub-arc asthenosphere thus contaminating the mantle source below Costa Rica and Panama (Figure 1.8b). In a manner similar to that suggested for the central Andes (Kay et al., 2005), the increase in subduction erosion rate during the last 6 Ma along the Central American margin could have overloaded the mantle wedge with this forearc material. Low degrees of partial melt from this source would dominate the adakitic lavas that reached the surface along the arc during this period. This model provides an alternative mechanism to explain the < 4 Ma episode of adakitic magmatism in the Cordillera de Talamanca and throughout west-central Panama.

Constraints and Limitations

Although the proposed subduction erosion model is a viable alternative to previous models, the source of the enriched Pb in the Central American lavas cannot be definitively constrained as the mantle, lower crust, and eroded forearc could all have similar Pb isotopic signatures.

Backarc lavas with elevated Pb-isotopic ratios and OIB-like geochemical characteristics in southern Central American arc lavas clearly show the presence of an enriched mantle below Costa Rica. While Pb-isotopic modeling indicates that the enriched Costa Rican arc lavas require a source similar to forearc ophiolites, the subduction erosion model does not explain the enriched Pb isotopic ratios in the backarc lavas. As suggested by Feigenson et al. (2004), a viable alternative is that plums of Galápagos mantle with Pb isotopic ratios similar to the forearc ophiolites exist below the southern Central American arc. These authors note a general correlation between the isotopic heterogeneity of the Central American subarc mantle to the isotopic provinces of the Galápagos hotspot. Melting of enriched mantle plums

via subduction-fluid fluxing or from back-arc upwelling could also explain the enriched isotopic ratios in both arc and backarc lavas. However, this model offers no explanation for < 4 Ma arrival of adakitic magmatism with enriched Pb isotopic signatures.

Geophysical and chemical data indicate that mafic Caribbean oceanic crust extends below the Costa Rican volcanic front (Sallarès et al., 1999; Hoernle et al., 2004). Assimilation of this lower-crust could impart Galápagos-like Pb isotopic signatures on the central Costa Rican lavas while producing the observed flat REE patterns and low Sr contents characteristic of the enriched Costa Rican arc lavas. Simply stated, the Pb-isotopic signature of lower crustal contamination may be indistinguishable from source contamination by forearc ophiolites. In contrast, contamination by this lower crust alone cannot explain the temporal shift to higher La/Yb and Sr/Y ratios in < 4 Ma Talamancan and Panamanian adakites. The appearance of adakites at 4 Ma with elevated 206 Pb/²⁰⁴Pb and 208 Pb/²⁰⁴Pb ratios suggests the Pb-isotopic signatures in volcanic front lavas are not controlled by preestablished mantle heterogeneities or the *in situ* crust but are better explained by a post-Miocene increase in subduction erosion rate.

VI CONCLUSIONS

Given the thin crust and low ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios of subducted Cocos plate basalts, transient adakitic geochemical signatures in southern Central American lavas are best explained by partial melting of tectonically-eroded forearc crust incorporated into the mantle wedge. Along-arc variations in Pb isotopic ratios correspond to isotopic patterns in Cretaceous and Tertiary ophiolites obducted onto the forearc of the southern Central American margin. Pb isotopic signatures in modern volcanic front lavas indicate source contamination with an enriched mantle component likely derived from the Galápagos hotspot plume. A potential radiogenic Galápagoslike source that spans the entire along-arc length of erupted magmas with elevated 206 Pb/ 204 Pb and 208 Pb/ 204 Pb ratios is the mafic forearc basement. Isotopic modeling of Costa Rican calc-alkaline arc lavas and < 4 Ma adakites with enriched Pb-isotopic signatures supports a subduction erosion source for the radiogenic Pb. Using established rates of subduction erosion along the Central American margin, mass balance calculations confirm that enough radiogenic forearc Pb has been transported into the mantle wedge in the past 6 Ma to sufficiently alter the isotopic character of the sub-arc mantle.

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CHAPTER 2

CENTRAL ANDEAN ADAKITES FROM THE NORTHERN EDGE OF THE CHILEAN FLATSLAB (27-28.5° S) ASSOCIATED WITH ARC MIGRATION AND FOREARC SUBDUCTION EROSION

ABSTRACT

Along the northern edge of the Chilean flatslab region (27°-28.5° S) in the Central Andes, the Pircas Negras (7-2 Ma) and Dos Hermanos (~ 7.7 Ma) andesites define a suite of glassy plagioclase phenocryst-free lavas that erupted spatially and temporally coincident with ~ 50 km of eastward frontal arc migration. These lavas are distinguished from early-middle Miocene and Quaternary andesites at the same latitude by greater HFSE depletion (La/Ta = 40-100; Ba/Ta=800-2400) and a pronounced adakitic character (La/Yb = 25-60; Sm/Yb = 5-9; Sr = 600-1400 ppm; Sr/Yb = 400-1300). During the height of arc migration, 5 to 3 Ma Pircas Negras lavas exhibit high-Mg numbers (Mg # = 50-61) and elevated Cr and Ni concentrations (Cr = 100-250 ppm; Ni = 40-70 ppm). More radiogenic 87 Sr/ 86 Sr ratios in the Pircas Negras andesites (0.7055-0.7065) compared to early-middle Miocene andesites (0.7048-0.7054) parallel a similar trend in Neogene mantle-derived southern CVZ basalts. These geochemical trends are best explained by contamination of the sub-arc mantle with crustal material eroded from the Chilean forearc followed by interaction of mantle-derived magmas with thickened continental crust. An isotopic mixing model shows that the contamination of the mantle wedge can be explained by partial melting of tectonically-eroded forearc material composed of 80-90 % Jurassic arc gabbros and cumulates and 10-20 % sialic Paleozoic crust. Mixing percentages are consistent with compositional estimates of the Chilean forearc from field and geophysical data. Adakitic melts generated at high pressures (> 2 GPa) in the mantle wedge reacted with mantle peridotite to produce high Mg #s and Cr and Ni concentrations. Pyroxene mineral equilibria and modeling using MELTS indicate that the Pircas Negras magmas had pre-eruptive temperatures of 1040-1080 °C. These *hybridized* adakitic melts then mixed with melts largely derived from anatexis of *in situ* eclogitic lower crust. Assuming a constant arc-trench gap over the last 8 Ma, $\sim 124 \text{ km}^3/\text{m.y./km}$ of crustal material needs to have been removed from the forearc to account for the late Miocene frontal arc migration. This material was thus available to contaminate the mantle wedge.

I INTRODUCTION

Continental subduction zones represent the only tectonic setting where continental crust is concurrently produced and consumed through the same tectonic process. The presence of an arc signature (low HFSE, elevated LREE and LILE) in bulk estimates of average continental crust (e.g., Rudnick and Fountain, 1995) suggests an important role for arc volcanism in generating primary continental crust, with lesser percentages from basaltic underplating and accreted oceanic crust (Rudnick, 1995). Moreover, the similarity of these estimates to compositions of high-Mg andesites, many with adakitic geochemical signatures, has led some authors to propose high pressure anatexis of mafic oceanic crust as a significant mechanism for crustal growth (Kelemen et al., 2003a). Processes responsible for the destruction of continental crust at convergent margins are less understood with lower crustal delamination (Kay and Kay, 1991; 1993; Jull and Kelemen, 2001), subduction of terrigeneous sediments (e.g., Armstrong, 1968; Kay et al., 1978; White and Dupré, 1986; Plank and Langmuir, 1998), and forearc subduction erosion (e.g., von Huene and Scholl, 1991; Ranero and von Huene, 2000; von Huene et al., 2004) as the dominant mechanisms. Tectonic processes controlling the destruction of the
continental crust have largely been decoupled from creation of new crust, with net crustal growth (or loss) a composite function of two independently operating processes.

A model of high-Mg adakite genesis (Mg #s 50-60) linked directly to accelerated forearc subduction erosion along the Andean margin provides a co-genetic relationship between generation and destruction of continental crust along convergent margins. Forearc margins characterized by net erosion such as the Central Andes (e.g., von Huene et al., 1999; von Huene and Ranero, 2003) and southern Central America (e.g., Vannucchi et al., 2001) may represent locations of large-scale crustal recycling as eroded forearc material is reprocessed as high-Mg andesite within the mantle wedge. At arcs worldwide, high-Mg adakites are rare and volumetrically minor components of the total magma erupted, leading to the conclusion that either small volumes of high-Mg magma are produced in or near the mantle wedge or that significant upper crustal processes (i.e., fractional crystallization and/or crustal assimilation) overprint the primary high-Mg adakitic signature.

In this paper, we present major and trace element analyses, isotopic data, and mineral chemistry for late Miocene to Pliocene adakitic andesites from the northern transition zone of the Chilean flatslab of the central Andes (Figure 2.1; 27°-28.5° S). These glassy hornblende phenocryst-dominated andesites erupted coincident with the eastward migration of the frontal arc between 7-4 Ma (Kay et al., 1999; Kay and Mpodozis, 2002; Goss et al., Chapter 4). The *transient* eruption of Andean high-Mg andesites with steep REE patterns, extreme HFSE depletion, and elevated Sr, Ni, and Cr contents is interpreted in the context of experimental data and models of adakite genesis. Mafic crust eroded from the forearc during short-lived periods of arc instability can explain the rapid frontal late Miocene arc migration along this section of the Andean margin. Isotopic modeling of mafic lavas shows that partial melting of



Figure 2.1 SRTM digital elevation model of the Central Andes showing main morphotectonic features. Nazca plate convergence direction is the long-term integrated NUVEL-1 rate from DeMets et al. (1990). Dark solid lines show contours of the subducting Nazca plate (Cahill and Isacks, 1992) with depths in kilometers to the Wadati-Benioff zone. Small yellow circles show late Miocene to Recent volcanic centers of the Andean Central (CVZ) and Southern (SVZ) Volcanic Zones. The blue box gives the approximate position of the early to late Miocene Maricunga belt volcanic arc (Kay et al., 1994b; Mpodozis et al., 1995). C = Volcán Copiapó (11-8 Ma). Open red boxes show (1) the general spatial extent of Pircas Negras adakitic andesites (Figure 2.2) and (2) the Ojos del Salado region of the southernmost CVZ (Figure 2.4).

eroded forearc material in the sub-arc mantle can explain the temporal nature of the adakitic trend and the progressive isotopic enrichment of Neogene mantle-derived basalts from the southernmost central volcanic zone (CVZ). This model is analogous to that presented for other temporally-restricted pulses of adakitic volcanism in erosive margins such as in the southern Andes (Kay et al., 2005) and in southeast Central America (Goss and Kay, 2006a).

II GEOLOGICAL SETTING

Andean tectonics

The Andean Cordillera is the type example of an orogenic mountain belt formed from the subduction of an oceanic plate below a continental margin (Figure 2.1). Beginning in the early-mid Jurassic, subduction of Pacific (Farallon) oceanic crust below the western Gondwana margin resulted in the formation of intrusive and extrusive arc sequences that now comprise much of the Coastal Cordillera along the Chilean forearc (Mpodozis and Ramos, 1989). Along the central and southern Andes (21°-40° S), progressive stages of Mesozoic volcanism migrated into the foreland with arc sequences becoming younger to the east (e.g., Mpodozis and Ramos, 1989). The deformation, uplift, crustal thickening, and magmatism associated with the modern Andes commenced in the late Oligocene with the breakup of the Farallon plate into the Nazca and Cocos plates (Pilger, 1984; Pardo-Casas and Molnar, 1987). This major kinematic reorganization at ~ 26 Ma resulted in accelerated subduction of the Nazca plate, a 40° change in convergence direction (Pardo-Casas and Molnar, 1987; Somoza, 1998), and re-initiation of arc magmatism along the margin. During the late Miocene, convergence slowed (Somoza, 1998), rapid uplift of the Puna-Altiplano plateau ensued (e.g., Isacks, 1988; Kay et al., 1999; Garzione et al.,

2006), and Laramide-style structural deformation spread deeper into the Andean foreland (Jordan et al., 1983).

Global plate motion models indicate that over the last 3 m.y. the Nazca plate has subducted below South America at an average rate of 84 mm/a at an azimuthal convergence direction of 075° N (DeMets et al., 1990). Below the Puna-Altiplano plateau (Figure 2.1; 20°-25° S), the Nazca plate is subducting at ~ 30°. To the south, the subducting plate gradually shallows in the backarc resulting in near-horizontal subduction at 100-125 km depth below the Argentine Precordillera and Sierras Pampeanas (Barazangi and Isacks, 1976; Cahill and Isacks, 1992). The Chilean flatslab region (28°-33° S; Figure 2.1) corresponds to a 500 km wide zone of intense crustal seismicity (Smalley and Isacks, 1990; Pardo et al., 2002), thick-skinned deformation with basement uplifts (Jordan et al., 1983), and a ~ 700 km gap in active arc volcanism along the margin extending from Ojos del Salado (26° S), the southernmost active volcanic center of the Central Volcanic Zone (CVZ), to Tupungatito (33° S), the northernmost active center of the Southern Volcanic Zone (SVZ).

The extent of Pircas Negras andesitic volcanism within the northern flatslab transition zone between 27°-28.5° S is shown on Figure 2.1. Late Miocene to Pliocene eruptions of the Pircas Negras andesites marked the terminal stages of mafic volcanism within the southernmost CVZ.

Crustal structure and composition

The thickness of the crust below the northern flatslab transition zone has a profound impact on the petrogenesis of the Pircas Negras andesites. The crustal structure of the Central Andes is a product of Neogene crustal shortening and structural thickening with known crustal thicknesses below the Puna ranging from 42-67 km (James, 1971; Isacks, 1988; Yuan et al., 2002; Heit, 2005). South of the transition zone, crustal thicknesses across the flat slab region at $\sim 30^{\circ}$ S (Figure 2.1; Fromm et al., 2004) reach a maximum of 62 km below the Frontal Cordillera. In the transition region between the southernmost Puna and the northern flatslab (25° to 30° S), there are few constraints on crustal thickness or composition. McGlashan et al. (2007), using depth phase precursors (pmP-phase), calculated a crustal thickness of 70 km at 28° S in the region of Pircas Negras volcanism.

There is limited outcrop of basement rocks within the region of Pircas Negras volcanism and no lower crustal or mantle xenoliths have been reported. Late Proterozoic gneisses and schists exposed east of the region in the Sierras de Toro Negro extend as far west as Las Tamberias near Cerro Bonete Chico (Figures 2.1 and 2.2; Caminos and Fauqué, 2000). East of Bonete Chico, deformed Carboniferous-Permian sedimentary units overlay Proterozoic metamorphic sequences. The Choiyoi Permo-Triassic granite-rhyolite province that extends from 21° S to 42° S (e.g., Mpodozis and Kay, 1992) is exposed south of Quebrada Veladero and all along the western side of the Rio Salado/Macho Muerto (Figure 2.2a). Kay et al. (1989) interpreted these rocks to record a large-scale crustal melting event associated with massive basaltic underplating following the break-up of Gondwana. Figure 2.3a shows an outcrop of Pircas Negras andesite at Paso Pircas Negras (location on Figure 2.2a) that intruded through and erupted on top of Choiyoi complex units. Like much of the Central Andes, Grenvillian age (~ 1.1 Ga) lower crust capped by a thick felsic Paleozoic and Permo-Triassic (Choiyoi) upper crust likely defines the structure of the crustal basement underlying the Pircas Negras andesites.

Figure 2.2 (A) Thematic Mapper satellite imagery of the Andean northern flat slab transition zone (27°-28.5° S) south of the Valle Ancho showing major volcanic centers. Dashed line shows international road through the Paso Pircas Negras.

(B) Map showing volcanic centers erupting during the 9-7 Ma pre-migration stage. Dos Hermanos and Pircas Negras-like lavas are mapped in dark grey. Ages are given in Table 2.2.

(C) Map showing volcanic centers erupting during the 7-3 Ma synmigration stage. Pircas Negras lavas are mapped in dark grey. Ages are given in Table 2.2. Dacites and rhyolites of the late Maricunga belt (e.g., Jotabeche) and late Miocene-Pliocene arc (e.g., Pissis, Bonete, and Veladero) are mapped in white.

(D) Map showing volcanic centers erupting during the 3-2 Ma post-migration stage. Pircas Negras lavas are mapped in dark grey. Ages are given in Table 2.2. Ignimbrites and domes of the 3-1 Ma Incapillo volcanic complex (Goss et al., Chapter 4) are mapped in white.



Figure 2.2 (continued)



Figure 2.2 (continued)



Figure 2.2 (continued)





Figure 2.3 A) Photo looking west from the Paso Pircas Negras showing a 4.2 Ma Pircas Negras flow (CO 413 and CO 414 in Table 2.1) directly overlying Permo-Triassic Choiyoi rhyolite.

B) Photo looking east across the upper Rio Salado. Fluvial Miocene conglomerates and coarse sandstones are unconformably overlain by the 6 Ma Jotabeche ignimbrite, which is overlain by 1.9 Ma Pircas Negras flows. These Pircas Negras flows are capped to the north by rhyodacitic domes of the Incapillo volcanic complex.

III EVIDENCE FOR LATE MIOCENE ARC MIGRATION

The magmatic history of the northern flatslab region records a late Miocene episode of frontal arc migration that was contemporaneous with the peak of crustal thickening and slab shallowing. At this latitude, arc volcanism initiated within the Maricunga belt (Figure 2.1) following the breakup of the Farallon plate at ~ 26 Ma (Pardo-Casas and Molnar, 1987) and persisted until the late Miocene (~ 6 Ma). The Neogene magmatic history of the Maricunga belt has been discussed by Kay et al. (1994b) and Mpodozis et al. (1995). Based on geochemical characteristics, these authors proposed that early Miocene Maricunga belt lavas erupted over a moderately-dipping slab and through a ~ 35-45 km thick crust. Further south in the flat slab region, rhyodacitic ignimbrites of the Tilito Formation (27-20 Ma) were unconformably overlain by the mafic Escabroso Formation (21-18 Ma) basaltic andesites (Figure 2.2a; Maksaev et al., 1984; Kay et al., 1987; 1991; 1994b; Mpodozis et al., 1995; Martin et al., 1997). These two formations collectively constitute the Doña Ana Group. A period of contractional deformation and crustal thickening accompanied a regional lull in arc magmatism between 20-18 Ma.

Within the Maricunga belt, a second phase of arc magmatism occurred between 17-12 Ma with the eruption of large stratovolcanic complexes. This magmatic episode was contemporaneous with a period of crustal thickening and terminated with the emplacement of gold porphyry deposits. During the late Miocene (11-7 Ma), magmatism was concentrated in the southern Maricunga belt at the Copiapó stratovolcanic complex (Figure 2.1). Volcanic activity in the Maricunga belt terminated at ~ 6 Ma with the eruption of the rhyodacitic Jotabeche caldera complex and ignimbrite (Figures 2.2c and 2.3b). Trace element indicators suggest crustal thicknesses > 60 km below Jotabeche during the late-Miocene. The first Pircas Negras lavas erupted at ~ 8 Ma within the terminating Maricunga arc south of the Jotabeche complex.

Following the cessation of Maricunga belt magmatism at ~ 6 Ma, the arc front was displaced ~ 50 km to the east with the eruption of the Bonete Chico (5.2-3.5 Ma), Pissis (6.5-3.0 Ma), and Veladero (5.6-3.6 Ma) dacitic volcanic centers (Figure 2.2c; Kay and Mpodozis, 2000). Surrounded by these stratovolcanic centers, the explosive Incapillo caldera and dome field (~ 3.0-0.5 Ma) marked the termination of Plio-Pleistocene arc volcanism at this latitude (Figure 2.2d; Kay and Mpodozis, 2000; Goss et al., Chapter 4). The spatial and temporal relationship between the Pircas Negras andesites and the migrating late Miocene-Pliocene arc is outlined below. A list of all sampled locations with available K-Ar ages is presented in Tables 2.1 and 2.2.

IV AGE AND GEOGRAPHICAL DISTRIBUTION OF NORTHERN FLATSLAB REGION MAFIC LAVAS

The earliest Neogene andesites from the northern flatslab region are 21-18 Ma flows from the Escabroso Formation that define the early Miocene arc. Escabroso units are found within and immediately west of Paso Pircas Negras, along the Rio Macho Muerto in Argentina (Figure 2.2b), and further to the south along the Rio del La Sal into the flatslab region. They are absent from the magmatic record east of the Rio Salado. Mafic volcanism persisted in the southern Maricunga belt during the middle Miocene with the eruption of hornblende- and pyroxene-bearing andesites from the Jotabeche Norte (18-16 Ma; Kay et al., 1994b; McKee et al., 1994) and La Laguna (15-14 Ma; Kay et al., 1994b) stratovolcanic centers (Figure 2.2a). South of Jotabeche Norte, hornblende-bearing andesites of the Cadillal-Yeguas Heladas complex erupted as elongated domes and lava flows between 15-13 Ma.

Table 2.1										
Sampled N	leogene basalts and a	ndesit	es from tl	he norther	n flatslab	o transition zone (~27°-28.5°)				
sample	21-18 Ma Dona Ana	type	lat (DD)	lon (DD)	elev (m)	location				
CO 291	Escabroso	А	28.804	69.631	4505	Rio de la Sal				
CO 292	Escabroso	А	28.771	69.638	4945	Rio de la Sal				
CO 293	Escabroso	А	28.776	69.634	4864	Rio de la Sal				
CO 294	Escabroso	А	28.787	69.630	4772	Rio de la Sal				
CO 295	Escabroso	BA	28.868	69.641	4162	Rio de la Sal				
CO 296	Escabroso	А	28.869	69.647	4264	Rio de la Sal				
CO 297	Escabroso	А	28.887	69.646	3997	Rio de la Sal				
CO 300	Escabroso	BA	28.867	69.570	4278	east side Rio de La Sal				
CO 335	Escabroso	А	27.963	69.341	3460	near Paso Pircas Negras				
CO 446	Escabroso	BA	27.938	69.359	3350	near Paso Pircas Negras				
CO 264	Escabroso	А	28.537	69.513	4384	Rio Macho Muerto				
	Pre-Migraton	type	lat (DD)	lon (DD)	elev (m)	location				
CO 428	Dos Hermanos	А	27.626	69.080	4563	minor lower flow				
CC 81 ^c	Dos Hermanos	А	27.615	69.065	4991	upper flow				
CC 82 ^c	Dos Hermanos	А	27.620	69.073	4840	upper flow				
CC 83 ^c	Dos Hermanos	Α	27.623	69.073	4837	upper flow				
CC 94 ^a	Redonda	D	27.491	69.039	4488	base of Dos Hermanos				
AC 406 ^b	Pircas Nergras	D	28.117	69.326	4170	Rio Comecaballos				
CO 72	Los Aparejos	В	27.660	68.336	4455	W of Portuzuelo La Coipa				
CO 24	Los Aparejos	В	27.629	68.339	4547	NE of Laguna Los Aparejos				
	Syn-Migration	type	lat (DD)	lon (DD)	elev (m)	location				
	Jotabeche/Gallina									
CC 17 ^a	Pircas Negras	Α	27.733	69.196	5014	La Gallina dome				
CC 11 ^a	Pircas Negras	Α	27.599	69.174	4400	La Gallina dome				
CC 15	Pircas Negras	Α	27.825	69.288	4129	at Casale mine, lower				
CO 415	Pircas Negras	Α	27.819	69.285	4157	at Casale mine, upper				
CO 416	Pircas Negras	Α	27.864	69.269	3579	along road to Casale				
CO 427	Pircas Negras	А	27.773	69.165	4695	Rio Gallina, SE of Jotabeche				
AC 556 ^b	Pircas Negras	А	27.815	69.298	4139	at Casale mine, upper				
AC 619A	Pircas Negras	А	27.825	69.256	3920	along road to Casale				
AC 623A	Pircas Negras	Α	27.788	69.203	4233	Rio Gallina ridge				
AC 624A	Pircas Negras	Α	27.789	69.206	4332	Rio Gallina ridge				
AC 625A	Pircas Negras	Α	27.792	69.206	4321	Rio Gallina ridge				
AC 626P	Pircas Negras	А	27.795	69.209	4252	Rio Gallina ridge				
	Paso Pircas Negras									
CO412	Pircas Negras	А	28.069	69.300	4179	at border near lake				
CO413	Pircas Negras	А	28.063	69.307	4042	at border along pass				
CO414	Pircas Negras	А	28.010	69.297	3976	on ridge north of pass				
AC 408 ^b	Pircas Negras	А	28.069	69.289	4145	at border along pass				
AC 409 ^b	Pircas Negras	А	28.069	69.289	4133	at border along pass				

^aKay et al., (1994b); ^bKay et al., (1991); ^cTittler, (1995) B = basalt; BA = basaltic andesite; A = andesite, D = dacite

	ampled Neogene basalts and andesites from the northern flatslab transition zone (~27°-28.5°) Syn-Migration (continued) type lat (DD) lon (DD) elev (m) location											
Sampled I	Neogene basalts and a	indesit	tes from the	ie norther	n flatslab	transition zone (~2/°-28.5°)						
Syn-N	Migration (continued) type	lat (DD)	lon (DD)	elev (m)	location						
L0	Wer Rio Salaao & Pasi	autos	20.042	(0.1(2	1075	and side Die Cale Is						
CO 163	Pircas Negras	A	28.043	69.162	4275	east side kio Salado						
CO 170	Pircas Negras	A	28.388	69.128	3799	lower Rio Salado at Pastillos						
CO 172	Pircas Negras	A	28.304	69.209	3629	lower Rio Salado						
CO 173	Pircas Negras	Α	28.235	69.188	3905	lower Rio Salado						
CO 175	Pircas Negras	А	28.113	69.208	4069	Rio Peñas Negras						
CO 176	Pircas Negras	D	28.101	69.156	4033	east side Rio Salado						
CO 309	Pircas Negras	А	28.101	69.215	4176	near refugio on road						
CO 310	Pircas Negras	А	28.114	69.184	4119	east side Rio Salado						
CO 327	Pircas Negras	А	28.430	69.309	3890	east side lower Rio Salado						
CO 329	Pircas Negras	А	28.398	69.160	3705	lowermost Rio Salado						
CO 331	Pircas Negras	Α	28.409	69.104	4004	near refugio Pastillos						
CO 332	Pircas Negras	А	28.416	69.043	3989	east of Pastillos north of road						
CO 504	Pircas Negras	А	27.952	69.119	4450	upper Rio Salado						
CO 507	Pircas Negras	D	27.939	69.051	4747	below western Incapillo dome						
	Laguna Brava											
CO 159	Pircas Negras	А	28.268	68.874	4449	NW of Laguna Brava						
CO 160	Pircas Negras	А	28.309	68.804	4283	east shore of Laguna Brava						
CO 161	Pircas Negras	D	28.274	68.746	4131	Laguna Mulas Muertas						
CO 333	Pircas Negras	A	28 405	68 927	4436	south shore of Laguna Brava						
CO 501a	Pircas Negras	BA	28 242	68 789	4453	north of Laguna Brava						
CO 502	Pircas Negras	D	28.220	69.021	4360	Barranças Blanças						
00 502	Ronata Chico	D	20.220	09.021	1500	Burraneus Blaneus						
CO 144	Direas Negras	٨	28 210	68 651	1286	NE of Loguna Mulas Muertas						
$\begin{array}{c} CO 144 \\ CO 145 \end{array}$	Pireas Negras	A	20.219	68 624	4280	NE of Laguna Mulas Muertas						
$\begin{array}{c} \text{CO} 143 \\ \text{CO} 146 \end{array}$	Pircas Negras	A	20.190	68 607	4112	SE of Como Donoto Chico						
CO 140	Plicas Negras	A	28.150	08.09/	4/31 5127	SE of Cello Bonete Chico						
0 324	Pircas Negras	А	27.995	08.808	5127	Quebrada Veladero						
~~	Valle Ancho/Los Pat	OS										
CC 252	Pircas Negras	D	27.251	68.792	4537	Los Patos						
CC 254	Pircas Negras	А	27.278	68.784	4899	Los Patos						
CC 270 ^e	Pircas Negras	D	27.296	68.959	4418	Rio Barros Negros						
CC 271 ^c	Pircas Negras	D	27.284	69.938	4709	Rio Lajitas						
CC 279	El Domo	А	27.045	68.895	4410	east of Tres Cruzes						
CC 101 ^c	Valle Ancho cone	BA	27.359	68.924	4697	south of Cerro Lajitas						
CC 102 ^c	Valle Ancho cone	BA	27.353	68.927	4678	south of Cerro Lajitas						
CC 262°	Valle Ancho cone	BA	27.347	68.954	4535	south of Cerro Lajitas						
00 202	Rodrigo		_,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,									
CC 2062	V Rodrigo	р	26 080	68 766	1753	north of Tree Cruzes						
CC 290a	V Rodrigo	ם ח	20.202	68 766	A752	north of Tres Cruzes						
CC 2900	v. Roungo V. Podrigo		20.202	68 766	4752	north of Tres Cruzes						
UU 291	v. Koungo	A	20.989	00.700	4/33							
	Post-Migration	type	lat (DD)	lon (DD)	elev (m)	location						
CO 179	Pircas Negras	D	27.904	69.093	4634	upper Rio Salado						
CO 177	Pircas Negras	А	28.001	69.168	4506	upper Rio Salado						
CO 312	Pircas Negras	А	27.993	69.148	4555	upper Rio Salado						
CO 313	Pircas Negras	Α	27.908	69.094	4623	upper Rio Salado						

Table 2.1 (continued)

K-Ar age	es for mafic lavas from t	he northe	rn flatslab	transition z	one (~2	7°-28.5	°)
sample	location	% K	Ar^{40}	% Ar atm	age	±	type
	Paso Pircas Negras/Con	mecaballo	s				
CO 413	P. Negras	1.956	0.350	78	4.6 =	± 0.4	WR
CO 414	P. Negras	2.187	0.356	81	4.2 =	± 0.5	WR
AC 409 ^a	P. Negras	1.699	0.345	87	5.2 =	± 0.9	WR
AC 407	P. Negras	2.410	0.814	56	8.7 =	⊾ 0.4	WR
	Jotabeche/Gallina						
CC 17 ^a	P. Negras				5.7 =	± 0.5	WR
CC 11	P. Negras	1.780	0.388	96	5.6 =	± 2.5	WR
CC 15	C. Maranceles	1.983	0.520	85	6.7 =	± 0.9	WR
AC 624	P. Negras-Gallina	1.711	0.416	84	6.2 =	± 0.9	WR
	Los Patos/Valle Ancho						
CC 270 ^b	P. Negras Barros Neg.	2.360	0.512	41	5.6 =	± 0.3	WR
CC 101 ^b	Valle Ancho Cone	1.300	0.295	84	5.8 =	± 0.7	WR
CC 262 ^b	Valle Ancho	1.336	0.294	56	5.6 =	± 0.3	WR
CO-24	Los Aparejos	1.321	0.047	62	9.1 =	± 0.6	WR
CO-72	Los Aparejos	1.315	0.488	59	9.5 =	± 0.5	WR
CC 296	Rodrigo	2.495	0.430	87	4.4 =	± 0.6	WR
	Rio Salado						
CO 170	P. Negras	1.633	0.300	74	4.7 =	± 0.5	WR
CO 179	P. Negras	2.350	0.178	82	1.9 =	± 0.2	WR
	Hombre Muerto/Mulas	s Muertas					
CO 144*	Eastern Pircas Negras	1.737	0.331	93	5.0 =	± 1.6	WR
CO 145	Eastern Pircas Negras	2.450	0.379	49	4.0 =	± 0.2	WR
CO 146	Eastern Pircas Negras	1.722	0.349	83	5.2 =	± 0.6	WR
	Dos Hermanos						
CC 84 ^b	Dos Hermanos	2.067	0.618	54	7.7 =	± 0.4	WR

Table 2.2

Ages obtained at the SERNAGEOMIN geochronology lab (Santiago, Chile) WR = whole rock analysis; *Average of two analyses

^aKay et al. (1994b), ^bTittler, (1995)

By the late Miocene, basalts and andesites from the northern flatslab region erupted contemporaneously with the migrating dacitic frontal arc and define the zone of active magmatism during the 7-3 Ma period of arc transition. Eruption of these mafic lavas can be divided into pre-, syn-, and post-migration periods corresponding to 9-7 Ma, 7-3 Ma, and 3-2 Ma respectively.

Pre-migration (9-7 Ma)

Isolated late Miocene mafic lavas along the Valle Ancho (Figure 2.2b) erupted in the waning Maricunga backarc between 9-7 Ma and are the first magmatic indication of the ensuing period of arc migration. The oldest of these lavas are the Los Aparejos backarc basaltic andesites that erupted between 9.5-9.1 \pm 0.6 Ma near Laguna Verde in the eastern Valle Ancho (Mpodozis et al., 1997). Further to the west are the 7.7 \pm 0.4 Ma Dos Hermanos mafic andesites that erupted near the headwaters of the Rio Salado. Both lower (CC 81-83 in Table 2.1; Kay et al., 1999) and upper (CO 428 in Table 2.1) units from this center are considered in this work. Slightly more evolved are lavas from the ~ 8 Ma Redonda center that erupted at the base of the Dos Hermanos. The oldest dated Pircas Negras-like lava is from an isolated flow in the Rio Comecaballos valley south of Paso Pircas Negras (8.7 \pm 0.4 Ma, age on AC 407 in Table 2.1, same flow as AC 406).

Syn-migration (7-3 Ma)

Pircas Negras andesites with ages of 7 to 3 Ma are the dominant syn-migration mafic volcanic sequence in the region. They include a broad suite of late Miocene-Pliocene adakitic lavas that erupted *between* the Maricunga belt and the late Miocene/Pliocene dacitic arc centers to the east (Kay et al., 1991; Mpodozis et al., 1995). The Pircas Negras andesites were first described by Mpodozis et al. (1988) near the Paso Pircas Negras within the Rio Comecaballos valley. Over 60 samples assigned to the Pircas Negras group (Figure 2.2c) are described below by region: (1) Gallina/Jotabeche, (2) Paso Pircas Negras, (3) Rio Salado valley, (4) Laguna Brava, (5) Bonete Chico, (6) and Los Patos/Valle Ancho (Figure 2.4). These andesites all exhibit chemical and petrographic characteristics similar to the older Pircas Negras lavas including glassy textures, plagioclase-poor modal abundances dominated by hornblende, and adakitic geochemical signatures.

Gallina-Jotabeche

Some of the earliest Pircas Negras flows erupted during the terminal pyroclastic eruption of Jotabeche at 6.0 ± 0.7 Ma (McKee et al., 1994; Mpodozis et al., 1995) that marked the end of Maricunga belt magmatism (Kay et al., 1994b). These flows are exposed at Cerro Casale along the Rio Nevado south of the Jotabeche center and the Aldebarán mining prospect (Figure 2.2c). They are dated at 6.7 ± 0.9 Ma (Table 2.2). Dacitic flows outcrop along the La Gallina fault south of Cerro de la Gallina and define a magmatic pulse at 6.2 ± 0.9 (Kay et al., 1994b; Mpodozis et al., 1995). North of Jotabeche, a series of younger Pircas Negras andesitic flows with ages of 5.7 ± 0.5 and 5.6 ± 2.5 Ma extend toward Lago Negro Francisco (Kay et al., 1994b).

Paso Pircas Negras

Late Miocene-Pliocene Pircas Negras andesites erupted between 5.2 ± 0.9 and 4.2 ± 0.5 Ma within the Paso Pircas Negras and along the Rio Pircas Negras (Figure 2.2c; Mpodozis et al., 1988; Kay et al., 1991). These dark glassy lava flows cap older Miocene sediments, early Miocene andesites of the Doña Ana Formation (Escabroso member), and Permo-Triassic Choiyoi granitoids (Figure 2.2b). Considering the oldest Pircas Negras lavas from the Rio Comecaballos at 8.7 Ma, a general age progression from south (older) to north (younger) characterizes the temporal spread of Pircas Negras lavas along the Chile-Argentina border.



Figure 2.4 Thematic Mapper imagery of the southernmost Andean CVZ north of the Valle Ancho showing major volcanic centers. Sample locations are for Pircas Negras-like andesites and dacites and Valle Ancho basaltic andesites (CC 101-2 and CC 262). Ages are given in Table 2.2.

Lower Rio Salado & Pastillos

The most voluminous Pircas Negras lava flows are located in the valley of the Rio Salado, which runs north-south for ~ 80 km between the Sierras de Veladero to the east and the Maricunga belt to the west. Within the Rio Salado (Figure 2.2c), the late Miocene sequence is exposed due to post-Miocene fluvial erosion. Pircas Negras flows unconformably overlay the Jotabeche ignimbrite, which itself caps mid-Miocene sandstones and conglomerates composed of clasts of Permo-Triassic Choiyoi granite and rhyolite (Figure 2.3b). These flows originate from within the Sierras de Veladero massif, ~ 5-10 km to the northeast, and reach thicknesses > 10 m along the Rio Salado canyon (Figure 2.2c). One of these flows has a ⁴⁰Ar/³⁹Ar age of 3.968 ± 0.192 (Goss et al., Chapter 4) and is overlain by ~ 2.5 Ma rhyodacitic domes associated with the Incapillo Caldera and Dome Complex. From the Rio Salado, a continuous chain of Pircas Negras lavas extends eastward past Barrancas Blancas towards Laguna Brava (Figure 2.2c).

The southernmost exposure of Pircas Negras andesites is near the confluence of the Rio Macho Muerto with the Rio Salado (Figure 2.2c). These lavas are K-Ar dated at 4.7 ± 0.5 Ma (Table 2.2) and overlay early Miocene Tilito ignimbrites (22-24 Ma) and/or mid-Miocene sedimentary units. A similar temporal sequence of younging Pircas Negras volcanism to the north parallels the sequence to the west within the Paso Pircas Negras and Jotabeche regions.

Laguna Brava

Isolated Pircas Negras-like flows erupted around Laguna Brava (Figure 2.2c), though K-Ar dating of the largest complex reveals that the some of these flows pre-date the main Pircas Negras magmatic event (i.e., sample CO 159, \sim 12.6 Ma). However, some of the undated lavas from this region exhibit chemical and petrographic characteristic similar to those from the Pircas Negras andesites further west and are therefore considered part of the Pircas Negras sequence.

Bonete Chico

The easternmost Pircas Negras lavas erupted contemporaneous with and on the flanks of the dacitic Cerro Bonete Chico center $(5.6 \pm 0.6 \text{ to } 3.5 \pm 0.1 \text{ Ma}; \text{Kay} \text{ and} Mpodozis, 2000})$ north of Laguna Mulas Muertas near Cerro Estanzuela (Figure 2.2c). These andesitic flows have K-Ar ages between 5.2 ± 0.6 and 4.0 ± 0.2 and are overlain by Miocene breccias and sediments. A Pircas Negras-like andesitic lava from the upper Rio Veladero (CO 324) on the western flank of Bonete Chico shares many geochemical and petrographic characteristics of the Pircas Negras suite and is capped by ~ 0.51 Ma Incapillo ignimbrite deposits (Goss et al., Chapter 4).

Valle Ancho

The 5.8 ± 0.7 Ma Valle Ancho basaltic andesites (CC 101-2 and CC 262) erupted at the northwestern end of the Valle Ancho and have been described by Kay et al. (1994b), Mpodozis et al. (1995) and Tittler (1995). Though these basaltic andesites erupted during the peak of frontal arc migration, they are petrographically and geochemically distinct from the Pircas Negras andesites. Also in the western Valle Ancho, Pircas Negras-like dacitic lava flows dated at 5.6 ± 0.3 Ma erupted between the Rio Lajitas and Rio Barros Negros in the western Valle Ancho (Figure 2.4; Tittler, 1995). To the east, andesitic (CC 254) and dacitic (CC 252) lavas with characteristics similar to the Pircas Negras suite erupted on the north flank of Volcán Los Patos (Figure 2.4; CO 254). Late Miocene mafic volcanism in the Ojos del Salado region with chemical affinities similar to the Pircas Negras lavas include a basaltic andesite cone west of Tres Cruces (CC 279) and the 4.4 ± 0.6 Ma Rodrigo and esitic center north of Tres Cruces (CC 296-7; Figure 2.4).

Post-Migration (3-2 Ma)

Following the main syn-migration pulse of Pircas Negras volcanism between 7-3 Ma, mafic magmatism waned and became localized in the upper Rio Salado (shown by a box in Figure 2.2d). The youngest and northernmost Pircas Negras flow in the upper Rio Salado (CO 179) has a K-Ar age of 1.9 ± 0.2 Ma. Flows from this post-migration stage stretch ~ 15 km N-S along the upper Rio Salado where they overlay late Miocene conglomerates. In sum, two episodes of mafic Pircas Negras volcanism are observed within the Rio Salado: a southern syn-migration pulse at 5-4 Ma followed by a post-migration pulse further north at ~ 3-2 Ma.

V BULK CHEMISTRY

We present 62 major and 52 trace element analyses of mafic and intermediate arc lavas from the northern transition of the flatslab region (Tables 2.3-2.5) as well as Sr, Nd, Pb, O isotopic data on a selected suite of samples (Tables 2.6-2.7). These data compliment published data for Pircas Negras flows near the Paso Pircas Negras (Kay et al., 1991) and Jotabeche regions (Kay et al., 1994b; Mpodozis et al., 1995). A description of the analytical methods is presented in Appendix 1. Major elements for both whole rock powders and *in situ* mineral grains were obtained by electron microprobe at Cornell University. Trace element data are from Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at Cornell University and from Atomic Absorption Spectrometry (AAS) at the Chilean Geological Survey (SERNAGEOMIN). Sr and Nd isotopic ratios were analyzed with a VG Sector 54° Thermal Ionization Mass Spectrometer (TIMS) at the Cornell University Keck Isotope Lab. Pb isotopic ratios were analyzed at the University of Florida on a Nu-Plasma[©] multi collector (MC) ICP-MS. Oxygen isotopes were analyzed by ArF laser fluorination on select olivine and quartz grains at the Universität Göttingen.

Major element data

For the Neogene Central Andes in general, arc volcanism has been dominantly andesitic to dacitic with scarce eruption of basalts or basaltic andesites. With the exception of a few late Miocene basaltic andesites from the Valle Ancho, the Pircas Negras and Dos Hermanos andesites are the most mafic arc lavas to have erupted over the northern flatslab transition zone. Whole rock major element analyses are presented in Table 2.3.

A range of major element compositions exists within each region of Pircas Negras volcanism and spatial patterns are generally not apparent in the data. The most basic Pircas Negras flows are from the Paso Pircas Negras and from the southern Rio Salado near Pastillos (SiO₂ = 57-59 wt %), whereas the most acidic flows are from the upper Rio Salado and at Los Patos (SiO₂ = 62-64 wt %). Pircas Negras lavas define linear differentiation trends with respect to FeO_t, MgO, and CaO concentrations on Si-variation diagrams (blue fields in Figure 2.5). TiO₂ concentrations are 0.7-1.3 wt %. Na₂O concentrations are high compared to typical arc andesites and range between 3.6-5.3 wt %. Al₂O₃ concentrations are between 15-18 wt % and do not correlate with SiO₂ or Mg number [molar ratio of Mg/(Mg + Fe²⁺total Fe)]. Based on the classification of Le Maitre et al. (1989), the Pircas Negras are high- to medium-K andesites and dacites (Figure 2.5).

Mg #s for the Pircas Negras andesites range from 36 to 61 and are plotted against SiO₂ content in Figure 2.5. Five samples have Mg $\# \ge 58$ and sample CO 412

from the Paso Pircas Negras has a Mg # = 61. The Pircas Negras are some of the least-evolved andesites from the Central Andes and have similar Mg #s to other high-Mg andesites (e.g., Kay, 1978; Kelemen, 1995; Yogodzinski et al., 1995; Grove et al., 2002). In contrast, Pircas Negras andesites from the upper Rio Salado, Los Patos, and on the flank of Cerro Bonete Chico, have Mg #s < 50 and SiO₂ \ge 60.

Dos Hermanos lavas are more potassic than the Pircas Negras at the same SiO₂ concentration (Figure 2.5; SiO₂ = 56-59 wt %; K₂O = 2.5-3.0 wt %) and are classified as high-K andesites (Figure 2.5). They have similar CaO (6.3-6.6 wt %), Al₂O₃ (16.6-17.6 wt %), TiO₂ (1.0-1.2 wt %), and Na₂O (4.5-5.0 wt %) concentrations, and slightly lower Mg #s (48-55) than the most mafic Pircas Negras lavas.

Table 2.4 shows major element analyses for mafic lavas from the Valle Ancho along with published data for basalts from the southernmost CVZ. The ~ 5 Ma Valle Ancho (Mg #s of 55-58) and 9 Ma Los Aparejos (Mg #s 66-68) basaltic andesites have lower alkali concentrations (Na₂O = 3.3-3.8 wt %; K₂O = 1.5-1.7 wt %) than the Pircas Negras and Dos Hermanos andesites. The Los Aparejos basaltic andesites have MgO concentrations of 8.4-8.7 wt %. North of the Valle Ancho, the ~ 24 Ma Segerstrom and < 2 Ma Incahuasi basalts and San Francisco basaltic andesite from the southernmost CVZ define the regional mafic endmember for Neogene volcanism (Figure 2.5; Mpodozis et al., 1996; Kay et al., 1999; in prep.). These lavas have MgO concentrations of 9-12 wt % and Mg #s ranging from 63 to 72. Also plotted on Figure 2.5 are the 21-18 Ma Escabroso (Table 2.5) and 18-13 Ma southern Maricunga andesites (data from Kay et al., 1991; Kay et al., 1994b; Mpodozis et al., 1995) that overlap the Pircas Negras fields with respect to most of the major elements. These older andesites are generally more aluminous (Al₂O₃ > 17 wt %) and have lower Mg #s than Pircas Negras lavas at the same SiO₂ content.

Major and trace eler	ment analyses of	late Miocene-I	Pliocene andesi	ites from the n	orthern flatslab	transition zone (~27°-28.5°)				
			Pre-Mi	gration		·`			Syn-Migration		
		Dos He	ermanos		Redonda	Rio CC		Jotab	eche-Gallina I	Region	
sample	CO 428	CC 81 ^c	CC 82 ^c	CC 83 ^c	CC 94 ^a	AC 406 ^b	CC 17 ^a	CC 11 ^a	CC 15	CO 415	CO 416
SiO ₂	58.95	57.34	56.08	58.24	63.41	64.15	58.39	59.05	59.96	60.94	58.91
TiO ₂	1.15	1.05	1.03	1.08	0.88	0.91	0.93	1.30	1.05	0.93	1.15
Al_2O_3	16.80	17.66	16.62	17.36	17.08	16.53	17.81	16.60	16.55	16.47	17.51
Fe ₂ O ₃	3.40				3.67			3.22	3.57	2.58	
FeO	1.63	5.52	5.56	5.49	0.66	4.17	5.60	2.82	1.67	1.57	5.14
FeOt	4.69	5.52	5.56	5.49	3.96	4.17	5.60	5.72	4.88	3.89	5.14
MnO	0.09	0.09	0.08	0.12	0.05	0.08	0.09	0.07	0.06	0.06	0.09
MgO	3.18	3.03	3.05	2.88	1.92	1.85	3.51	3.61	2.59	2.66	2.77
CaO	6.50	6.37	6.62	6.34	4.03	4.49	6.00	6.28	5.96	6.69	6.86
Na ₂ O	4.50	4.62	4.69	4.89	4.58	4.71	4.42	4.33	4.60	4.50	4.8
K ₂ O	2.86	2.61	2.58	2.64	3.05	2.80	2.34	1.86	2.58	2.83	2.18
P_2O_5	0.40	0.45	0.43	0.46	0.28	0.30	0.40	0.35	0.33	0.31	0.57
Total	99.12	98.74	96.74	99.50	99.24	99.99	99.49	99.17	98.56	99.28	99.98
Mg #	54.7	49.5	49.4	48.3	46.3	44.2	52.8	53.0	48.6	54.9	49.0
La	66.8	58.4	59.8	61.5	44.1	45.6	42.2	40.2		43.1	30.8
Ce	128.5	120.0	123.0	128.1	92.3	91.9	84.5	83.6		87.3	68.5
Nd	65.3	55.5	56.2	58.7	38.4	39.2	37.8	36.7		46.1	38.6
Sm	9.68	8.23	8.30	8.60	5.92	6.5	5.99	6.12		7.15	6.50
Eu	2.21	2.16	2.29	2.34	1.58	1.69	1.63	1.73		1.64	1.55
Tb	0.606	0.554	0.607	0.652	0.370	0.509	0.555	0.503		0.463	0.504
Yb	1.103	1.02	1.04	1.00	0.685	0.79	1.01	1.20		0.892	0.846
Lu	0.147	0.137	0.128	0.136	0.101	0.096	0.137	0.148		0.112	0.112
Y	13.7	14	12	12	9.5		11	12		9	11.7
Rb	64.2	66	59	62	79.4	71	55	55		49	59.0
Sr	1436	1243	1330	1221	602	800	740	679		1016	765
Sr*	1402	1278	1500	1400	793		870	944			1063
Ba	1591	1146	1147	1167	1126	1103	854	897		1312	946
Ba*	1231	1156	1100	1100	1034		910	922			825
Pb	13.0	14.6	9	8	13.8		7	6		9	9.1
Cs	0.9	1.7	1.0	0.8	1.9	0.9	1.5	2.2		0.7	1.6

Table 2.3

		Dos He	ermanos		Redonda	Rio CC		Jotab	eche-Gallina I	Region	
sample	CO 428	CC 81 ^c	CC 82 ^c	CC 83 ^c	CC 94 ^a	AC 406 ^b	CC 17 ^a	CC 11 ^a	CC 15	CO 415	CO 416
U	1.3	1.4	1.5	1.5	1.5	1.1	1.2	1.3		1.2	1.3
Th	9.2	8.7	8.6	9.1	8.4	6.8	6.4	6.2		5.3	4.0
Zr	256	246	237	251	223		231	236		239	264
Nb	12.7	12.9	12	13	9.9		12	11		9	12.3
Hf	5.4	5.6	5.6	5.9	6.2	6.9	5.3	5.3		5.6	5.3
Та	0.66	0.64	0.63	0.65	0.68	0.46	0.67	0.74		0.57	0.62
Sc*	9.3	9.5			7.2					10.6	8.4
Sc	9.9	9.9	9.8	9.6	6.5	6.0	12.5	12.7		10	8.1
Cr	52	55	55	50	17	96	46	58		72	47
Cr*	55	57	132	82	17		131	54		61	49
Ni	25	30	23	23	10	15	26	25		24	19
Ni*	26.3	20	22	18	8.8		21	19		19	22.8
Co	17	16	17	17	11	10	19	19		15	12
Co*	17.4	16			9.3					12	13.5
Cu	27	22	23	20	22		24	21		92	
Zn		88	86	114	89		92	92		107	
V	121	115	118	109	92		121	131		25	108
Rb/Sr		0.05	0.04	0.04	0.10		0.06	0.06		0.05	0.08
Ba/La	23.8	19.6	19.2	19.0	25.5	24.2	20.2	22.3		30.4	30.7
La/Sm	6.9	7.1	7.2	7.1	7.4	7.0	7.0	6.6		6.0	4.7
La/Yb	60.5	57.3	57.4	61.2	64.4	57.6	41.8	33.5		48.3	36.4
Eu/Eu*	0.97	1.09	1.11	1.08	1.13	1.02	1.01	1.10		0.97	0.94
Sm/Yb	8.8	8.1	8.0	8.6	8.6	8.3	5.9	5.1		8.0	7.7
Ba/Th	174	132	134	128	134	162	134	146		247	239
Ba/Ta	2409	1796	1824	1790	1651	2408	1282	1219		2316	1516
La/Ta	101	92	95	94	65	99	63	55		76	49
Th/U	6.8	6.2	5.9	6.1	5.7	6.5	5.2	4.6		4.5	3.1
Sr/Yb	1302	1219	1278	1216	879	1011	733	566		1139	905
Sr/Y	102.4	88.5	125.0	116.7	83.1		79.1	78.7			90.5

Table 2.3 (continued)

^aKay et al., (1994b), ^bKay et al., (1991); ^cTittler, (1995); Major element data from electron microprobe at Cornell University. Trace elements analyzed by INAA at Cornell University following methods outlined in Kay et al., (1987); Other trace elements (Yb, Rb, Sr*, Ba*, Pb, Zr, Nb, Sc*, Cr*, Ni*, Co*, Cu, Zn, V) from ICPMS at Cornell University (Appendix 3 for full analyses) or by atomic adsorption at SERNAGEOMIN (italicized)

Major and tr	ace element an	alyses of late l	Miocene-Plioce	ene andesites f	rom the northe	ern flatslab tra	nsition zone (~2	7°-28.5°)					
	Indicate Piocene andesites from the northern Flatlab transition zone (-277-28.5°) Syn-Migration Syn-Migration Piocene callina Region (conspan="6") Syn-S AC 619A AC 623A AC 625A AC 626P C0412 C0413 C0414 AC 408 ^b AC 409 ^b Syn-S 61.06 61.04 AC 629A AC 626P C0412 C0414 AC 408 ^b AC 409 ^b Syn-S 61.06 61.08 60.22 57.38 Syn-Migration 104 10.8 AC 619A AC 629A AC 626P C0412 C0414 AC 408 ^b AC 409 ^b 104 16.33 1.04 AC 629A AC 625A AC 626P C0412 C0413 AC 4028 AC 402												
Major and trace element analyses of late Miocenee Pliconee andesites from the northern Ratshab transition zone (-27*-28.57) Syn-Migration syn-Migration zone (-27*-28.57) manple Ot 427 AC 6356 ^b AC 619A AC 624A AC 625P CO412 CO413 CO414 AC 409 ^b Sinple Ot 427 AC 6256 ^b AC 624A AC 625P CO412 CO413 CO414 AC 409 ^b Sinple CO 427 AC 6256 AC 625A AC 626P CO413 CO414 AC 409 ^b Sinple CO 427 AC 625 AC 626P CO413 CO414 AC 409 ^b AC 610 Sinple CO441 AC 626 CO413 CO44 AC 627 AC 610 Single faither													
sample	CO 427	AC 556 ^b	AC 619A	AC 623A	AC 624A	AC 625A	AC 626P	CO412	CO413	CO414	AC 408 ^b	AC 409 ^b	
SiO ₂	59.25	61.06	61.44	60.56	60.15	61.08	60.22	57.38	58.94	61.97	57.54	57.36	
TiO ₂	1.04	1.08	0.88	0.95	0.95	0.93	1.02	1.01	0.96	0.85	0.99	1.01	
Al_2O_3	17.63	16.94	16.37	16.68	16.26	16.53	16.47	18.02	17.32	16.82	16.92	17.22	
Fe ₂ O ₃	2.41		4.36	3.21	5.04	3.94	2.84	2.15	2.27	1.52			
FeO	2.13	4.67	0.24	1.80	0.22	1.45	2.40	3.38	4.63	2.47	5.54	5.79	
FeOt	4.30	4.67	4.16	4.69	4.75	5.00	4.96	5.31	6.67	3.84	5.54	5.79	
MnO	0.09	0.08	0.06	0.08	0.08	0.08	0.08	0.10	0.09	0.08	0.10	0.10	
MgO	3.51	2.49	2.12	3.33	3.30	3.32 3.56 4.71 3.67 2.69 4.54							
CaO	5.88	6.12	5.36	5.64	5.96	5.72	5.95	6.48	6.10	5.19	8.10	7.60	
Na ₂ O	4.46	4.65	4.61	4.33	4.30	4.27	4.26	4.02	4.05	4.22	3.97	4.10	
K ₂ O	2.26	2.52	2.21	2.16	2.14	2.01	2.01	2.32	2.66	2.93	1.98	1.93	
P_2O_5	0.32	0.38	0.27	0.31	0.25	0.24	0.31	0.27	0.26	0.24	0.32	0.33	
Total	98.74	99.99	97.48	98.73	98.14	99.18	98.84	99.63	100.73	98.82	100.00	100.00	
Mg #	59.3	48.7	47.6	55.9	55.3	54.2	56.2	61.2	49.5	55.5	59.4	58.4	
La	35.1	39.7						37.3	43.0	42.2	36.0	37.4	
Ce	74.8	80.8						78.2	88.3	89.5	73.8	74.1	
Nd	37.5	37.0						42.6	47.2	42.0	29.8	34.9	
Sm	6.11	6.4						6.54	7.46	6.78	5.9	6.3	
Eu	1.55	1.64						1.58	1.78	1.64	1.65	1.70	
Tb	0.545	0.467						0.599	0.653	0.557	0.610	0.640	
Yb	1.036	0.81						1.41	1.43	1.10	1.41	1.36	
Lu	0.130	0.097						0.183	0.193	0.149	0.180	0.190	
Y	13.7							17.2	14	11			
Rb	47.1	59						47.0	52	57	51	53	
Sr	761	1050						890	995	705	800	830	
Sr*	934							912					
Ba	925	996						928	1139	1156	711	866	
Ba*	840							791					
Pb	8.3							8.0	9	10			
Cs	1.2	1.2						1	1.7	1.7	1.5	1.8	

Table 2.3 (continued)

Jotabeche-Gallina Region (continued) sample CO 427 GSA 556 ^b AC 619A AC 623A AC 624A AC 625A AC 6 U 1.0 1.1 1							Pa	aso Pircas Neg	gras			
sample	CO 427	GSA 556 ^b	AC 619A	AC 623A	AC 624A	AC 625A	AC 626P	CO412	CO413	CO414	GSA 408 ^b	GSA 409 ^b
U	1.0	1.1						1	1.4	1.6	1.4	1.6
Th	4.6	5.1						5.7	7.0	7.3	4.8	5.1
Zr								229	247	259		
Nb								11.2	9	9		
Hf	5.4	5.6						5.3	5.8	6.1	5.2	5.5
Та	0.55	0.55						0.64	0.72	0.63	0.59	0.66
Sc*	11.2							16	14.4	10.1		
Sc	11.6	9.6						15.9	14	9	16.2	16.8
Cr	74	131						147	100	57	210	247
Cr*	73							141	87	48		
Ni	23	21						43	18	25	53	63
Ni*	27.3							47	41	23		
Co	15	14						21	18	13	20	21
Co*	14.8							19.6	17	11		
Cu	30							33	95	95		
Zn	96							94	127	94		
V	117							142	29	24		
Rb/Sr	0.05							0.05	0.05	0.08		
Ba/La	26.3	25.1						24.9	26.5	27.4	19.7	23.1
La/Sm	5.7	6.2						5.7	5.8	6.2	6.1	5.9
La/Yb	33.9	49.1						26.4	30.0	38.5	25.5	27.6
Eu/Eu*	0.96	1.04						0.90	0.91	0.94	1.00	0.97
Sm/Yb	5.9	7.9						4.6	5.2	6.2	4.2	4.7
Ba/Th	200	194						163	164	157	150	170
Ba/Ta	1674	1825						1450	1592	1848	1215	1304
La/Ta	64	73						58	60	67	62	56
Th/U	4.6	4.6						5.7	4.8	4.7	3.4	3.1
Sr/Yb	734	1296						631	695	642	566	612
Sr/Y	68.4							52.9				

Table 2.3 (continued)

^aKay et al., (1994b), ^bKay et al., (1991); ^cTittler, (1995); Major element data from electron microprobe at Cornell University. Trace elements analyzed by INAA at Cornell University following methods outlined in Kay et al., (1987); Other trace elements (Yb, Rb, Sr*, Ba*, Pb, Zr, Nb, Sc*, Cr*, Ni*, Co*, Cu, Zn, V) from ICPMS at Cornell University (Appendix 3 for full analyses) or by atomic adsorption at SERNAGEOMIN (italicized)

Major and	lajor and trace element analyses of late Miocene-Pliocene andesites from the northern flatslab transition zone (~27°-28.5°)Syn-Migration													
						S	Syn-Migration							
							Rio Salac	lo Region						
sample	CO 163	CO 170	CO 172	CO 173	CO 175	CO 176	CO 309	CO 310	CO 327	CO 329	CO 331	CO 332	CO 504	CO 507
SiO_2	62.76	57.40	56.78	58.89	60.57	63.40	61.71	59.10	61.68	59.00	61.48	59.33	60.20	63.04
TiO ₂	0.96	1.03	1.22	0.91	0.93	0.68	0.95	1.00	1.02	1.06	0.95	1.00	0.96	0.91
Al_2O_3	16.62	16.78	16.23	16.36	16.67	16.11	16.23	16.11	16.69	16.26	16.09	16.00	17.18	16.54
Fe ₂ O ₃	2.89		3.75	2.76	3.14	2.85								
FeO	2.21	6.10	3.73	3.47	2.14	1.91	4.83	5.45	5.00	5.98	4.91	5.65	4.99	4.67
FeOt	4.82	6.10	7.10	5.95	4.96	4.48	4.83	5.45	5.00	5.98	4.91	5.65	4.99	4.67
MnO	0.06	0.10	0.12	0.10	0.08	0.08	0.08	0.09	0.07	0.11	0.10	0.10	0.07	0.08
MgO	2.11	4.77	4.44	4.11	2.55	2.34	2.61	3.24	2.25	4.22	2.58	3.65	3.51	2.35
CaO	4.63	6.58	7.30	6.34	5.74	4.77	6.46	6.67	5.28	5.91	6.07	7.05	5.89	5.08
Na ₂ O	4.82	3.76	4.12	4.07	4.68	4.17	4.52	5.19	5.15	4.50	4.91	4.31	4.44	4.10
K ₂ O	2.48	2.15	1.72	2.09	2.30	2.88	2.51	2.59	2.40	2.36	2.70	2.39	2.37	2.89
P_2O_5	0.33	0.30	0.35	0.26	0.37	0.17	0.36	0.34	0.38	0.38	0.34	0.36	0.40	0.35
Total	99.58	98.97	99.37	99.08	98.86	99.09	100.25	99.79	99.92	99.78	100.12	99.85	100.00	100.00
Mg #	43.8	58.2	52.7	55.2	47.8	48.2	49.0	51.5	44.5	55.7	48.3	53.6	55.6	47.3
La	45.0	31	29.2	25.7	41.8	38.7	39.1	40.4	43.2	40.5	43.6	44.5	42.0	46.8
Ce	94.6	72.0	61.1	56.1	86.4	70.9	82.2	86.8	90.2	83.3	91.9	95.3	85.2	89.7
Nd	49.8	44.5	35.4	28.7	37.7	32.7	45.7	46.3	36.7	39.3	46.9	47.2	40.9	41.1
Sm	7.41	6.7	6.7	5.4	6.48	5.8	6.74	7.23	7.47	6.88	7.19	7.53	7.3	7.1
Eu	1.70	1.69	1.86	1.47	1.68	1.21	1.61	1.83	1.97	1.83	1.77	1.96	2.11	1.85
Tb	0.562	0.641	0.8	0.6	0.523	0.5	0.485	0.552	0.524	0.597	0.611	0.711	0.61	0.58
Yb	0.95	1.3	1.57	1.2	0.82	1.2	0.83	0.92	1.06	1.32	1.09	1.28	1.09	1.13
Lu	0.127	0.181	0.222	0.169	0.110	0.164	0.120	0.138	0.134	0.169	0.130	0.164	0.157	0.163
Y	13.7	17.3	19	15	11	14	11.0	11	12.1	15.8	13.0	17.6	15.0	15.3
Rb	61.9	48.5	40	54	56	95	60	61	44.1	61.1	78.0	71.3	51.3	81.1
Sr	843	741.8	728.0	625.5	897	736.9	931	1006	873	790	776	881	932	901
Sr*	835	848	735	656	920	738	899	820	990	882	789	991	932	901
Ba	1048	756.9	608.0	699.6	1002	925.1	1057	1155	1142	819	1062	1001	884	952
Ba*	989	744	596	662	931	887	920	918	1016	882	949	968	884	952
Pb	10.4	8.8	6	8	8	13	10.5	10.2	9.3	9.8	12.1	10.6	9.0	11.3
Cs	10.8	1.3	2.5	2.5	1.7	1.9	1.72	2.76	3.56	1.94	1.61	1.61	1.061	1.969

 Table 2.3 (continued)

							Rio Salao	lo Region						
sample	CO 163	CO 170	CO 172	CO 173	CO 175	CO 176	CO 309	CO 310	CO 327	CO 329	CO 331	CO 332	CO 504	CO 507
U	1.3	1.1	1.0	0.9	1.5	2.3	1.5	1.5	1.2	1.1	1.5	1.5	1.1	1.4
Th	6.1	4.4	3.1	3.3	5.2	9.2	4.9	5.1	5.6	5.3	8.0	7.1	5.8	9.2
Zr	310	250	236	201	249	215	254	253	337	302	300	317	270	253
Nb	13.0	11.9	12.9	10	12	9	12	11	11.5	11.8	11.8	12.5	12.6	12.1
Hf	6.7	5.7	5.3	4.9	5.8	5.0	5.8	6.8	7.4	6.6	6.7	6.5	6.23	5.92
Та	0.62	0.7	0.7	0.6	0.70	0.6	0.69	0.75	0.66	0.66	0.70	0.70	0.69	0.67
Sc*	11.5	17.8	18	16	8	10	8	8	7.4	13.5	8.5	13.1	11.5	9.4
Sc		15.7	18.7	16.1	8.2	10.7	7.8	9.2	8.3	14.2	9.0	13.3	11.5	9.4
Cr	49	208.8	134.6	159.9	61	29	56	84	46	139	36	130	100	30
Cr*	60	210	129	153	64	31	59	71	42	132	36	131	100	30
Ni	15	61.9	39.3	46.1	24	9.9	23	27	15	41	10	44	36.4	13.8
Ni*	18.5	61.7	33	40	19	5	19	21	17.0	40.7	17.9	64.9	36.4	13.8
Co	11	21.0	23.0	20.9	14	12.4	13	15	11	18	11	17	15.4	11.2
Co*	12.3	21.5	21	17	14	12	13	13	10.7	18.5	11.3	18.3	15.4	11.2
Cu	20	32	31	32	30	17								
Zn	91	106	96	85	89	70								
V	132	162	166	148	107	117	101	99	95	128	94	136	115	101
Rb/Sr	0.07	0.07	0.05	0.08	0.06	0.13							0.06	0.09
Ba/La	23.3	24.4	20.8	27.3	24.0	23.9	27.0	28.6	26.4	20.2	24.3	22.5	21.0	20.4
La/Sm	6.1	4.6	4.3	4.7	6.5	6.7	5.8	5.6	5.8	5.9	6.1	5.9	5.7	6.6
La/Yb	47.5	23.4	18.6	21.0	50.9	31.4	47.2	44.0	40.7	30.6	40.0	34.8	38.4	41.5
Eu/Eu*	0.91	0.93	0.95	0.95	1.01	0.78	0.97	1.01	1.01	0.96	0.86	0.86	1.35	1.35
Sm/Yb	7.8	5.0	4.3	4.4	7.9	4.7	8.1	7.9	7.0	5.2	6.6	5.9	6.7	6.3
Ba/Th	172	173	194	212	191	100	217	226	203	155	133	141	152	103
Ba/Ta	1700	1157	815	1238	1435	1649	1535	1540	1719	1245	1528	1437	1276	1426
La/Ta	73	47	39	45	60	69	57	54	65	62	63	64	61	70
Th/U	4.7	4.0	3.3	3.9	3.5	4.0	3.3	3.5	4.8	4.7	5.5	4.7	5.5	6.4
Sr/Yb	889	559	464	512	1091	598	1123	1097	822	597	711	688	852	799
Sr/Y	61.0	49.1	38.7	43.7	83.6	52.7			81.8	55.9	60.5	56.3	62.3	59.0

Table 2.3 (continued)

^aKay et al., (1994b), ^bKay et al., (1991); ^cTittler, (1995); Major element data from electron microprobe at Cornell University. Trace elements analyzed by INAA at Cornell University following methods outlined in Kay et al., (1987); Other trace elements (Yb, Rb, Sr*, Ba*, Pb, Zr, Nb, Sc*, Cr*, Ni*, Co*, Cu, Zn, V) from ICPMS at Cornell University (Appendix 3 for full analyses) or by atomic adsorption at SERNAGEOMIN (italicized)

Major and	d trace eleme	nt analyses of l	late Miocene-l	Pliocene andes	ites from the 1	northern flatsla	b transition zon	e (~27°-28.5°)				
						Syn-Migratio)n					
			Laguna B	rava Region				Bonete Cl	nico Region		L. Patos/	V. Ancho
sample	CO 159	CO 160	CO 161	CO 333	CO 501a	CO 502	CO 144	CO 145	CO 146	CO 324	CC 252	CC 254
SiO ₂	62.21	59.21	63.80	61.95	53.42	63.26	58.20	62.74	57.45	59.11	63.56	57.11
TiO ₂	0.98	0.78	0.95	0.90	1.21	0.92	1.03	0.88	1.03	0.85	0.88	1.11
Al_2O_3	16.23	15.83	16.08	15.86	17.86	16.43	17.27	16.96	16.50	14.65	15.64	16.42
Fe ₂ O ₃	2.57	2.89	1.98					3.18	2.73			
FeO	2.82	2.67	2.87	4.72	9.55	4.29	5.72	1.47	3.89	5.70	4.66	6.54
FeOt	5.13	5.28	4.65	4.72	9.55	4.29	5.72	4.33	6.35	5.70	4.66	6.54
MnO	0.08	0.09	0.06	0.09	0.20	0.04	0.09	0.04	0.10	0.10	0.08	0.12
MgO	2.37	4.33	2.03	2.46	5.97	2.24	3.55	1.36	4.53	3.93	2.25	4.20
CaO	4.83	6.03	3.97	6.09	6.79	4.87	6.10	4.00	6.58	6.14	5.05	7.46
Na ₂ O	4.26	3.78	4.24	5.13	4.28	4.66	4.28	4.62	3.72	5.09	4.03	4.01
K ₂ O	2.67	2.32	2.90	2.77	0.55	2.93	2.39	3.02	2.25	3.48	2.71	1.98
P_2O_5	0.25	0.24	0.29	0.34	0.16	0.35	0.32	0.30	0.29	0.30	0.26	0.32
Total	99.01	97.90	98.98	100.30	100.00	100.00	98.95	98.25	98.80	99.36	99.12	99.27
Mg #	45.2	59.4	43.7	48.2	52.7	48.3	52.5	35.9	56.0	55.2	46.3	53.4
La	41.8	32.5	47.4	43.2			39.6	42.8	36.2	53.0	38.2	35.1
Ce	91.6	69.5	99.3	89.0			83.8	88.5	75.8	113.9	78.4	67.6
Nd	36.6	32.3	43.3	34.3			44.5	41.8	38.0	48.1	35.2	34.2
Sm	7.0	4.93	7.3	6.79			7.16	7.3	7.2	9.23	6.42	6.12
Eu	1.59	1.42	1.70	1.63			1.77	1.68	1.76	1.91	1.36	1.61
Tb	0.7	0.908	0.6	0.484			0.594	0.5	0.722	0.794	0.501	0.653
Yb	1.3	1.47	1.1	1.06			1.07	0.9	1.7	1.80	1.26	1.34
Lu	0.2	0.214	0.152	0.127			0.146	0.107	0.232	0.344	0.151	0.181
Y	17	17	14	13.1			15.0	11.7	21.5	16		
Rb	80	77	74	87.1			43.0	70.1	49.6	138	104	46
Sr	664.5	699	731.8	724			839	805.7	698.7	779	540	778
Sr*	663	736	730	831			935	849	828	588	540	830
Ba	852.3	727	1024.8	1137			954	961.1	706.5	1033	757	759
Ba*	803	716	982	998			885	952	717	720	670	730
Pb	11	9	12	15.5			9.3	11.3	9.4	17.0	12	6
Cs	2.1	4.0	1.8	3.01			1.0	0.7	1.4	7.55	3.5	0.7

Table 2.3 (continued)

			Laguna Bi	ava Region				Bonete Ch	ico Region		L. Patos/	V. Ancho
sample	CO 159	CO 160	CO 161	CO 333	CO 501a	CO 502	CO 144	CO 145	CO 146	CO 324	CC 252	CC 254
U	1.9	2.7	1.5	2.0			1.1	1.7	1.3	7.4	3.6	1.0
Th	7.8	6.0	7.5	7.3			4.8	7.2	5.0	20.8	15.0	5.4
Zr		222	291	305			263	243	244	239	197	172
Nb	12	10	11	11.5			14.9	12.4	12.9	16	9.4	9.9
Hf	7.1	5.2	6.9	6.7			6.0	6.7	5.8	8.6	5.9	5.1
Та	0.8	0.76	0.7	0.69			0.79	0.6	0.8	1.49	0.900	0.667
Sc*	9	15	8	7.8			12.1	7.9	17.3	10	8.4	
Sc	9.1	14.3	7.7	7.8			12.0	7.6	17.6	14.3		17.7
Cr	38.3	207	41.7	33			91	57.0	201.8	136	39	100
Cr*	37	194	45	39			82	56	201	105	33	101
Ni	12.6	63	19.6	9			35	17.1	60.3	27	17	32
Ni*	6	62	13	16.1			28.8	16.0	59.9	28	12	31
Co	12.0	18	11.7	10			17	8.1	22.7	17	13	22
Co*	12	20	10	10.9			16.1	7.5	21.1	14		
Cu	16	31	20				28	15	37		17	29
Zn	90	80	92				107	87	103		93	94
V	107	124	100	88			126	86	146	103	108	157
Rb/Sr	0.12	0.11	0.10				0.05	0.09	0.07	0.23	0.19	0.06
Ba/La	20.4	22.4	21.6	26.3			24.1	22.4	19.5	19.5	19.8	21.6
La/Sm	6.0	6.6	6.5	6.4			5.5	5.9	5.0	5.7	6.0	5.7
La/Yb	33.1	22.1	43.0	40.9			37.0	49.4	21.5	29.5	30.3	26.2
Eu/Eu*	0.84	0.85	0.92	0.90			0.96	0.95	0.89	3.35	1.13	1.13
Sm/Yb	5.5	3.4	6.6	6.4			6.7	8.4	4.3	5.1	5.1	4.6
Ba/Th	109	121	137	156			199	134	142	50	50	140
Ba/Ta	1086	958	1526	1637			1201	1531	928	694	841	1138
La/Ta	53	43	71	62			50	68	48	36	42	53
Th/U	4.2	2.2	5.1	3.7			4.3	4.2	3.7	2.8	4.2	5.3
Sr/Yb	526	476	664	685			783	929	414	433	428	580
Sr/Y	39.0	43.3	52.1	63.6			62.1	72.4	38.4	35.8		

Table 2.3 (continued)

^aKay et al., (1994b), ^bKay et al., (1991); ^cTittler, (1995); Major element data from electron microprobe at Cornell University. Trace elements analyzed by INAA at Cornell University following methods outlined in Kay et al., (1987); Other trace elements (Yb, Rb, Sr*, Ba*, Pb, Zr, Nb, Sc*, Cr*, Ni*, Co*, Cu, Zn, V) from ICPMS at Cornell University (Appendix 3 for full analyses) or by atomic adsorption at SERNAGEOMIN (italicized).

Major and	l trace elemer	nt analyses of a	indesites from t	he northern flat	slab transition	zone (~27°-28.5	°)			
			Syn-Migrati	on				Post-m	igration	
]	LP/Valle Anch	10		Rodrigo			Upper R	io Salado	
sample	CC 270 ^c	CC 271 ^c	CC 279	CC 296a	CC 296b	CC 297	CO 177	C0 179	CO 312	CO 313
SiO ₂	63.88	64.77	59.73	62.90	62.90	60.91	61.90	63.33	60.89	62.23
TiO ₂	0.83	0.73	0.78	0.74	0.74	0.79	0.89	0.84	1.00	0.90
Al_2O_3	15.67	16.19	15.51	15.97	15.97	16.32	16.82	16.62	16.45	16.31
Fe ₂ O ₃							2.20	2.27		
FeO	4.54	3.97	4.71	4.11	4.26	4.23	2.37	1.94	4.91	4.39
FeOt	4.54	3.97	4.71	4.11	4.26	4.23	4.35	3.98	4.91	4.39
MnO	0.10	0.05	0.09	0.08	0.08	0.07	0.06	0.06	0.08	0.07
MgO	1.75	2.32	3.34	2.16	2.16	2.45	1.92	1.81	2.43	2.20
CaO	4.77	3.96	6.76	4.71	4.71	5.14	4.73	4.60	5.87	5.45
Na ₂ O	4.50	4.28	3.96	4.28	4.23	4.23	4.67	4.54	5.06	5.29
K ₂ O	2.92	3.37	2.45	3.10	3.10	3.08	2.90	2.64	2.90	2.83
P_2O_5	0.24	0.22	0.26	0.25	0.25	0.24	0.30	0.29	0.35	0.33
Total	99.20	99.86	97.59	98.30	98.40	97.46	98.55	98.72	99.94	100.00
Mg #	40.7	51.0	55.8	48.4	47.5	50.8	44.0	44.7	46.9	47.2
La	41.0	42.6	46.9	38.8	40.1	39.5	46.1	45.6	49.4	49.3
Ce	85.8	87.2	89.7	79.9	94.7	72.6	92.8	91.4	103.3	102.8
Nd	36.3	35.4	39.3	32.0	36.3	32.6	43.2	39.9	53.9	55.8
Sm	6.04	5.73	6.71	5.67	5.87	5.42	7.3	6.89	7.90	7.65
Eu	1.46	1.33	1.47	1.28	1.41	1.24	1.42	1.45	1.78	1.70
Tb	0.456	0.315	0.542	0.382	0.460	0.445	0.5	0.482	0.547	0.510
Yb	0.723	0.76	1.056	0.797	0.865	0.829	0.8	0.83	0.97	0.98
Lu	0.093	0.094	0.132	0.096	0.100	0.100	0.109	0.108	0.133	0.153
Y		8					11	11	11.6	11.6
Rb	95	116	80	78		74	65	76	67.9	76.5
Sr	690	458	875	651	681	657	824.4	866	877	892
Sr*	600	605	780	710		680	758	783	863	921
Ba	986	1029	737	905	946	901	1032.5	1092	1252	1386
Ba*	860	820	660	880		830	946	1070	984	1121
Pb	11	13	9	9		7	10	12.1	11.5	12.2
Cs	2.15	3.3	4.67	1.13	1.45	1.35	1.0	1.2	0.99	1.11

Table 2.3 (continued)

	LP/Valle Ancho			Rodrigo			-	Upper Rio Salado			
sample	CC 270 ^c	CC 271 ^c	CC 279	CC 296a	CC 296b	CC 297		CO 177	C0 179	CO 312	CO 313
U	1.95	2.4	3.51	1.54	1.50	1.49	-	1.3	1.5	1.4	1.6
Th	10.73	14.0	10.98	9.7	9.7	8.6		7.2	7.3	7.9	8.2
Zr	93	218	154	217		213		289	303.8	350	325
Nb	6.9	7	9.1	7.5		6.9		10	11	10.9	11.1
Hf	6.6	5.6	5.2	5.4	5.8	5.5		6.8	6.5	7.8	7.4
Та	0.6	0.57	0.8	0.5	0.5	0.5		0.6	0.60	0.63	0.61
Sc*								6	6	7.0	6.5
Sc	8.2	7.9	12.3	8.0	9.0	7.6		6.5	6.1	7.7	7.1
Cr	42	31	97	57	65	53		25.3	23	28	25
Cr*	43	30	96	54		54		25	29	29	28
Ni	10	11	37	18	18	16		8.9	9	10	9
Ni*	12	21	46	17		17		2	8	23.2	12.1
Co	14	12	17	11	13	11		10.3	9	12	10
Co*								10	9	11.3	28
Cu	19	19	26	19		18		16			
Zn	93	65	83	93		78		85			
V	99	97	113	89		59		89	82	94	82
Rb/Sr	0.16	0.19	0.10					0.09			
Ba/La	24.0	24.2	15.7	23.3	23.6	22.8		22.4	24.0	25.4	28.1
La/Sm	6.8	7.4	7.0	6.8	6.8	7.3		6.3	6.6	6.3	6.4
La/Yb	56.8	56.3	44.4	48.7	46.4	47.6		57.5	54.8	50.9	50.5
Eu/Eu*	1.13	1.13	1.13	0.94	0.95	0.89		0.82	0.86	0.93	0.92
Sm/Yb	8.4	7.6	6.4	7.1	6.8	6.5		9.1	8.3	8.1	7.8
Ba/Th	92	74	67	93	98	105		142	150	159	170
Ba/Ta	1638	1818	952	1917	1758	1989		1815	1835	1974	2254
La/Ta	68	75	61	82	75	87		81	77	78	80
Th/U	5.5	5.7	3.1	6.3	6.4	5.8		5.5	4.7	5.6	5.2
Sr/Yb	955	606	829	817	788	793		1028	1040	904	913
Sr/Y		75.6						68.9		74.6	79.6

 Table 2.3 (continued)

in the second the second the	Pre-mi		Syn-migration				
	Los A	pareios	Valle Ancho basaltic andesites				
sample	CO 72	CO 24	CC 101°	CC 102 ^c	CC 262		
SiO ₂	52.64	53.25	55.47	55.48	54.96		
TiO ₂	1.09	1.04	1.21	1.31	1.28		
Al ₂ O ₃	15.23	15.33	16.46	16.94	16.59		
Fe ₂ O ₃	3.69	3.38					
FeO	3.93	4.76	7.31	7.53	7.44		
FeOt	7.25	7.80	7.31	7.53	7.44		
MnO	0.13	0.13	0.13	0.13	0.12		
MgO	8.64	8.37	5.70	5.39	5.10		
CaO	8.47	8.02	7.55	7.04	7.96		
Na ₂ O	3.49	3.36	3.39	3.78	3.75		
K_2O	1.77	1.68	1.58	1.50	1.60		
P_2O_5	0.28	0.24	0.29	0.36	0.28		
Total	98.99	99.22	99.09	99.46	99.08		
Mg #	68.0	65.7	58.2	56.1	55.0		
La	32.0	31.1	23.2	24.2	25.1		
Ce	65.3	66.4	52.2	54.7	52.6		
Nd	31.9	33.2	27.6	27.8	30.6		
Sm	5.58	6.02	5.22	5.48	5.80		
Eu	1.50	1.58	1.63	1.82	1.62		
Tb	0.561	0.672	0.638	0.661	0.653		
Yb	1.49	1.83	1.43	1.33	1.39		
Lu	0.223	0.252	0.193	0.172	0.186		
Y	18	19.9	18.3		16.8		
Rb	32	31.5	34.9	32	35.2		
Sr	897	720	477	523	593		
Sr*	923	767	612	600	672		
Ba	744	632	506	482	598		
Ba*	724	624	555	500	588		
Pb	9	8.3	7.1	2	6.6		
Cs	0.4	0.8	1.1	1.2	0.9		

Table 2.4

	Los A	parejos	Valle Ancho basaltic andesites				
sample	CO 72	CO 24	CC 101 ^c	CC 102 ^c	CC 262 ^c		
U	0.9	0.9	0.7	0.7	0.8		
Th	3.5	3.8	2.6	2.6	2.8		
Zr	133	185	190		192		
Nb	8	10.2	9.9		10.3		
Hf	3.7	4.3	4.5	5.0	4.8		
Та	0.58	0.56	0.53	0.57	0.65		
Sc*	25	22.2	23.0		18.5		
Sc	23.7	23.9	20.3	19.7	18.4		
Cr	632	672	198	201	195		
Cr*	519	575	196	187	188		
Ni	228	174	46	53	59		
Ni*	210	175	46.4	46	49.5		
Co	40	39	26	28	27		
Co*	36	36.8	26.2		25.4		
Cu	51	45	13	28	30		
Zn	86	90	81	103	96		
V	191	169	211	157	203		
Rb/Sr	0.03	0.04	0.06	0.05	0.05		
Ba/La	23.3	20.3	21.8	19.9	23.8		
La/Sm	5.7	5.2	4.4	4.4	4.3		
La/Yb	21.5	17.0	16.2	18.2	18.1		
Eu/Eu*	-0.08	0.92	1.06	1.13	0.98		
Sm/Yb	3.8	3.3	3.7	4.1	4.2		
Ba/Th	211	165	192	189	217		
Ba/Ta	1285	1126	960	849	918		
La/Ta	55	55	44	43	39		
Th/U	3.9	4.3	3.8	3.7	3.4		
Sr/Yb	604	394	333	393	426		
Sr/Y	51.3	38.5	33.5		40.1		

Data sources and analytical methodologies are the same as in Table 2.3
					21-18 M	la Escabroso :	andesites				
sample	CO 291	CO 292	CO 293	CO 294	CO 295	CO 296	CO 297	CO 300	CO 335	CO 446	CO 264
SiO ₂	60.56	58.33	60.57	61.02	55.94	60.55	60.27	54.53	59.41	56.82	59.32
TiO ₂	0.90	0.71	1.01	0.61	1.13	0.79	0.70	0.73	0.85	0.89	0.75
Al_2O_3	16.92	18.48	17.98	17.04	18.82	17.54	18.11	19.96	18.62	18.38	18.36
Fe ₂ O ₃										2.30	
FeO	5.67	6.50	6.00	4.83	7.51	5.72	5.31	6.47	6.85	3.12	6.11
FeOt	5.67	6.50	6.00	4.83	7.51	5.72	5.31	6.47	6.85	5.18	6.11
MnO	0.14	0.19	0.12	0.16	0.14	0.17	0.15	0.17	0.16	0.13	0.13
MgO	1.96	3.06	2.05	1.78	3.25	2.35	2.10	2.59	3.19	2.83	3.65
CaO	5.48	6.96	5.57	5.83	7.78	5.94	5.48	9.74	5.44	7.83	5.23
Na ₂ O	4.93	3.15	4.80	5.03	3.87	4.09	4.12	3.57	3.72	3.49	3.79
K ₂ O	2.95	1.55	2.09	2.28	1.69	1.82	2.14	1.51	1.55	2.15	1.82
P_2O_5	0.36	0.28	0.30	0.37	0.24	0.34	0.31	0.24	0.36	0.27	0.26
Total	99.87	99.22	100.51	98.94	100.38	99.32	98.69	99.51	100.16	97.97	99.41
Mg #	38.2	45.7	37.8	39.7	43.6	42.2	41.3	41.7	45.4	49.3	51.6
La	34.3	22.4	30.3	33.1	22.2	22.8	26.2	20.4	22.7	21.6	18.0
Ce	77.0	46.7	67.2	71.0	48.3	51.6	63.4	45.4	48.0	48.0	39.3
Nd	34.4	21.5	34.6	32.4	25.1	23.7	19.1	23.4	18.8	20.7	17.9
Sm	7.30	4.78	6.45	6.01	5.34	5.21	5.62	4.79	5.03	4.71	3.78
Eu	1.78	1.26	1.47	1.41	1.46	1.27	1.45	1.32	1.32	1.218	1.005
Tb	0.923	0.619	0.634	0.685	0.761	0.715	0.778	0.668	0.637	0.610	0.509
Yb	2.17	2.23	1.35	2.03	2.46	2.13	1.90	2.26	2.09	1.843	1.50
Lu	0.316	0.329	0.186	0.277	0.359	0.310	0.293	0.329	0.280	0.295	0.197
Y										18	
Rb										46	
Sr	548	542	645	604	539	489	540	594	588	575	474
Sr*											
Ba	774	353	652	763	447	455	507	409	491	589	561
Ba*											
Pb										9	
Cs	2.92	1.09	2.17	2.08	3.95	1.67	7.01	2.13	1.80	2	2.0

Table 2.5

Major and trace element analyses of early Miocene Escabroso (Doña Ana) andesites

	21-18 Ma Escabroso andesites													
sample	CO 291	CO 292	CO 293	CO 294	CO 295	CO 296	CO 297	CO 300	CO 335	CO 446	CO 264			
U	2.0	0.8	1.5	1.5	1.1	1.4	1.5	0.8	1.1	1.2	1.1			
Th	7.8	4.2	5.6	5.7	4.4	5.3	5.7	3.8	3.5	4.1	3.9			
Zr										153				
Nb										8				
Hf	7.3	4.3	6.3	6.3	4.9	4.7	6.3	3.9	4.3	4.1	3.6			
Та	0.85	0.58	0.71	0.71	0.53	0.52	0.67	0.52	0.58	0.61	0.56			
Sc*														
Sc	9.6	13.1	7.5	5.3	19.2	9.6	539.7	15.6	13.9	14	19.8			
Cr	2	5	19	2	5	2	2	5	7	9	10			
Cr*														
Ni	1	6	11	1	5	1		4	6	2	10			
Ni*														
Co	10	15	14	1	22	11	11	16	17	15	19			
Co*														
Cu										32				
Zn										87				
V										135				
Rb/Sr														
Ba/La	22.6	15.8	21.5	23.1	20.1	19.9	19.3	20.0	21.6	27.3	31.2			
La/Sm	4.7	4.7	4.7	5.5	4.2	4.4	4.7	4.3	4.5	4.6	4.8			
La/Yb	15.8	10.0	22.4	16.3	9.0	10.7	13.8	9.0	10.9	11.7	12.0			
Eu/Eu*	0.82	0.88	0.83	0.82	0.88	0.80	0.84	0.89	0.88	0.86	0.87			
Sm/Yb	3.4	2.1	4.8	3.0	2.2	2.4	3.0	1.2	2.4	2.6	2.5			
Ba/Th	100	85	117	133	101	86	89	109	138	142	144			
Ba/Ta	908	609	917	1082	851	867	752	792	842	970	996			
La/Ta	40	39	43	47	42	44	39	40	39	36	32			
Th/U	3.9	5.2	3.7	3.9	4.2	3.8	3.8	4.9	3.3	3.4	3.5			
Sr/Yb	253	242	477	298	219	229	284	262	282	312	317			

 Table 2.5 (continued)

Data sources and analytical methodologies are the same as in Table 2.3 Additional trace elements for sample CO 446 obtained by atomic adsorption at SERNAGEOMIN (italics)

Figure 2.5 Harker diagrams showing differentiation trends for mafic and intermediate lavas associated with late Miocene frontal arc migration at 28° S. Blue circles = 21-18 Ma Escabroso andesites; white circles = 18-13 Ma southern Maricunga andesites (data from Kay et al., 1991; 1994b; Mpodozis et al., 1995); blue diamonds = 9-2 Ma Pircas Negras adakites; pink boxes = \sim 8 Ma Dos Hermanos; yellow triangles = \sim 5 Ma Valle Ancho basaltic andesites; yellow diamonds = 9 Ma Los Aparejos basalts. Open diamonds show values for primitive CVZ basalts including \sim 24 Ma Segerstrom and < 2 Ma Incahuasi and San Francisco centers (Kay et al., 1999). K₂O classification is from Le Maitre et al. (1989). Data are in Tables 2.3-2.5.



Trace element data

The Pircas Negras lavas exhibit trace element characteristics that distinguish them from most other central and southern Andean andesites. The ubiquitous trace element signatures of the Pircas Negras andesites are their steep REE patterns and high degree of HFSE depletion relative to the LREE as shown on chondrite normalized REE and MORB-normalized incompatible element diagrams (Figures 2.6 and 2.7). The Dos Hermanos andesites exhibit the greatest degree of LREE enrichment, yet have HREE depletion trends similar to most Pircas Negras andesites. The Valle Ancho basaltic andesites have markedly flatter LREE with HREE that overlap the easternmost Pircas-Negras lavas from the Bonete Chico region. REE patterns from the late Miocene Rodrigo center to the north (CO 296a; Mpodozis et al., 1996) exhibit LREE concentrations characteristic of the majority of Pircas Negras and have amongst the greatest extent of MREE and HREE depletion of all analyzed samples from the region (Figure 2.7a,b). Europium anomalies are minimal in most Pircas Negras high-Mg and esites and range from 0.88 to 1.10 with an average Eu/Eu* = 1.028 (σ = 0.05; n = 24). Dos Hermanos lavas have slightly positive Eu/Eu* from 1.06-1.11.

All samples exhibit a strong "arc signature" with enriched LILE relative to uniformly depleted HFSE (Figures 2.6 and 2.7). The 5-4 Ma Pircas Negras from the Rio Salado display the greatest degree of LILE enrichment relative to MORB, whereas backarc Valle Ancho basaltic andesites have the least. Dos Hermanos lavas have LILE concentrations intermediate between these two but have higher Sr concentrations. Similarly, Th and U enrichment is less in the Valle Ancho basaltic andesites compared to the Pircas Negras and Dos Hermanos andesites. All lavas are characterized by anomalously high Pb concentrations (7-17 ppm) relative to the incompatible element trend.



Figure 2.6 (A) C1 Chondrite normalized (McDonough and Sun, 1995) REE diagram and (B) MORB-normalized (Sun and McDonough, 1989) incompatible element spider diagram showing general ranges for Pircas Negras, Dos Hermanos, and Valle Ancho lavas. Data are from ICP-MS (Appendix 3). Also shown are LA-ICPMS data from Rapp et al. (1999) for high-P (3.8 GPa) experimental melts of a basaltic amphibolite (AB-1) that reacted with depleted and primitive mantle (circles and diamonds respectively).



Figure 2.7 (A) C1 Chondrite-normalized (McDonough and Sun, 1995) REE diagrams and (B) MORB-normalized (Sun and McDonough, 1989) incompatible element spider diagrams for representative Pircas Negras samples (ICP-MS data in Appendix 3). Shaded fields show REE ranges for high-Mg andesites from Adak (Kay, 1978; Kay and Kay, 1994) and dacites from Mt. Shasta in the Cascades (Grove et al., 2002). Figures 2.7c and 2.7d show similar diagrams for representative Dos Hermanos andesites, Valle Ancho and Los Aparejos basaltic andesites, and mantle-derived CVZ basalts (Kay et al., 1999).

Temporal trace element relationships

The trace element signatures that characterize the Pircas Negras and Dos Hermanos andesites are a *transient* feature confined to the late Miocene period of rapid frontal arc migration. These andesites are chemically distinguishable from lavas that erupted within a tectonically-stable arc including (1) spatially contiguous early Miocene (21-18 Ma) Escabroso and middle Miocene (18-13 Ma) southern Maricunga andesites (Kay et al., 1991; 1994b; Mpodozis et al., 1995) and (2) Quaternary andesites from the southernmost CVZ near 27° S (e.g., V. Peinado, Falso Azufre, Volcán San Francisco; Mpodozis et al., 1996; Kay and Mpodozis, 2000).

Stable arc – early-mid Miocene (21 to 13 Ma) and < 2 Ma CVZ

The 21-18 Ma Escabroso andesites exhibit the flattest REE patterns (Figures 2.8a and 2.9; La/Yb = 10-22; La/Sm = 4.2-5.9; and Sm/Yb = 2.2-2.6) among Neogene lavas from the northern flatslab region and have a HFSE-depletion signature like that of the modern Andean CVZ (Figure 2.8; La/Ta = 32-47 and Ba/Ta = 609-1082). Sr concentrations and Sr/Yb ratios (Figure 2.10; Sr = 569-645 ppm; Sr/Yb = 219-477) fall within the range for the modern CVZ arc. Escabroso andesites have low Cr and Ni contents (e.g., Cr = 5-10 ppm; Ni = 2-10 ppm) compared to Pircas Negras and modern CVZ andesites (Figures 2.5 and 2.11).

Compared to the 21-18 Ma Escabroso andesites, the 18-13 Ma southern Maricunga andesites have slightly steeper REE patterns (Figures 2.8a and 2.9; La/Yb = 13-26; La/Sm = 5.1-6.0; and Sm/Yb = 2.3-5.2) and a stronger arc signature as evidenced by higher Ba/La ratios. They also have somewhat higher Sr and Cr concentrations (Figure 2.10; Sr = 530-820 ppm; Sr/Yb = 480-770; Cr = 3-106 ppm) than the Escabroso andesites.

Figure 2.8 (A) Graph of La/Ta vs. La/Yb and (B) La/Ta vs. Ba/Ta for mafic and intermediate lavas from the northernmost flatslab transition zone (~ 27-28.5° S). Blue = pre-migration andesites (9-7 Ma); yellow = synmigration andesites (7-3 Ma); and green = post-migration andesites (3-2 Ma). Data are given in Tables 2.3-2.5. Mid-Miocene field (18-13.5 Ma) includes data from southern Maricunga belt andesites (Jotabeche Norte, La Laguna, Cadillal-Yeguas Heladas shown in Figure 2.2; Kay et al., 1991; 1994b; Mpodozis et al., 1995). Field labeled "CVZ" is for Quaternary andesites from the Ojos del Salado region (Peinado, V. Falso Azufre, Las Grutas, and V. San Francisco; data from Mpodozis et al., 1996; Kay et al., 1999). Data for ~ 24 Ma Segerstrom and < 2 Ma CVZ basalts are from Kay et al. (1999).





Figure 2.9 Graphs of (A) La/Yb vs. wt % SiO₂ and (B) La/Sm vs. Sm/Yb for mafic and intermediate lavas from the northern flatslab transition zone ($\sim 27^{\circ}-28.5^{\circ}$ S). Fields and colors are the same as in Figure 2.8.



Figure 2.10 Graphs of (A) Sr (ppm) vs. Sr/Yb and (B) Yb (ppm) vs. Sr/Yb for mafic and intermediate lavas from the northern flatslab transition zone ($\sim 27^{\circ}$ -28.5° S). Fields and colors are the same as in Figure 2.8.



Figure 2.11 Graphs of (A) Sm/Yb vs. Cr (ppm) and (B) Ni (ppm) for mafic and intermediate lavas from the northern flatslab transition zone (~ 27° -28.5° S). Fields, symbols, and colors are the same as in Figure 2.8. The ~ 9 Ma Los Aparejos and < 2 Ma CVZ basalts (Segerstrom, Incahuasi, and San Francisco; Kay et al., 1999) are not plotted and have Cr and Ni concentrations of 600-700 ppm and 150-230 ppm respectively.

Trace element ratios from Quaternary CVZ andesites are similar to the 18-13 Ma southern Maricunga andesites (Figure 2.8a and 2.9; La/Yb = 15-27; La/Ta = 25-41; Sm/Yb = 2.9-4.1). Compared to the Pircas Negras lavas, CVZ andesites have more subdued arc signatures (Figure 2.8b; Ba/Ta = 375-730; Ba/La = 9-17), lack an adakitic signature (Figure 2.10; Sr < 660 ppm; Sr/Yb < 360), and have lower Cr and Ni contents (Figure 2.11; Cr = 3-113 ppm and Ni = 6-57 ppm).

Pre-migration – 9 to 7 Ma

The 7.7 Ma Dos Hermanos, 8.8 Ma Pircas Negras, and ~ 8 Ma Redonda andesites are chemically distinct from early-mid Miocene andesites and the 7-3 Ma of Pircas Negras lavas. These andesites have very steep REE patterns (La/Yb = 58-64; Figure 2.9) and high La/Ta ratios (La/Ta = 92-101; Figure 2.8) that fall off the trends defined by the 7-3 Ma Pircas Negras. Figure 2.9b shows that the steep REE patterns characteristic of these andesites are dominantly controlled by extreme HREE depletion (Sm/Yb = 8.0-8.8), not LREE enrichment, as La/Sm ratios are similar to modern CVZ and slightly greater than the early-mid Miocene andesites. Despite strong HFSE depletion (Ba/Ta = 1800-2400), extreme LREE enrichment in 7.7 Ma Dos Hermanos andesites is coupled with Ba/La ratios (19-24) that are lower than most Pircas Negras andesites (Figure 2.8b).

Pre-migration andesites are clearly differentiated from early-mid Miocene and Quaternary CVZ andesites by their high Sr contents and adakitic Sr/Yb ratios (Figure 2.10a,b). The most extreme enrichment is observed in the Dos Hermanos andesites, which have higher Sr concentrations than the Pircas Negras (Sr = 1220-1436 ppm) and a strong adakitic signature (Sr/Yb = 1216-1302). The 8.8 Ma Comecaballos Pircas Negras has similarly high Sr concentrations and Sr/Yb ratios as

the Dos Hermanos. Pre-migration andesites generally have Cr and Ni concentrations typical of the Quaternary CVZ (Cr < 100 ppm and Ni < 25 ppm).

The 9 Ma Los Aparejos backarc basaltic andesites from the eastern Valle Ancho have relatively flat REE patterns (La/Yb = 17-22; La/Sm = 5.2-5.7; Sm/Yb = 3.3-3.8), typical arc signatures (La/Ta = 55; Ba/Ta = 1126-1285), elevated Sr contents (Sr = 720-897), and high transition metal concentrations (Cr = 632-672 ppm; Ni = 174-228 ppm).

Syn-migration - 7 to 3 Ma

Most of the Pircas Negras andesites are chemically distinguishable from the early-mid Miocene and Quaternary CVZ andesites. Steep REE patterns (La/Yb = 19-57) and strong HFSE-depletions (La/Ta = 36-76; Ba/Ta = 700-2300) characterize their trace element signatures (Figure 2.8). They have a strong adakitic geochemical signature (Figure 2.10; Sr = 460-1050 ppm; Sr/Yb = 400-1300) that is more subdued than that of the pre-migration Dos Hermanos andesites (Figures 2.8a and 2.10). Despite a slightly positive correlation between La/Yb and SiO₂, the 7-3 Ma Pircas Negras andesites fall within the same SiO₂ concentration range as the older and younger andesites that have distinctly lower La/Yb ratios (Figure 2.9a). As with the pre-migration andesites, the variability in La/Yb ratios is dominantly a function of HREE depletion (Sm/Yb = 4.0-8.5).

Cr and Ni contents are anomalously enriched (Cr = 15-250 ppm; Ni = 7-63 ppm) in some syn-migration Pircas Negras andesites compared to andesites that erupted before and after the main episode of arc migration (Figure 2.11). The highest concentrations occur in the 5-3 Ma Pircas Negras from the Paso Pircas Negras and Rio Salado regions. As with HREE depletion, high Cr and Ni concentrations are an *ephemeral* feature confined to high-Mg andesitic melts erupting during the peak of

frontal arc migration. A negative correlation exists between the extent of HREE depletion (Sm/Yb) and Cr and Ni enrichment. Syn-migration Pircas Negras andesites with intermediate HREE depletion (Sm/Yb = 4-6) and high Cr and Ni concentrations contrast with pre-and post-migration andesites with extreme HREE depletion and lower Cr and Ni concentrations.

The trace element characteristics of the ~ 5 Ma Valle Ancho basaltic andesites have been discussed by Tittler (1995). REE patterns of these lavas exhibit lower degrees of LREE enrichment and HREE depletion than most of the Pircas Negras andesites and are broadly similar to the 9 Ma Los Aparejos basalts (Figures 2.9 and 2.10). They share the high Cr and Ni contents exhibited by some syn-migration Pircas Negras high-Mg andesites (Figure 2.11, Cr = 195-201; Ni = 46-59), but lack a strong adakitic signature (Figure 2.10; Sr = 477-593 ppm and Sr/Yb = 333-426).

Post-migration – 3 to 2 Ma

The 3-2 Ma post-migration Pircas Negras lavas from the upper Rio Salado exhibit trace element signatures broadly similar to the pre-migration andesites. These flows, though slightly more evolved than the pre- or syn-migration Pircas Negras, have steep REE patterns (Figures 2.8a and 2.9; La/Yb = 51-58 and Sm/Yb = 7.8-9.1) and extreme HFSE-depletion (La/Ta = 77-81; Ba/Ta = 1815-2250). Like the pre-migration lavas, post-migration upper Rio Salado Pircas Negras flows have low (i.e., typical) Cr and Ni contents (Figure 2.11; Cr = 23-28 ppm and Ni = 9-10 ppm) like early-mid Miocene and Quaternary CVZ andesites. These lavas have an adakitic character that is similar to that of the 7-3 Ma Pircas Negras andesites (Figure 2.10; Sr = 824-892; Sr/Yb = 913-1040).

Isotopic data

Sr, Nd, and Pb isotopic ratios for selected Pircas Negras and Dos Hermanos andesites, 21-18 Ma Escabroso andesites, and Valle Ancho basaltic andesites are presented in Tables 2.6 and 2.7 and plotted in Figures 2.12-2.14.

A temporal trend towards more enriched ratios in both mafic and intermediate lavas erupting during and after the late Miocene period of arc instability is evident from the isotopic data. Figure 2.12a shows that discrete increases in isotopic ratios occur in spatially-coincident lavas of similar SiO₂ content. Higher ⁸⁷Sr/⁸⁶Sr ratios in the Dos Hermanos and Pircas Negras andesites (0.7055–0.7065) contrast with lower ratios in 21-18 Ma Escabroso (0.7047-0.7051) and in 18-13 southern Maricunga andesites (0.7048-0.7054; Kay et al., 1991; 1994b). Valle Ancho basaltic andesites exhibit high ⁸⁷Sr/⁸⁶Sr ratios (0.7057-0.7059; Tittler, 1995) that are broadly similar to the majority of Pircas Negras andesites. The 9 Ma Las Aparejos basaltic andesite has the highest ⁸⁷Sr/⁸⁶Sr ratio (0.7062) of all analyzed lavas from Valle Ancho. These temporal increases in Sr isotopic ratios are superimposed upon a larger-scale positive trend with ⁸⁷Sr/⁸⁶Sr and SiO₂ content seen in the isotopic data of mafic to silicic magmas of the same age (Figure 2.12a). Similarly, there is a positive correlation between ⁸⁷Sr/⁸⁶Sr and Sr concentration (Figure 2.12b), though the Dos Hermanos andesites fall off this trend towards higher Sr concentrations (1200-1400 ppm).

Nd-isotopic data exhibit a negative correlation with 87 Sr/ 86 Sr and a similar temporal trend towards lower ε Nd contemporaneous with the migration of the Andean volcanic front (Figure 2.14a). The 21-18 Ma Escabroso (-0.5 to -0.8) and 18-13 Ma southern Maricunga andesites (+0.1 to -1.7) have higher ε Nd values than both the 7-3 Ma Pircas Negras (-2.6 to -4.1) and the ~ 8 Ma Dos Hermanos (-3.4; Tittler, 1995) andesites. Valle Ancho basaltic andesites and the 9 Ma Los Aparejos basalt isotopically resemble the Pircas Negras with low ε Nd (-2.3 to -3.3; Tittler, 1995).

Sr, Nd, and I	Sr, Nd, and Pb isotopic analyses of basalts and andesites from the northern flatslab transition zone (~27°-28.5°)													
sample	unit	age	⁸⁷ Sr/ ⁸⁶ Sr	error	143Nd/144Nd	error	End	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb				
CO 412	Pircas Negras	~ 5	0.7057666	0.0007	0.5125012	0.0010	-2.67	18.650	15.611	38.654				
CC 17 ^a	Pircas Negras	5.7 ± 0.5	0.7055690	0.0007	0.5125130	0.0014	-2.44	18.640	15.600	38.578				
GSA 409 ^b	Pircas Negras	5.2 ± 0.9	0.7057990	0.0006	0.5124650	0.0010	-3.37							
GSA 406 ^b	Pircas Negras	~ 8.8	0.7064030	0.0007	0.5124540	0.0013	-3.59							
CO 427	Pircas Negras	~ 6	0.7055601	0.0009	0.5125027	0.0010	-2.64	18.644	15.616	38.627				
CO 179	Pircas Negras	1.9 ± 0.2	0.7062547	0.0005	0.5124258	0.0009	-4.14	18.663	15.612	38.698				
CO 309	Pircas Negras	~ 5	0.7055645	0.0008	0.5125049	0.0007	-2.60	18.631	15.611	38.603				
CO 310	Pircas Negras	~ 5	0.7057134	0.0007	0.5124774	0.0008	-3.13							
CO 324	Pircas Negras	~ 5	0.7061927	0.0008	0.5124510	0.0008	-3.65	18.726	15.617	38.731				
CO 332	Pircas Negras	~ 5	0.7064063	0.0008	0.5124282	0.0010	-4.09							
CO 507	Pircas Negras	~ 4						18.675	15.615	38.704				
CO 428	Dos Hermanos	~ 8	0.7057378	0.0010	0.5124673	0.0008	-3.33							
CC 81 ^c	Dos Hermanos	7.7 ± 0.4	0.7058710	0.0008	0.5124910	0.0009	-2.87	18.640	15.610	38.612				
CC 271 ^c	Pircas Negras	~ 5.6	0.7064152	0.0008	0.5124310	0.0009	-4.04	18.680	15.620	38.761				
CC 296a	Rodrigo	4.4 ± 0.6	0.7062780		0.5123960		-4.72	18.656	15.610	38.709				
CC 297	Rodrigo	~ 4.4	0.7062728											
CC 101 ^c	Valle Ancho	5.8 ± 0.7	0.7056670		0.5124780		-3.12							
CC 262 ^c	Valle Ancho	5.6 ± 0.3	0.7059427	0.0007	0.5124930	0.0012	-2.83	18.680	15.610	38.619				
CO 24	Los Aparejos	9.1 ± 0.6	0.7062286	0.0008	0.5124766	0.0022	-3.15	18.688	15.613	38.588				
CO 446	Escabroso	~ 21	0.7050527	0.0009	0.5125970	0.0009	-0.80							
CO 292	Escabroso	~ 21	0.7047840	0.0007	0.5125840	0.0010	-1.05							
CO 264	Escabroso	21.9 ± 0.8	0.7048574	0.0006	0.5126249	0.0009	-0.26							
CO 335	Escabroso	~ 21	0.7049475	0.0009	0.5126088	0.0008	-0.57							

Table 2.6

^aKay et al., (1994b); ^bKay et al., (1991); ^cTittler, (1995), ^dKay et al., (1999) - Segerstrom Pb values from sample CC 320f

Isotopic ratios were obtained on a VG sector thermal mass spectrometer at Cornell University and reflect measured values. Sr isotopic ratios were normalized to an 86 Sr/ 88 Sr ratio of 0.1184. Cornell value for 87 Sr/ 86 Sr for NBS 987 is 0.7102957 ± 0.00006 (2 sigma error; n = 40 from 6/2003 to 9/2004), 143 Nd/ 144 Nd for Ames is 0.5121436 ± 0.000028 (2 sigma error; n = 28 from 2/2004 to 5/2004); and 143 Nd/ 144 Nd for La Jolla is 0.5118496 ± 0.000015 (n = 13 from 2/2004 to 4/2004). Epsilon Nd is based on a CHUR value of 0.512614. Errors for 87 Sr/ 86 Sr and 143 Nd/ 144 Nd are reported as percent standard error. Italicized Pb isotope ratios were obtained via MC-ICPMS at the University of Florida and are relative to reported NBS Pb standard values of 206 Pb/ 204 Pb = 16.937 (+/-0.004), 207 Pb/ 204 Pb = 15.491 (+/-0.004), and 208 Pb/ 204 Pb = 36.695 (+/-0.009). Uncertainty on NBS Pb isotopic ratios is 2x standard error.



Figure 2.12 Graphs of 87 Sr/ 86 Sr vs. (A) SiO₂ (wt %) and (B) Sr concentration (in ppm) for (1) Pircas Negras and Dos Hermanos andesites, (2) basaltic andesites from the Valle Ancho, (3) 21-18 Ma Escabroso Formation andesites, (4) 24 Ma Segerstrom primitive basalt (Kay et al., 1999), (5) mid-Miocene Maricunga belt andesites (Jotabeche Norte, La Laguna, Cadillal-Yeguas Heladas; Kay et al., 1991; 1994b; Mpodozis et al., 1995), (6) < 2 Ma primitive basalts from the southernmost CVZ (Kay et al., 1999), and (7) ~ 9 Ma Los Aparejos basaltic andesite. Data are in Table 2.6. Forearc Mesozoic units (purple crosses) are measured values from mafic volcanics and plutons from the Coastal Cordillera (Lucassen and Thirlwall, 1998; Lucassen et al., 2002). Average isotopic values of Early to Late Paleozoic metamorphic and magmatic rocks between 21° and 27° S are from Lucassen et al. (2001).

Graphs of ²⁰⁶Pb/²⁰⁴Pb vs. (A) ²⁰⁷Pb/²⁰⁴Pb and (B) ²⁰⁸Pb/²⁰⁴Pb showing Figure 2.13 (1) adakitic andesites (Pircas Negras and Dos Hermanos) from the southernmost Andean Puna, (2) a basaltic andesite from the Valle Ancho, (3) a ~ 20 Ma Escabroso Formation and esite from the main cordillera of the Chilean flatslab-El Indio belt (Kay et al., 1999), (4) 24 Ma Segerstrom primitive basalt (Kay et al., 1999), (5) < 2 Ma primitive basalts from the southernmost CVZ (Kay et al., 1999), and (6) \sim 9 Ma Los Aparejos basalt from the Valle Ancho. Data are in Table 2.6. Forearc Mesozoic units (crosses) are measured values from exposed mafic volcanics and plutons from the Coastal Cordillera (Lucassen and Thirlwall, 1998; Lucassen et al., 2002). Open diamond and triangle show average values of Jurassic forearc gabbros (Lucassen et al., 2002) and Paleozoic crust (Lucassen et al., 2001) respectively. Pb isotopic data for Permo-Triassic Choiyoi grano-rhyolite province are from Moscoso et al. (1993). Hatched field shows range of lavas from the Chilean flatslab (28°-33° S) and southern CVZ (Kay et al., 1999 and references therein). Isotopic data for Precordillera and Sierras Pampeanas lavas are shown by striped fields and are from (Kay and Abbruzzi, 1996; Kay et al., 1999). NHRL = Northern Hemisphere Reference Line (Zindler and Hart, 1986). Dashed box shows isotopic field shown in Figure 2.14.



Graphs showing multi-stage isotope mixing model for adakitic Figure 2.14 andesites from the northern flat slab transition zone and mantle-derived basalts from the southernmost CVZ. (A) 87 Sr/ 86 Sr vs. ϵ Nd (B) 206 Pb/ 204 Pb vs. 207 Pb/ 204 Pb and (C) 206 Pb/ 204 Pb vs. 208 Pb/ 204 Pb for samples discussed in Figures 2.12-2.13 and from Table 2.6. Stage one of the model (solid black line) shows possible isotopic concentrations of a mixture of mafic Jurassic gabbros and sialic average Paleozoic rocks of the Chilean forearc. Values for Paleozoic crust are from Lucassen et al. (2001) (Sr = 189 ppm, Nd = 24.3 ppm, Pb = 16 ppm, ${}^{87}Sr/{}^{86}Sr = 0.732064$, $\epsilon Nd = -8.72$; ${}^{87}Sr/{}^{86}Sr = 0.732000$; $\epsilon Nd = -8.72$; ${}^{206}Pb/{}^{204}Pb = 18.95$; ${}^{207}Pb/{}^{204}Pb = 15.69$; ${}^{208}Pb/{}^{204}Pb = 38.90$) and Jurassic gabbros (Sr = 319 ppm, Nd = 2.06 ppm, Pb = 1.22 ppm, 87 Sr/ 86 Sr = 0.703309, ϵ Nd = +6.57; 206 Pb/ 204 Pb = 18.23; 207 Pb/ 204 Pb = 15.59; 208 Pb/ 204 Pb = 38.08) are from Lucassen et al. (2002). Large circles represent mixtures of these two forearc end-members in ratios of 9:1, 8.5:1.5, and 8:2. Stage two of the model (dashed lines) involves contamination of the pre-migration Andean mantle represented by the 24 Ma Segerstrom basalt (CC 320c) with forearc material. Three mixing lines, one for each possible forearc contaminant from stage one, are shown in dashed lines. Hatch marks represent 10 % mixing Open regions in Pb isotope diagrams represent isotopic intervals. values for the Pircas Negras/Dos Hermanos predicted by Figure 2.14a (Sr-Nd) without the effect of Pb isotopic buffering by in situ crustal basement (i.e., Choiyoi). Dark arrow points toward Choiyoi isotopic values shown in Figure 2.13.



Pb isotopic ratios from the Pircas Negras and Dos Hermanos andesites overlap the general field for Chilean flatslab and southern CVZ lavas (Kay et al., 1999 and references therein) and range from ${}^{206}Pb/{}^{204}Pb = 18.63-18.72$, ${}^{207}Pb/{}^{204}Pb = 15.60-$ 15.62, ${}^{208}Pb/{}^{204}Pb = 38.56-38.76$ (Figure 2.13a,b). The Valle Ancho basaltic andesite and 9 Ma Los Aparejos basalt, have Pb isotopic ratios that generally agree with those of the Pircas Negras and Dos Hermanos andesites. No Pb isotopic data are available for the 21-18 Ma Escabroso or 18-13 Ma southern Maricunga andesites that erupted within the northern flatslab transition zone (27°-29° S). However, a ~ 20 Ma Escabroso andesite from the Frontal Cordillera of the flatslab region (~ 29.5°) exhibits ${}^{206}Pb/{}^{204}Pb$ (18.64) similar to the Pircas Negras, whereas ${}^{207}Pb/{}^{204}Pb$ (15.63) and ${}^{208}Pb/{}^{204}Pb$ (38.39) are more and less radiogenic respectively than the Pircas Negras andesites (Figure 2.14a,b; Kay and Abbruzzi, 1996).

Oxygen isotopes on mineral separates from two Pircas Negras andesites and from the Valle Ancho basaltic andesite are given in Table 2.7. Olivines from the Valle Ancho basaltic andesite (CC 101) and the upper Veladero Pircas Negras andesite (CO 324) have near mantle-like oxygen isotopic ratios of $\delta^{18}O_{ol} = +6.2 \% \pm 0.2$. A quartz xenocryst from the La Gallina high-Mg Pircas Negras andesite (CO 427) yielded a crustal oxygen isotopic value of $\delta^{18}O_{qz} = +8.35 \% \pm 0.2$.

Table 2.7														
Oxygen isotopic data for Pircas Negras and Valle Ancho mineral separates														
sample	unit	age	$\delta^{18}O_{ol}$	error	$\delta^{18}O_{qz}$	error								
CO 324	Veladero Pircas Negras	~ 5	6.2	0.2										
CO 427	Gallina Pircas Negras	~ 6			7.8 8.9									
				mean	8.35	0.20								
CC 101	Valle Ancho cone	58 ± 07	62	0.2										

Oxygen isotopic data were obtained by ArF laser fluorination at Universität Göttingen. Individual olivine and whole rock analyses were corrected to the UWG-2 garnet standard ($\delta^{18}O = 5.7$). The Doerndrop quartz was run as a secondary standard with mean values of $\delta^{18}O = 12.32 \pm 0.47$ ‰ (n = 3) and $\delta^{18}O = 12.65 \pm 0.45$ ‰ (n = 3). In-run machine error is estimated at ± 0.2 ‰ with analytical precision of 0.2 - 0.5 ‰. Reported error for mineral separates is from in-run machine error.

VI PETROGRAPHY AND MINERAL CHEMISTRY

The 7-2 Ma Pircas Negras andesites are composed of uniformly hypocrystalline and melanocratic glassy lava dominated by acicular porphyritic phenocrysts of oxy-amphibole with minor clinopyroxene and olivine in a cryptocrystalline groundmass of plagioclase microlites, rhombic Fe-Ti oxide phases, and translucent grey glass. Plagioclase phenocrysts are rare and are completely absent in most samples. Estimated phenocryst abundances in the Pircas Negras lavas range from 10 to 30 %. Representative major element mineral analyses are in Table 2.8 and all of the analyses are in Appendices 5 to 10.

Amphibole and oxy-amphibole are the dominant mafic phases (85-100 %) in the Pircas Negras andesites from the northern transition zone. They form euhedral accilar laths (0.1-4 mm) and basal pyramids (0.1-1 mm) with thick opaque reaction rims that occasionally penetrate to the core of the crystal (Figure 2.15a). Amphiboles are typically aligned and rarely form glomeroporphyritic cumulates. Following the classification scheme of Leake et al. (1997), amphiboles from Pircas Negras andesites (samples CO 412, CO 427, CO 324, and CO 309) have $(Ca+Na)_B \ge 1.00$ and Na_B < 0.50 and are thus sodic-calcic amphiboles. With the exception of a few tschermakitic amphiboles with $(Na + K)_A < 0.5$ from CO 427 and CO 324, the majority of the amphiboles are magnesiohastingites (pargasites) (Table 2.8 and Figure 2.16). Compositions define a trend from the most magnesian amphiboles in sample CO 427 (Rio de La Gallina; $Mg\#_{amph} = 0.66-0.80$) to the least magnesian in sample CO 309 (Rio Salado; Mg $\#_{amph}$ = 0.62-0.72). Alumina concentrations are generally high ($Al_2O_3 = 11.5-13.0$ wt %), except for those in sample CO 427 ($Al_2O_3 =$ 10.72-12.5 wt %). A few amphiboles from CO 324 have completely resorbed cores while retaining rims that exhibit a skeletal euhedral basal form.

Representative major element inmeral analyses from selected rifes regras and bos fremanos andesites										olivine analyses					
analysis #	83	85	150	152	222	223	3	4		55	56	238	241	272	
type	с	r	с	r	с	r	с	с		с	r	с	r	с	
sample	309-1	309-1	427-7	427-7	324-3	324-3	412-3	412-3		101-1	101-1	324-3	324-3	412-1	
SiO ₂	40.98	42.29	43.24	43.59	43.64	42.61	42.86	42.89		39.21	37.55	39.31	38.18	39.16	
TiO ₂	2.92	2.74	2.09	2.26	2.24	3.04	1.90	2.08		0.02	0.03	0.01	0.02	0.05	
Al_2O_3	13.36	12.04	11.59	11.15	12.68	12.17	12.65	12.48		0.05	0.02	0.00	0.05	0.05	
FeO	13.08	10.96	7.75	8.32	9.18	10.17	7.85	8.77		16.19	26.86	16.20	23.66	17.34	
MnO	0.13	0.10	0.09	0.09	0.12	0.06	0.13	0.14		0.23	0.45	0.24	0.44	0.36	
MgO	12.60	14.85	16.52	16.80	15.97	15.73	16.71	16.58		44.05	35.19	44.64	38.05	42.78	
CaO	11.15	11.41	11.04	11.21	11.18	12.12	11.72	11.48		0.11	0.18	0.11	0.11	0.18	
Na ₂ O	2.70	2.60	2.58	2.49	2.40	2.56	2.48	2.46		0.01	0.00	0.00	0.00	0.00	
K ₂ O	0.78	0.78	0.71	0.65	0.71	0.59	0.68	0.77		0.00	0.00	0.00	0.00	0.01	
Cr ₂ O ₃	0.01	0.03	0.72	0.18	0.17	0.09	0.95	0.22		0.04	0.00	0.02	0.03	0.01	
Total	97.72	97.80	96.34	96.76	98.29	99.13	97.94	97.87		99.92	100.27	100.53	100.53	99.93	
Si	6.001	6.112	6.229	6.251	6.169	6.066	6.087	6.094		0.992	0.997	0.988	0.995	0.996	
Ti	0.322	0.297	0.227	0.244	0.238	0.325	0.203	0.222		0.000	0.001	0.000	0.000	0.001	
Al (iv)	1.999	1.888	1.771	1.749	1.831	1.934	1.913	1.906		0.001	0.001	0.000	0.001	0.001	
Al (vi)	0.307	0.162	0.197	0.135	0.280	0.108	0.205	0.183		-	-	-	-	-	
Fe ²⁺	0.966	0.606	0.158	0.153	0.204	0.562	0.113	0.104		0.342	0.596	0.341	0.515	0.369	
Fe ³⁺	0.635	0.719	0.776	0.845	0.880	0.649	0.819	0.938		-	-	-	-	-	
Mn	0.016	0.012	0.011	0.011	0.014	0.007	0.016	0.017		0.005	0.010	0.005	0.010	0.008	
Mg	2.752	3.200	3.548	3.591	3.364	3.338	3.538	3.512		1.661	1.393	1.673	1.478	1.622	
Ca	1.750	1.768	1.706	1.724	1.694	1.851	1.785	1.749		0.003	0.005	0.003	0.003	0.005	
Na _(B)	0.250	0.232	0.294	0.276	0.306	0.149	0.215	0.251		0.000	0.000	0.000	0.000	0.000	
Na _(A)	0.515	0.497	0.426	0.417	0.353	0.558	0.469	0.428		-	-	-	-	-	
K	0.146	0.144	0.130	0.119	0.129	0.107	0.122	0.140		0.000	0.000	0.000	0.000	0.000	
Cr	0.002	0.004	0.083	0.021	0.019	0.010	0.107	0.024		0.001	0.000	0.000	0.001	0.000	
Total	15.874	15.889	15.824	15.826	15.783	15.889	15.874	15.891		3.007	3.002	3.011	3.004	3.002	
(Na + K) _A	0.661	0.641	0.557	0.536	0.481	0.665	0.591	0.567	Fo	82.7	69.7	82.9	73.8	81.2	
$(Ca + Na)_B$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	Fa	17.0	29.8	16.9	25.7	18.4	
Mg ²⁺ /(Mg ²⁺ +Fe _T)	0.632	0.707	0.792	0.783	0.756	0.734	0.791	0.771	Тр	0.2	0.5	0.2	0.5	0.4	

 Table 2.8

 Representative major element mineral analyses from selected Pircas Negras and Dos Hermanos andes

All unknown mineral analyses were corrected by deviation from Smithsonian standards JDF and A99 and in-house standard RHA. Replicated analyses of USGS secondary standards are reported in Appendices 5-10 relative to published values by Jarosewich et al. (1980). Amphiboles, olivines, pyroxenes, and plagioclase phenocrysts were calculated on the basis of 23, 4, 6, and 32 oxygens respectively. Cation totals assume all Fe as Fe^{2+} and the Fe^{2+}/Fe^{3+} ratio was calculated from the cation total following Droop (1987). Na (B) is calculated following Leake et al. (1997) for all amphibole analyses. Olivines: Fo = Forsterite; Fa = Fayalite; Tp = Tephroite, Pyroxenes: En = Enstatite; Fs = Ferrosilite; Wo = Wollastonite; Jd = Jadite; FeCaTs = Fe Ca Tschermak calculated following Lindsley (1983); Plagioclase: An = Anorthite; Ab = Albite Or = Orthoclase.

analysis #	31	34	14	16	67	69	97	114	121	137	263	268	9	242	226
type	с	r	с	r	с	r	cum	с	r-az	r-qz	с	r	cum	с	с
sample	428-2	428-2	81-1	81-1	101-1	101-1	309-1	309-7	309-9	427-1	412-1	412-2	412-4	324-3	324-1
SiO ₂	50.11	50.34	50.76	50.98	51.70	47.52	52.47	50.95	53.30	52.89	52.36	51.94	52.99	50.97	51.39
T1O ₂	0.76	0.74	0.90	0.73	0.53	1.71	0.40	0.67	0.19	0.25	0.43	0.74	0.18	0.50	0.41
Al ₂ O ₃	4.51	3.24	4.27	3.08	2.14	5.65	2.47	4.59	0.24	0.88	3.29	1.13	0.92	3.28	3.15
FeO	6.75	6.82	6.80	6.09	6.57	9.98	7.16	7.58	8.51	8.02	5.82	8.65	8.67	10.85	10.40
MnO	0.13	0.17	0.10	0.12	0.15	0.23	0.13	0.11	0.26	0.25	0.17	0.35	0.19	0.32	0.26
MgO	14.54	15.50	14.97	15.41	16.56	13.52	16.13	14.78	14.80	15.34	16.66	15.90	15.55	13.17	13.66
CaO	22.30	22.69	21.64	22.49	20.98	20.00	20.32	20.76	22.04	21.10	21.15	20.47	21.15	20.03	20.14
Na ₂ O	0.67	0.43	0.60	0.43	0.22	0.40	0.59	0.78	0.35	0.38	0.50	0.46	0.54	0.85	0.85
K_2O	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.02	0.03	0.00	0.00	0.00	0.00	0.00
Cl_2O_3	100.25	100.02	0.51	0.40	0.24	0.10	0.26	0.20	0.01	0.00	0.25	0.00	0.02	0.05	0.14
Total	100.55	100.02	100.57	99.74	99.08	99.13	99.95	100.47	99./1	99.14	100.60	99.04	100.20	100.00	100.41
Si	1.837	1.849	1.860	1.878	1.914	1.785	1.926	1.864	1.984	1.972	1.900	1.926	1.953	1.900	1.903
Ti	0.021	0.021	0.025	0.020	0.015	0.048	0.011	0.018	0.005	0.007	0.012	0.021	0.005	0.014	0.012
Al (iv)	0.163	0.140	0.140	0.122	0.086	0.215	0.074	0.136	0.011	0.028	0.100	0.049	0.040	0.100	0.097
Al (vi)	0.032	0.000	0.044	0.011	0.008	0.035	0.033	0.062	0.000	0.010	0.041	0.000	0.000	0.044	0.040
Fe ²⁺	0.088	0.059	0.128	0.097	0.147	0.205	0.167	0.148	0.229	0.217	0.112	0.176	0.184	0.249	0.231
Fe ³⁺	0.119	0.150	0.080	0.090	0.057	0.109	0.053	0.084	0.036	0.033	0.064	0.092	0.083	0.089	0.091
Mn	0.004	0.005	0.003	0.004	0.005	0.007	0.004	0.004	0.008	0.008	0.005	0.011	0.006	0.010	0.008
Mg	0.795	0.849	0.818	0.846	0.914	0.757	0.883	0.807	0.821	0.852	0.901	0.879	0.855	0.731	0.754
Ca	0.877	0.894	0.850	0.888	0.833	0.806	0.800	0.815	0.880	0.843	0.823	0.814	0.836	0.800	0.800
Na _(B)	0.047	0.031	0.043	0.031	0.015	0.029	0.042	0.055	0.025	0.028	0.035	0.033	0.038	0.061	0.061
Na _(A)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.000	0.000
Cr	0.017	0.002	0.009	0.012	0.007	0.003	0.008	0.007	0.000	0.000	0.007	0.000	0.001	0.001	0.004
Total	4.040	4.051	4.027	4.030	4.019	4.037	4.018	4.028	4.012	4.011	4.022	4.031	4.028	4.030	4.031
Fn	53.9	55.9	51.8	52.1	52.1	50.5	50.9	51.9	43.3	45.6	54.2	50.5	48.1	45.1	46.5
Fs	5.9	3.9	8.1	6.0	8.3	13.7	9.6	9.5	12.1	11.6	6.8	10.1	10.4	15.4	14.2
Wo	40.2	40.1	40.1	41.8	39.6	35.8	39.5	38.6	44.7	42.8	39.0	39.4	41.5	39.5	39.3
Ac	0.047	0.031	0.043	0.031	0.015	0.029	0.042	0.055	0.025	0.028	0.035	0.033	0.038	0.061	0.061
FeCaTs	0.072	0.119	0.038	0.059	0.041	0.080	0.011	0.029	0.011	0.006	0.029	0.059	0.044	0.028	0.030
AlCaTs	0.032	0.000	0.044	0.011	0.008	0.035	0.033	0.062	0.000	0.010	0.041	0.000	0.000	0.044	0.040

 Table 2.8 (continued)

 Representative major element mineral analyses from selected Pircas Negras and Dos Hermanos andesites

Représentative n		orthopyroxen	e analyses		egras and Do.	5 1101 1141									
analysis #	6	8	255	256	211		156	168	195	241	253	219	144	181	205
type	с	r	с	r	r-oliv		r	с	r	с	с	с	xeno-r	xeno-c	xeno-c
sample	412-1	412-1	324-4	324-4	324-2		324-4	412-1	427-2	309-3	101-2	81-1	324-2	412-9	427-9
SiO ₂	54.11	53.71	52.88	52.87	53.85		54.16	53.01	54.07	56.03	52.84	53.48	60.48	62.26	61.10
TiO ₂	0.19	0.22	0.17	0.18	0.41		0.06	0.03	0.05	0.07	0.11	0.05	0.03	0.01	0.00
Al_2O_3	3.06	2.89	1.18	1.19	1.10		29.45	29.91	29.02	27.45	28.61	29.31	25.04	23.90	25.73
FeO	10.63	10.65	21.16	21.24	17.00		0.62	0.58	0.73	0.75	1.06	0.88	0.40	0.03	0.08
MnO	0.23	0.20	0.55	0.53	0.49		0.00	0.00	0.02	0.01	0.00	0.02	0.00	0.00	0.01
MgO	30.22	29.27	23.00	22.90	26.19		0.04	0.06	0.08	0.04	0.12	0.05	0.02	0.00	0.01
CaO	1.12	1.64	1.35	1.29	1.58		12.01	12.89	11.83	9.62	12.56	11.93	6.33	5.30	6.25
Na ₂ O	0.04	0.04	0.05	0.02	0.03		4.26	4.04	4.58	5.40	4.05	4.35	6.68	7.40	7.03
K ₂ O	0.00	0.00	0.00	0.01	0.01		0.38	0.27	0.27	0.51	0.35	0.40	1.31	1.30	1.06
Cr ₂ O ₃	0.70	0.53	0.01	0.03	0.04		-	-	-	-	-	-	-	-	-
Total	100.29	99.14	100.38	100.27	100.72		100.99	100.78	100.66	99.87	99.69	100.46	100.30	100.21	101.26
Si	1.902	1.914	1.951	1.954	1.941		9.719	9.561	9.744	10.116	9.656	9.672	10.768	11.038	10.745
Ti	0.005	0.006	0.005	0.005	0.011		0.008	0.004	0.007	0.009	0.015	0.007	0.004	0.001	0.000
Al (iv)	0.098	0.086	0.049	0.046	0.047		6.229	6.357	6.163	5.840	6.163	6.248	5.253	4.994	5.332
Al (vi)	0.028	0.035	0.002	0.006	0.000		-	-	-	-	-	-	-	-	-
Fe ²⁺	0.270	0.291	0.612	0.626	0.463		0.093	0.088	0.111	0.114	0.162	0.133	0.060	0.005	0.012
Fe ³⁺	0.043	0.026	0.041	0.031	0.050		-	-	-	-	-	-	-	-	-
Mn	0.007	0.006	0.017	0.017	0.015		0.000	0.000	0.003	0.001	0.000	0.003	0.000	0.000	0.002
Mg	1.583	1.555	1.265	1.262	1.408		0.011	0.017	0.022	0.011	0.031	0.013	0.005	0.000	0.002
Ca	0.042	0.063	0.054	0.051	0.061		2.312	2.493	2.287	1.862	2.462	2.313	1.209	1.007	1.178
Na _(B)	0.002	0.003	0.004	0.002	0.002		1.483	1.411	1.599	1.891	1.434	1.524	2.307	2.543	2.398
Na _(A)	-	-	-	-	-		-	-	-	-	-	-	-	-	-
K	0.000	0.000	0.000	0.000	0.001		0.088	0.061	0.061	0.116	0.083	0.093	0.298	0.295	0.237
Cr	0.019	0.015	0.000	0.001	0.001		-	-	-	-	-	-	-	-	-
Total	4.014	4.009	4.014	4.010	4.017		19.944	19.993	19.997	19.959	20.006	20.005	19.904	19.883	19.906
En	2.2	3.3	2.8	2.6	3.2	An	59.5	62.87	57.94	48.12	61.88	58.86	31.7	26.19	30.90
Fs	83.5	81.5	65.5	65.1	72.9	Ab	38.2	35.59	40.51	48.87	36.04	38.78	60.5	66.15	62.89
Wo	14.2	15.2	31.7	32.3	24.0	Or	2.3	1.54	1.55	3.01	2.07	2.35	7.8	7.66	6.21

 Table 2.8 (continued)

 Representative major element mineral analyses from selected Pircas Negras and Dos Hermanos andesites



Figure 2.15 Photomicrographs of Pircas Negras and Dos Hermanos andesites: (A) ~ 5.2 Ma Paso Pircas Negras (CO 414) showing oxidized magnesiohastingitic amphiboles, (B) ~ 6.2 Ma Gallina Pircas Negras (CO 427) showing a resorbed quartz xenocryst with a cpx reaction corona, (C) glomeroporphyritic clots of olivine in ~ 5 Ma Rio Veladero Pircas Negras (sample CO 324), (D) cpx as the only phenocrystic phase in 7.7 Ma Dos Hermanos (sample CO 428). Major phenocrystic and xenocrystic phases are labeled



Figure 2.16 Analyses of Pircas Negras amphiboles plotted on the classification diagram of Leake et al. (1997). Pircas Negras samples include: CO 427 (~ 6 Ma La Gallina), CO 324 (~ 5 Ma Quebrada Veladero), CO 412 (5.2 Ma Paso Pircas Negras), and CO 309 (~ 4 Ma Barrancas Blancas). Representative data are in Table 2.8 and all data are in Appendix 5. Cation concentrations have been corrected for $Fe^{2+/}Fe^{3+}$ following Droop (1987) where $Fe^{3+} = 2*X(1-T/S)$ in which X is the number of oxygens per formula unit; T is the ideal number of cations per formula unit, and S is the measured cation totals.

Clinopyroxene exists in approximately two-thirds of the sampled Pircas Negras lavas, occurring as < 5 % of the total phenocryst population. The grains are typically < 1 mm sub-to-anhedral crystals often found in glomeroporphyritic clots surrounded by euhedral hornblende laths. Within the Pircas Negras suite, there is little compositional variability between clinopyroxene phenocrysts with most plotting between $En_{45-55}Fs_{5-15}Wo_{38-41}$ on the pyroxene ternary diagram (Table 2.8 and Figure 2.17a,b). Clinopyroxene cores from CO 412 have the lowest Fe-contents (< Fs₂₋₉). These crystals are normally-zoned with Fe-rich rims (< Fs₁₀₋₁₁) that are compositionally similar to cumulitic clinopyroxenes ($En_{47-49}Fs_{10-12}Wo_{40-42}$). Core compositions from sample CO 309 overlap the rim and cumulitic clinopyroxenes in sample CO 412. Rims from these clinopyroxenes as well as cores from CO 427 are more Fe-rich (Fs₁₀₋₁₅). Reversely zoned clinopyroxenes from CO 324 are distinct from the bulk of the Pircas Negras population due to their Fe-rich (Fs₁₃₋₁₅) cores and compositionally bimodal rims (Fe₇₋₉ and Fe₁₂₋₁₃).

Clinopyroxene is the only phenocrystic phase in the Dos Hermanos andesites and exists as small (< 1 mm) tabular crystals in a cryptocrystalline glassy matrix (Figure 2.15d). Dos Hermanos clinopyroxenes in samples CC 81 and CO 428 are normally-zoned and are generally more enstatitic than those in the Pircas Negras andesites ($En_{48-54}Fs_{6-10}Wo_{39-43}$; Figure 2.17c). They are similar to cpx cores from sample CO 412 and cpx rims from CO 324. Clinopyroxene cores from the Valle Ancho basaltic andesite (CC 101) are compositionally similar to those of the Dos Hermanos and Pircas Negras, whereas the rims are distinctively more Fe-rich (Fs_{10-15}) and have similar enstatite contents as cores from reversely-zoned clinopyroxenes from sample CO-324 (Figure 2.17c).



Figure 2.17 Pyroxene and olivine analyses of selected Pircas Negras, Dos Hermanos, and Valle Ancho samples plotted in the pyroxene ternary diagram (at bottom right). (A) Pircas Negras samples CO 324 (~ 5 Ma Quebrada Veladero) and CO 412 (5.2 Ma Paso Pircas Negras) showing tie-lines between cpx-opx pairs used to calculate pre-eruptive temperatures from two pyroxene geothermometry (Table 2.9), (B) Pircas Negras samples CO 427 (~6 Ma La Gallina) and CO 309 (~4 Ma Barrancas Blancas), (C) Dos Hermanos samples CO 428 and CC 81 (\sim 7.7 Ma). Also plotted in (C) are mineral data from the Valle Ancho basaltic andesites. Representative analyses are in Table 2.8 and all data are in Appendices 6 (cpx), 7 (opx), and 8 (olivines). Pyroxene cation totals have been corrected for $Fe^{2+7}Fe^{3+}$ (Droop, 1987). Filled and open symbols are cores and rim analyses respectively. Red open symbols represent pyroxene cumulates. Pyroxene endmember compositions are En = Enstatite (MgSi₂O₃), Fs = Ferrosilite (FeSiO₃). Vertical axis (Z) is $Wo = Wollastonite (CaSiO_3)$. Olivine endmember compositions are Fo = Forsterite (Mg₂SiO₄), $Fa = (Fe_2SiO_4)$ and are plotted on the lower binary axis (Fo-Fa).

Orthopyroxene exists as a trace phase in only a few samples forming small (< 1 mm) subhedral independent phenocrysts. Two populations of orthopyroxene occur (Table 2.8 and Figure 2.17a). Those in sample CO 412 with high Mg contents (> En_{82-84}) contrast with phenocrysts in sample CO 324 with lower Mg (En_{65-66}). Sample CO 324 also contains high-Mg orthopyroxene microphenocrysts (En_{73-91}) that occur as aggregate rims around subhedral olivine phenocrysts.

Olivine phenocrysts are rare in the Pircas Negras andesites but occur in a few samples (CO 309; CO 412; CO 413; CO 324) as cumulates of 10-20 anhedral crystals (Figure 2.15c). No correlation exists between whole rock SiO₂ content and the presence of cumulitic olivine. Pircas Negras olivines are normally zoned and exhibit a narrow compositional range with Fo₇₉₋₈₃ cores and Fo₇₄₋₇₉ rims (Table 2.8; Figure 2.17a). In contrast to the Pircas Negras, the Valle Ancho basaltic andesites contain olivine as an abundant phase (> 10 %). These olivines exhibit a wider compositional range of than Pircas Negras olivines with cores ranging from Fo₇₃₋₈₃ and rims from Fo₆₆₋₇₄ (Figure 2.17c).

A defining petrographic characteristic of the Pircas Negras andesites is the general lack of phenocrystic plagioclase. However, plagioclase does occur as groundmass microlites or microphenocrysts (< 0.5 mm) or as larger sub- to anhedral xenocrysts (1-10 mm). Plagioclase compositions are shown in Table 2.8 and plotted in Figure 2.18. Microphenocrystic plagioclase is generally An_{48-65} and shows little compositional zoning. A few of the microlites have < An_{40} . Microlites from andesite CO 412 have the highest average An-content (An_{61} ; n=18) and those from CO 309 have the lowest (An_{57} ; n=10). Dos Hermanos microlites exhibit a wider compositional range (An_{17-59}) than those in the Pircas Negras or from the Valle Ancho basaltic andesite (CC 101; An_{46-65}). The single plagioclase phenocryst in Dos Hermanos

sample CC 81 is highly zoned and compositionally similar to Pircas Negras groundmass plagioclase (An_{46} - An_{66}).

Xenocrystic plagioclases display extensive resorbtion, reverse zoning, and sieve textures indicative of chemical disequilibrium with the Pircas Negras melt. Only in the Rio Veladero flow (CO 324) do plagioclase xenocrysts exceed > 5 % of the total crystal population. Cores of the xenocrysts (An₂₆₋₄₁) are significantly more albitic than plagioclase microphenocrysts, whereas the rims (An₂₈₋₄₉) approach the An content of the microlitic plagioclase.



Figure 2.18 Plagioclase analyses of selected Pircas Negras, Dos Hermanos, and Valle Ancho lava flows plotted in the An-Ab-Or ternary diagram (only Or_{0-20} is shown). Pircas Negras samples are the same as in Figure 2.17. Data for representative analyses are shown in Table 2.8 and all data are given in Appendix 9. Red symbols represent xenocrystic plagioclase compositions. Filled and open symbols represent core and rim compositions respectively. Ab = Albite (NaAlSi₃O₈), An = Anorthite (CaAl₂Si₂O₈), and Or = Orthoclase (KalSi₃O₈).

Quartz xenocrysts exist in many Pircas Negras lavas and are evident in hand specimen. These xenocrysts are highly fractured resorbed crystals rimmed by coronas of radiating acicular clinopyroxene microlaths (Figure 2.15b). Lithic agglomerates resembling a sandstone or siltstone xenolith composed of randomly-oriented and severely-resorbed albite and quartz xenocrysts are also found in a flow from the Paso Pircas Negras (CO 415). Xenocrysts and xenoliths in Pircas Negras lavas provide petrographic evidence for assimilation of pre-existing felsic crust.

Magnetite is the dominant oxide phase in the Pircas Negras lavas occurring as small (< 0.1 mm) equant rhombs within the groundmass or as inclusions within silicate phases. Ilmentite is absent from most flows although it was found in contact with magnetite and as an independent phase in a few samples (Appendix 10 and Figure 2.19). One sample, the Rio Veladero Pircas Negras (CO 324), contains abundant in-contact ilmenite-magnetite pairs (Figure 2.19). Other trace phases qualitatively identified include apatite, zircon, and chromite.

VII GEOTHERMOMETRY

Pre-eruptive crystallization temperatures were calculated from two Pircas Negras flows (CO 412 and CO 324) using two pyroxene (Lindsley, 1983) and magnetite-ilmenite (Anderson and Lindsley, 1988) phase equilibria (Tables 2.9 and 2.10). To calculate Wo-Fs-En endmember compositions (Table 2.8), non-quadrilateral components were subtracted from analyses of co-existing cpx and opx phenocrysts following Lindsley (1983). Two pyroxene and magnetite-ilmenite temperatures were calculated using the algorithms in the QUILF95 program (Anderson et al., 1993). Two-pyroxene temperatures were calculated at 0.5 kbar, 1 kbar, 2 kbar, and 5 kbar due to the pressure dependency on pyroxene equilibrium compositions. For chemically pure end-member phases crystallizing in equilibrium, the error of the two-pyroxene

and magnetite-ilmenite geothermometers are \pm 50 °C and \pm 10 °C respectively. Estimates of pre-eruptive f_{O2} obtained via magnetite-ilmenite equilibria are presented in Table 2.10. Only in-contact oxide pairs (Figure 2.19) were used to calculate temperature and f_{O2} in order to minimize error due to phase disequilibrium.



Figure 2.19 Electron microprobe backscatter images of in-contact magnetite-ilmenite grains from Pircas Negras andesites (CO 324 and CO 412). Dots show sites of microprobe analyses. Concentrations and calculated pre-eruptive temperatures are in Appendix 10 and Table 2.10 respectively.
Table 2.9												
Two pyroxene geothermometry ¹ for sample CO 412 calculated with average phenocrystic opx ²												
		v			0.5 kbar		1 kbar		2 kbar		5 kbar	
cpx analysis	#	En	Fs	Wo	T° C	±	T° C	±	T° C	±	T° C	±
cores			<u>CO 412</u>									
412-1 (cpx1)	263	0.542	0.068	0.390	1049	66	1051	67	1054	68	1064	72
412-1 (cpx1)	265	0.506	0.091	0.404	1059	50	1061	50	1064	50	1074	50
412-2 (cpx2)	266	0.528	0.075	0.397	1053	50	1055	50	1058	50	1068	50
rims			<u>CO 412</u>									
412-2 (cpx1)	268	0.505	0.101	0.394	1066	60	1068	60	1071	59	1082	56
412-2 (cpx1)	269	0.493	0.104	0.403	1065	74	1065	76	1068	75	1078	72
cumulates			<u>CO 412</u>									
412-4 (cum1)	9	0.481	0.104	0.415	1058	86	1060	85	1063	84	1072	82
412-5 (cum2)	10	0.491	0.112	0.397	1065	96	1067	96	1070	95	1081	92
² average opx	6-9	0 824	0 149	0.027								

¹Two-pyroxene geothermometry obtained using the QUILF95 program of Anderson et al. (1993). Clinopyroxene (cpx) endmember composition calculated following Lindsley (1983) with reported errors a minimum of \pm 50 °C. ²Average orthopyroxene (opx) endmember compositions are from average of 2 rim and 2 core analyses of sample 412-1 (opx1)

Two pyroxene geothermometry ¹ for sample CO 324 calculated with phenocrystic opx ²													
					0.5 kb	0.5 kbar		1 kbar		2 kbar		5 kbar	
cpx analysis	#	En	Fs	Wo	T° C	±	T° C	±	T° C	±	T° C	±	
cores ³			<u>CO 324</u>										
324-3 (cpx1)	242-3	0.451	0.154	0.395	962	50	964	50	967	50	977	50	
324-4 (cpx1)	258-9	0.456	0.130	0.414	940	52	942	53	945	54	954	57	
average opx core ²	254-5	0.657	0.316	0.027									
rims			<u>CO 324</u>										
324-4 (cpx1)	260-1	0.452	0.124	0.425	922	54	923	54	926	55	934	58	
average opx rim ²	256-7	0.651	0.323	0.026									

Table 2.9 (continued)

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Two pyroxene geothermometry ¹ for sample CO 324 calculated with opx rims on olivine												
					0.5 kb	ar	1 kba	ır	2 kba	ır	5 kba	ır
		En	Fs	Wo	T° C	±	T° C	±	T° C	±	T° C	±
cores ³			<u>CO 324</u>									
324-1 (cpx1)	225-7	0.467	0.140	0.393	1052	50	1054	50	1057	50	1067	50
324-2 (cpx1)	230-1	0.470	0.140	0.390	1053	50	1055	50	1058	50	1069	50

opx-rims 4 2110.7290.2400.032¹Two-pyroxene geothermometry obtained using the QUILF95 program of Anderson et al. (1993). Clinopyroxene (cpx) endmember composition calculated
following Lindsley (1983) with reported errors a minimum of \pm 50 °C.

²Orthopyroxne (opx) core and rim compositions are from average of 2 analyses of 324-4 (opx1)

³Cpx cores are averages of two analyses ⁴Opx-rim endmember composition are from sample 324-2 (opxolrim1)

Two oxide geothermometry ¹ for Pircas Negras in contact mt-ilm pairs										
		<u>CO 412</u>	T° C	±	fO_2	±	ΔQMF			
Pair 1	Ilm1 (312)	Mt1 (314)	880	23	-10.44	0.26	2.47			
	Ilm1 (313)	Mt1 (314)	882	41	-10.41	0.46	2.46			
		<u>CO 324</u>	T° C	±	fO_2	±	ΔQMF			
Pair 1	Ilm1 (292)	Mt1 (294)	855	45	-11.70	0.45	1.69			
		Mt1 (295)	860	41	-11.63	0.41	1.65			
	Ilm1 (293)	Mt1 (294)	846	13	-11.93	0.14	1.63			
		Mt1 (295)	851	10	-11.86	0.09	1.60			
Pair 2	Ilm2 (298)	Mt2 (296)	855	34	-12.15	0.34	1.21			
		Mt2 (297)	858	55	-12.11	0.56	1.22			
		Mt2 (299)	831	32	-12.52	0.33	1.35			
Pair 3	Ilm (303)	Mt1 (301)	788	10	-13.55	0.03	1.24			
Pair 4	Ilm4 (306)	Mt1 (#304)	896	51	-11.04	0.50	1.57			
		Mt1 (#305)	884	10	-11.21	0.07	1.63			
	Ilm4 (307)	Mt1 (#304)	900	31	-11.00	0.30	1.55			
		Mt1 (#305)	885	12	-11.19	0.12	1.63			
Pair 5	Ilm5 (311)	Mt1 (#308)	841	25	-12.25	0.26	1.41			
	()	Mt1 (#309)	861	27	-11.98	0.27	1.30			

Table 2.10

¹Two-oxide geothermometry at 1 kbar using the QUILF95 program of Anderson et al. (1993) with reported errors a minimum of ± 10 °C.

Full oxide analyses and endmember compositions are in Appendix 10

Backscatter images of in-contact mt-ilm pairs are shown in Figure 2.19.

For the 5.2 Ma high-Mg andesite from the Paso Pircas Negras (CO 412), two pyroxene temperatures were obtained using the average composition of an opx phenocryst (412-1) with analyses of phenocrystic cpx in textural equilibrium with the opx. This approach is satisfactory due to similar opx core and rim compositions (Table 2.8; Figure 2.17a). Equilibrium conditions are satisfied as both cpx and opx phenocrysts share similar extents of resorbtion and disequilibrium textures with the host melt. Calculated temperatures using phenocrystic cpx cores range from 1064 °C \pm 72 to 1074 °C \pm 50 at 5 kb. Cpx rims and cumulates record slightly higher temperatures with higher errors (1072-1082 °C \pm 57-92 °C) that may reflect disequilibrium with the orthopyroxene. The single in-contact mt-ilm pair from CO 412 yielded a lower temperature of 880-882 °C \pm 23-41 with an f_{O2} \sim 2.5 log units above the quartz-magnetite-fayalite (QMF) buffer at 1 kbar (Table 2.10).

Estimation of pre-eruptive temperatures for the ~ 5 Ma Upper Rio Veladero Pircas Negras (CO 324) are complicated by bimodal opx compositions (Figure 2.17a), reverse zoning in cpx phenocrysts, and petrographic evidence for thermal disequilibrium. Phenocrystic opx and cpx cores that could be in equilibrium record temperatures of 954-977 °C \pm 50-57 °C at 5 kbar. High-Mg opx rims on olivine phenocrysts (324-2) paired with nearby cpx phenocrysts give higher temperatures of 1067-1069 °C \pm 50 C° at 5 kbar similar to two-pyroxene temperatures obtained for sample CO 412. In-contact mt-ilm pairs yield cooler temperatures at 1 kbar than the two-pyroxene temperatures ranging from 788 °C \pm 10 °C to 900 °C \pm 31 °C.

VIII DISCUSSION

Trace element, isotopic, and petrologic observations suggest that the genesis of the Pircas Negras and Dos Hermanos adakitic melts involved equilibration with garnet at depths outside of the plagioclase stability field within or near the sub-arc mantle. These lavas are geochemically similar to adakitic andesites from other Pacific margins that have been related to high-pressure melting of eclogitic or garnet-amphibolitic crust. The spatially and temporally-confined eruption of the Pircas Negras high-Mg andesites during the peak of tectonic instability and arc migration along the Central Andean margin permits an evaluation of these lavas against competing hypothesis for high-Mg andesite and adakite formation.

The ubiquitous geochemical characteristic that distinguishes the Pircas Negras and Dos Hermanos andesites from most other Central Andean Neogene calc-alkaline andesites are their steep REE patterns, particularly the extreme depletion of the HREE with respect to the MREE (high Sm/Yb). Along with the high-Mg andesites from the Aleutians (Kay, 1978; Kay and Kay, 1994; Yogodzinski et al., 1994; Yogodzinski et al., 1995; Kelemen et al., 2003b) and adakitic dacites from Central America (Defant and Drummond, 1990; Defant et al., 1991b; de Boer et al., 1995), the Pircas Negras and Dos Hermanos record some of the steepest REE patterns from Phanerozoic arc lavas on Earth and are similar to those reported for the Archean tonalite-trondhjemite-dacite suite (TTDs; Martin, 1987; Drummond and Defant, 1990; Martin, 1999).

To generate these exceptionally steep REE patterns in andesitic melts, the HREE must preferentially partition into garnet in a high-pressure residual mineral assemblage, thereby leaving the magma depleted in these elements (e.g. Barker and Arth, 1976; Gromet and Silver, 1987). Lattice strain theory models (Blundy and Wood, 1994; van Westrenen et al., 2001) predict effective partitioning (Dgt/melt > 1) of isovalent trace elements including the HREE (X^{3+}) into the garnet dodecahedral X-site that are consistent with experimentally-obtained partition coefficients for REE fractionation into garnet in equilibrium with basaltic (e.g., Green et al., 2000; Klemme et al., 2002) and andesitic (Klein et al., 2000) melts. Experimental evidence indicates that eclogitic and garnet granulitic residues are in equilibrium with intermediate composition liquids resulting from $\sim 20-40$ % vapor-absent partial melting of an olivine-normative tholeiitic amphibolite at 1.2-3.2 GPa (Rapp and Watson, 1995). These authors also show that low-MgO mafic liquids result from 40-60 % melting of the same source at 1.2-2.8 GPa. The amphibole melting reaction above the garnet-in phase boundary at >1.2 GPa (Wyllie and Wolf, 1993; Wolf and Wyllie, 1994) generates a small amount of water and a garnet residue (Sen and Dunn, 1994; Rapp and Watson, 1995). The residual assemblages reported by these authors are broadly similar to lower crustal xenoliths from Australia (Kay and Kay, 1983; Rudnick and Taylor, 1991) as well as modal abundances of exposed lower crustal sections of the Kohistan arc (Garrido et al., 2006). Near-solidus 10-50 % partial melting experiments

of basaltic eclogites at 1250-1335 °C and 2-3 GPa generated basaltic to andesitic melts with rutile-bearing eclogitic residues (Pertermann and Hirschmann, 2003).

The general lack of phenocrystic plagioclase, negligible Eu anomalies, and high Na₂O and Sr concentrations leads to the conclusion that the Pircas Negras and Dos Hermanos lavas formed, ponded, and equilibrated outside of the stability field of plagioclase (Kay et al., 1991). Within the plagioclase crystal lattice, Sr^{2+} and Eu^{2+} substitute for Ca²⁺ and significant fractionation of plagioclase will dramatically lower both the Sr and Eu concentrations in fractionated melts. Two factors, increasing pressure and water content, can suppress plagioclase fractionation in a basaltic melt. At pressures in excess of 1.2 GPa, plagioclase is not stable within an anhydrous basaltic melt (Green and Ringwood, 1968; Ito and Kennedy, 1968). In hydrous arc magmas, plagioclase is not stable in gabbroic and tonalitic melts at 900 - 1100 °C and 1.5 GPa with $H_2O > 3$ and 7 wt % respectively (Huang and Wyllie, 1986). In water saturated P-T experiments conducted at 1050 °C (Moore and Carmichael, 1998), plagioclase was unstable in a western Mexico basaltic and esite at pressures > 1.3 GPa with 2.0-5.5 wt % H₂O and in and esite at > 1.0 GPa with 3.5 – 4.5 wt % H₂O. Similarly, plagioclase was suppressed in water saturated ($H_2O > 3$ wt %) experimental melts of Mt. Shasta high-Mg basaltic andesite at 1.2 GPa that simultaneously produced residual amphibole and garnet cumulates (Müntener et al., 2001).

With respect to the petrogenesis of the Pircas Negras and Dos Hermanos andesites, experimental results are consistent with the observed HREE depletion indicating these melts equilibrated at depths > 1.3 GPa within the stability field of garnet and outside of the field for plagioclase. Assuming crustal densities, these pressures correspond to depths of > 40 km within the ~ 70 km thick crust below the northernmost flatslab region. The geochemistry suggests that these lavas did not reside in upper crustal magma chambers, but rose from lower crustal depths to the surface sufficiently fast to prevent crystallization of plagioclase. Furthermore, this is consistent with the glassy nature of these lavas compared to most Andean andesites. The source of these lavas is best explained by a small percentage melting of an eclogitic (cpx + garnet) or garnet-bearing amphibolitic (Kay et al., 1991) mafic source.

The strong HFSE depletion in the Pircas Negras andesites (e.g., high Ba/Ta and La/Ta) compared to early Miocene and Quaternary CVZ arc andesites (Figure 2.8a and b) is testament to the changing physical conditions of the mantle and crust during arc migration and slab shallowing. As discussed by Kay et al. (1994b), the increase in LILE in 7-3 Ma Pircas Negras lavas is likely due to an increased concentration of slab-derived fluids in these magmas resulting from the dehydration of the shallowing Nazca slab and subsequent loss of asthenospheric wedge volume. This interpretation is consistent with the abundance of phenocrystic amphibole with thick reaction rims in these lavas, suppression of plagioclase, and $f_{\mbox{O}_2} \sim$ 1-3 log units above the QMF buffer. Moreover, higher Ba/Ta and La/Ta in syn-migration (5-3 Ma) rhyodacitic domes associated with the Incapillo Caldera and Dome Complex compared to evolved arc and backarc lavas from the CVZ of similar age have been attributed to a greater concentration of slab fluids in magmas erupting during the height of slab shallowing (Goss et al., Chapter 4). In contrast, lower Ba/La ratios (18-25) and lack of amphibole in the ~ 8 Ma Dos Hermanos are consistent with lower slab fluid concentrations resulting from its slightly backarc position and eruption before the main pulse of shallowing and migration.

Depletion of Ta with respect to the LILE and LREE has been explained either by melt equilibration with a HFSE-bearing phase, such as rutile or amphibole, present in oxidized eclogitic/amphibolitic mafic crustal sources (Green and Pearson, 1986; Foley et al., 2000; Schmidt et al., 2004) or by the immobile nature of the HFSE in slab-derived fluids compared to the mobile LILE and LREE (e.g., McCulloch and Gamble, 1991; Pearce and Peate, 1995). The strong adakitic signature, extreme LILE concentrations, and association with a hydrous fluid-fluxed mantle suggests both mechanisms can potentially explain the high La/Ta and Ba/Ta in these lavas (Kay et al., 1994b). However, near-chondritic Nb/Ta ratios (17.9-19.9) in pre-migration Pircas Negras and Dos Hermanos lavas contrast with dominantly subchondritic Nb/Ta ratios (11-18) in < 6 Ma Pircas Negras lavas (Goss and Kay, Chapter 3). These authors concluded that a HFSE-bearing residual phase was responsible for the strong Ta depletions observed in these lavas as slab-derived fluids cannot significantly fractionate Nb from Ta (Schmidt et al., 2004).

High Mg #s combined with elevated Cr and Ni contents attest to the involvement of sub-arc mantle or mantle melts in the genesis of the 5-3 Ma Pircas Negras adakites (Figure 2.11). In contrast, somewhat lower Mg #s and transition metal contents in pre- and post-migration adakites suggest a reduced mantle component in these lavas. The inverse relationship between Cr and Ni content and HREE depletion leads to the interpretation that the garnet signature is largely decoupled from mantle contamination processes. In this sense, the syn-migration lavas are unlike the low-Mg adakitic melts (Mg # 37-44) that result from melting a basaltic source at 3.2 GPa (Rapp and Watson, 1995; Rapp et al., 1999). Instead, they are more comparable to experimental "hybridized" high-Mg adakitic melts (Mg # 53-56) generated by reacting low-Mg adaktic melts with 10-20 wt % depleted peridotite to produce a Mg-rich garnet and opx residue (Figure 2.6; Rapp et al., 1999). This model was initially proposed by Kay (1978) as "adakitic" melt generated from anatexis of the subducting Pacific plate back-reacted with the overlying Aleutian mantle peridotite to produce the Adak high-Mg andesite. Both the Pircas Negras andesites and experimental high-Mg adakitic melts (Rapp et al., 1999) have similar Mg #s as adakites from Mindanao (Mg # 45-60; Sajona et al., 1994) and western

Panama (Mg # = 42-63; Defant et al., 1992). High-magnesian andesites from the western Aleutians (Yogodzinski et al., 1994; Yogodzinski et al., 1995) and from the Setouchi volcanic belt in Japan (Tatsumi, 1982; Tatsumi and Ishizaka, 1982), have higher Mg #s of 70-72 and 67-76 respectively and have been explained by melting of mantle metasomatized by adakitic melts. Other high-Mg andesites and dacites from Mt. Shasta in the Cascades are modeled as melts of a hydrated mantle wedge that subsequently equilibrated with a shallow depleted mantle residue (Grove et al., 2002). These melts however have significantly flatter REE patterns than the Pircas Negras and Adak high-Mg andesites (Figure 2.7).

Mineral equilibria and thermal considerations

Though the general lack of co-existing pyroxene or oxide phases in the majority of Pircas Negras andesites complicates estimation of pre-eruptive temperatures, the presence of these phases in two flows (CO 412 and CO 324) permits a first-order interpretation of magmatic temperatures. The two-pyroxene temperatures calculated for the Pircas Negras andesites (~ 1059-1068 °C at 5 kb; Table 2.9) are similar to experimentally-determined andesite liquidus temperatures with 5 wt % H₂O (~ 1050 °C; Green, 1982). Moreover, isobaric (5 kb) equilibrium crystallization modeling using whole rock analyses of these two Pircas Negras andesites in MELTS (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) at 5 wt % H₂O and f_{O2} fixed at 2 + FMQ stabilizes both opx and cpx at temperatures between 1089-1097 °C. At 7 wt % H₂O, opx and cpx are simultaneously saturated at temperatures between 1063-1071 °C. The highly resorbed textures of both Pircas Negras opx and cpx are attributed to decreased pyroxene stability at lower temperatures and pressures. These MELTS-modeled two-pyroxene temperatures agree with those calculated via chemical equilibria on analyzed opx-cpx pairs (Table 2.9). Of note, at the same modeled

pressure and f_{O_2} conditions, orthopyroxene could not be saturated from bulk compositions of opx-free Pircas Negras (e.g., CO 309, CO 310) and Dos Hermanos (CC 81) and esites.

Calculated pre-eruptive temperatures are ~ 50-80 °C cooler than temperatures expected to generate hybridized high-Mg # (> 55) adakitic melts in equilibrium with eclogitic residues (1100-1150 °C; Rapp et al., 2007). According to these authors, mantle temperatures are generally 100-200 °C warmer than the adakite solidus temperature (~ 850-1000 °C) and rising low-Mg primary adakitic melts must entrain thermal energy to prevent complete back-reaction with the mantle. However, the Pircas Negras erupted during the peak of slab shallowing and sub-arc mantle temperatures may reflect the cooling caused by loss of asthenospheric wedge volume (Kay et al., 1991). Within a cooler mantle wedge (< 1100 °C), higher melt:rock ratios (> 1:1) are required to generate "hybridized" high-Mg andesites that retain their original adakitic trace element signature (Kelemen et al., 1998). This observation is consistent with the general lack of opx in the majority of Pircas Negras lavas. The rare occurrence of resorbed orthopyroxenes in a few Pircas Negras samples can be explained as either "metasomatic" opx at low melt:rock ratios (Rapp et al., 1999) or as an early liquidus phase unstable during decompression at lower pressures.

Experimental work on the crystallization sequence of a basaltic andesite from Mt. Shasta (at NNO with $P_{H2O} = P_{total}$; Grove et al., 2003) indicates that at 0.8 GPa and 1065 °C, pargasitic amphibole (Mg # = 0.80) is the dominant silicate phenocrystic phase in equilibrium with cpx, opx, and andesitic melt (SiO₂ = 57.2 wt %; Al₂O₃ = 17.1 wt %; MgO = 4.9 wt %). At higher temperatures (1077 °C), olivine and cpx are the only phenocrystic phases, whereas at lower temperatures (1054 °C), opx reacts with amphibole and disappears from the assemblage. Based on melt inclusion data

and the linear relationship between Mg # in hornblende and H₂O content, Grove et al. (2003) estimate the pre-eruptive H₂O contents in these magmas to be > 10 wt %.

The crystallization sequence, pre-eruptive temperatures, mineral compositions, and modal assemblage recorded in the high pressure crystallization experiments by Grove et al. (2003) are highly similar to those of the Pircas Negras andesites. Based on these experiments, the high-Mg amphiboles that dominate the Pircas Negras assemblage may have crystallized at ~ 1060 °C from water-rich adakitic precursor melts ponded at pressures > 0.8 GPa within the Andean crust. Though no independent estimates of pre-eruptive H₂O or depth of crystallization exist for the Pircas Negras andesites, their glassy texture and strong slab signature are consistent with high pre-eruptive water contents. The thick magnetite rims that typify Pircas Negras amphiboles likely resulted from a late-stage oxidation reaction as these hydrous adakitic melts rose to the surface through the thick Andean upper crust.

Unlike most Pircas Negras lavas, the Rio Veladero flow (CO 324) shows evidence for storage at shallower depths in the crust. Lower temperatures recorded with phenocrystic orthopyroxene (~ 950-980 °C) and mt-ilm pairs (~ 840-900 °C) reflect a cooler magma, though higher temperatures obtained using opx rims around resorbed olivines imply secondary injection of a new batch of hotter Pircas Negras magma (~ 1060 °C) into the magma chamber. This is consistent with other petrographic evidence for mixing including the presence of euhedral skeletal relict amphiboles replaced by cpx, reversely zoned plagioclase xenocrysts, and plagioclase microlites with compositions of An_{60} . At 5 kb, this injected magma likely had a pre-eruptive temperature similar to the two-pyroxene temperature calculated for Pircas Negras sample CO 412, between 1064-1081 °C, which reflects the initial pre-eruptive temperature of the Pircas Negras lavas.

Petrogenesis of the Pircas Negras and Dos Hermanos adakites

Based on the available geochemical and petrologic data, we interpret the bulk of the 7-3 Ma Pircas Negras lavas to be the result of low-degree melting of a mafic crustal source at pressures in excess of 1.2 GPa within the garnet stability field. Four potential mechanisms are evaluated in the context of these interpretations: (1) partial melting of the subducted Nazca plate slab, (2) high-pressure fractionation of garnet from hydrous mantle-derived basaltic and andesitic melts, (3) partial melting of the thick Andean lower crust, and (4) partial melting of forearc crust removed and transported to the sub-arc mantle via subduction erosion processes.

Slab melting

Melting of subducted eclogitic oceanic crust was proposed by Kay (1978) to explain steep REE patterns, high Sr contents (up to 1800 ppm), and non-radiogenic Sr and Pb isotopes of a high-Mg andesite from Adak Island in the Aleutian island arc (Figure 2.7b). In an attempt to explain andesites and dacites from western Panama with similar geochemical signatures, Defant and Drummond (1990) proposed that lavas with these "adakitic" characteristics represented melts of subducted oceanic lithosphere. Standard thermal models suggest that melting of subducted oceanic crust can occur only during subduction of very young (< 7 Ma) and cold oceanic lithosphere (Peacock et al., 1994), however recent non-isoviscous modeling of the Central American subduction zone generated higher slab-mantle interface temperatures that no longer preclude melting of older slabs (Peacock et al., 2005). In the past, several geodynamic mechanisms have been proposed to surmount this thermal barrier to slab melting such as the introduction of a slab window (Kay et al., 1993; Johnston and Thorkelson, 1997; Yogodzinski et al., 2001; Thorkelson and Breitsprecher, 2005) and melting of the leading front of a newly subducted slab (Sajona et al., 1994). Specific

to the Andes, lavas with adakitic signatures at Cerro Pampa and other back arc centers from the Southern Volcanic Zone (Kay et al., 1993), and Cerro Cook from the Austral Volcanic Zone (Stern and Killian, 1996) have been modeled as melts of subducting oceanic lithosphere.

Arguments against large-scale slab melting as a mechanism to explain adakitic geochemical signatures from the central Chilean flatslab were outlined by Kay and Mpodozis (2002) and are directly applicable to the genesis of the Pircas Negras adakitic andesites. First, the subducting Nazca plate is ~ 50 Ma old at the Chile Trench (Yañez et al., 2001) and is therefore too cold to melt from top-down mantle conduction (Peacock et al., 1994). Second, adakitic lavas occur in a narrow spatial and temporal range that corresponds to the region and timing of migration of the Andean volcanic front. These signatures contrast strongly with flatter REE in both early- to mid-Miocene and Quaternary CVZ andesites. If slab melting was a important process generating Central Andean magmas, Neogene lavas with strong adakitic signatures would be uniformly present along the entire central Andean margin. Lastly, the Sr and Nd isotopic ratios of these adakitic lavas are too evolved (87 Sr/ 86 Sr > 0.7050; ϵ Nd < -2) to be derived from altered oceanic crust interacting with overriding mantle.

High-P garnet fractional crystallization

Garnet fractionation from basalts at pressures > 0.8 GPa has been proposed as a mechanism to generate adakitic magmas from the Surigao peninsula in the Philippines (MacPherson et al., 2006). Experimental work on hydrous (5-10 wt % H₂O) basaltic (Müntener et al., 2001) and andesitic (Ulmer et al., 2003; Alonso-Perez et al., 2004) magmas at these elevated pressures indicate the potential for 5-15 wt % garnet fractionation. MacPherson et al. (2006) used 30-50 % fractionation of a high-pressure mafic assemblage containing ~ 12 % garnet from a mafic andesite with flat HREE to model the adakitic signature (Sr/Y = 50-150; Sm/Yb 4-7) in < 1 Ma Surigao lavas.

High-P fractionation of garnet from basaltic precursor melts ponded below or within the Andean lower crust is an unrealistic model to produce the exceptional HREE depletion of the Pircas Negras and Dos Hermanos adakites. Table 2.11 shows results for a high-pressure fractional crystallization model for a hydrous basalt consistent with the experimental assemblage stabilized by Müntener et al. (2001).

Table	2.11										
High-P (1.2 GPa) fractional crystallization model of mantle-derived CVZ basalt*											
	Los Aparej	os			Incahuasi						
	CO 24	F = 0.40	F = 0.50	F = 0.53	CC 339	F = 0.40	F = 0.50	F= 0.57			
		$F_g = 0.10$	$F_{g}=0.13$	$F_{g}=0.14$		$F_{g}=0.10$	$F_{g}=0.13$	$F_{g}=0.15$			
SiO2	53.25	58.27	60.58	61.46	53.08	57.92	60.15	62.34			
TiO2	1.04	1.27	1.39	1.43	1.19	1.53	1.69	1.85			
Al_2O_3	15.33	16.70	17.33	17.57	14.81	15.81	16.25	16.69			
FeO	7.80	6.38	5.63	5.35	7.40	5.70	4.82	3.96			
MnO	0.13	0.12	0.11	0.11	0.15	0.15	0.15	0.15			
MgO	8.37	3.56	1.11	0.18	8.99	4.59	2.36	0.18			
CaO	8.02	5.47	4.16	3.66	8.36	6.03	4.84	3.68			
Na ₂ O	3.36	5.03	5.86	6.17	3.14	4.66	5.40	6.13			
K ₂ O	1.68	2.80	3.35	3.56	1.86	3.09	3.71	4.30			
P_2O_5	0.24	0.40	0.48	0.52	0.31	0.52	0.62	0.73			
Total	99.22	100.00	100.00	100.00	99.29	100.00	100.00	100.00			
La/Sm	5.2	5.8	6.2	6.4	4.4	7.5	8.1	8.6			
La/Yb	17.0	30.7	37.3	39.8	16.2	36.3	44.1	51.5			
Sm/Yb	3.3	5.3	6.0	6.2	3.7	4.8	5.5	6.0			

*F = percent (%) fractional crystallization of a high-pressure assemblage from a basaltic melt composed of cpx, opx, gt, and amphibole in the proportions 45.0:14.6:25.5:14.8 in equilibrium with basaltic andesitic melt (SiO₂ = 56.7 wt%) at 1.2 GPa (experimental Run B726 from Müntener et al., 2001). Distribution coefficients used are from Martin (1987). Fg reflects % fractional crystallization of garnet as part of the high-P fractionating assemblage. Starting basaltic compositions are from samples CO 24 (~ 9 Ma Los Aparejos basalt) and CC 339 (< 2 Ma) Incahuasi basalt (Kay et al., 1999). Initial trace element ratios are shown in bold font. Highest F reported shows the upper limit of fractional crystallization due to the exhaustion of available MgO.

Using the mantle-derived 9 Ma Los Aparejos and < 2 Ma CVZ Incahuasi basalt (Kay et al., 1999) as starting compositions, between 45-85 % fractionation of this assemblage (or 11-22 % total garnet) would be required to reproduce the range of HREE depletion in the Pircas Negras adakites. However, fractionation of this mafic assemblage is limited by the availability of MgO in the precursor basalts (8.37-8.99 wt %) that only permits a maximum of 57 % fractionation (or 15 % total gt). Residual magmas would be extremely alkaline (K₂O+Na₂O > 10 wt %) and highly depleted in Mg and Fe (MgO = 0.0-2.3; FeO = 0.0-4.8) as well as Cr and Ni. Therefore, we conclude that fractional crystallization of a garnet-bearing mafic assemblage from basaltic precursor melts cannot reasonably explain the transient adakitic signatures from the northernmost flatslab region associated with frontal arc migration.

Melting in situ eclogitic lower crust

The extreme crustal thicknesses below the Andean Puna plateau require the existence of a mafic eclogitic or garnet-granulitic lower crust that may have contributed to the strong adakitic signatures in the Dos Hermanos and Pircas Negras lavas. Melting of this *in situ* tectonically- and magmatically-thickened crust by ponding mantle-derived mafic lavas in deep crustal "hot zones" (e.g., Annen et al., 2006) is conceptually analogous to basalt melting experiments at 2-2.5 GPa, or 60-75 km depth (Rapp and Watson, 1995). Eclogitic lower crust has been proposed as the source of adakitic lavas in the Central Andes and similar regions with thick crust including Tibet (Wang et al., 2005) and the western US (e.g., Conrey et al., 2001). In the Andes, adakitic lavas from (1) the Chilean flatslab region (Kay et al., 1987; Kay and Mpodozis, 2002), (2) the Miocene Maricunga volcanic belt (Kay et al., 1994b; Mpodozis et al., 1995), (3) the northernmost SVZ (Hildreth and Moorbath, 1988; Kay

et al., 2005), (4) the Cordillera Blanca in Peru (Atherton and Petford, 1993; Petford and Atherton, 1996), and (5) in southern Ecuador (Garrison and Davidson, 2003) have been attributed to *in situ* melting of thick eclogitic lower crust under compressional stress. In this context, we attribute the extreme HREE depletion, elevated Sr concentrations, lower Mg #s (< 55), and lower Cr and Ni concentrations of the Dos Hermanos and pre- and post-migration Pircas Negras (9-7 and 3-2 Ma) to result from *in situ* melting of the eclogitic Andean lower crust. Moreover, the eruption of these lavas temporally brackets the peak of frontal arc migration (7-3 Ma) and the coincident pulse of Pircas Negras adakites with higher Mg #s.

Kay et al. (1991) modeled three Pircas Negras lavas from the Paso Pircas Negras as 10-22 % partial melts of a two-pyroxene garnet-granulite with a primitive arc basalt chemistry. According to their model, basalts accumulating at the crust-mantle boundary in the mid-late Miocene dehydrated and heated the lower crust, facilitating ductile deformation and rapid crustal thickening (Isacks, 1988). By the late Miocene, a refractory amphibolite residue at the base of the crust reacted to a plagioclase-poor garnet granulite, which subsequently melted to form the Pircas Negras magmas. An *in situ* crustal contamination model is supported by the positive correlation between ⁸⁷Sr/⁸⁶Sr and both SiO₂ and Sr concentrations in spatially coincident Neogene andesites from the northern flatslab transition zone (Figure 2.12a,b). A similar isotopic trend was discussed by Kay et al. (1991) for Neogene andesites from the Central flatslab region. The abundance of quartz and plagioclase xenocrysts in the Pircas Negras adakites is petrographic evidence of secondary crustal contamination acquired during ascent through the upper crust (Figures 2.15 and 2.18).

A number of geochemical and tectonic considerations indicate melting of eclogitic lower crust may not be the *only* process involved in the genesis of the syn-

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migration Pircas Negras high-Mg andesites. The steep REE patterns characteristic of these andesites are confined to magmas erupting during the *transient* unstable period of rapid frontal arc migration and are not present in either 18-13 Ma southern Maricunga or Quaternary southern CVZ andesites that erupted through a similarly thick (~ 60-70 km) Andean crust (Figure 2.9a,b). Crustal thickening associated with the uplift of the Puna plateau was largely complete by the end of the middle Miocene $(\sim 10 \text{ Ma})$ based on the (1) deposition of thick mid-Miocene Atacama gravels derived from the Puna that cease in accumulation by 10 Ma (Cornejo et al., 1993), and (2) establishment of disconnected internal drainage systems within the southern Puna characterized by thick evaporate deposits by the middle Miocene (Alonso et al., 1991; Vandervoort et al., 1995; Carrapa et al., 2005). Kay et al. (1994b; 2002) attributed the change toward steeper La/Yb ratios in 18-13 Ma southern Maricunga Belt andesites compared to 21-18 Escabroso andesites (Figures 2.8 and 2.9) to the onset of a higher-pressure residual mineralogy in the lower crust associated with this middle Miocene period of crustal thickening and plateau uplift. For the 7-3 Ma Pircas Negras andesites and as shown by Kay et al. (2005) for a transect through the northern SVZ (~ 34° S), the steepness of the REE pattern in erupted arc lavas is effectively decoupled from crustal thickness during tectonically-unstable periods that correspond to peak episodes of frontal arc migration.

In addition to the transient steep REE patterns, an entirely *in situ* lower crustal genesis cannot explain geochemical evidence for mantle involvement evident in 7-3 Ma Pircas Negras adakites. Elevated Cr and Ni concentrations inversely correlated with Sm/Yb, high Mg #s, and mantle-like olivine δ^{18} O values all signify some degree of mantle interaction with the primary adakitic lava. Isotopic trends, specifically the discrete increases in 87 Sr/ 86 Sr ratios in Pircas Negras adakites compared to spatially contiguous early-middle Miocene (21-13 Ma) andesites (Figure 2.12), also cannot be

easily justified by *in situ* crustal assimilation or by a spatial change in the isotopic character of the underlying basement units. Mantle contamination is strongly supported by a similar change towards more radiogenic Sr isotopic ratios in < 2 Ma southernmost CVZ basalts (San Francisco and Incahuasi; 87 Sr/ 86 Sr = 0.7052-0.7058) compared to early Miocene basalts (24 Ma Segerstrom 87 Sr/ 86 Sr = 0.7039-0.7042) from the same region (Figure 2.12; Kay et al., 1999). These Neogene basalts have a primitive mantle-derived nature with high MgO (9-12 wt %; Figure 2.5), Cr (570-700 ppm), and Ni (156-250 ppm) concentrations, olivines with Fo₈₈₋₈₉ and trace element ratios similar to the modern CVZ (Figures 2.7-2.10). In light of these observations, the geochemistry of the 7-3 Ma Pircas Negras lavas reflect contamination of the sub-arc mantle with crustal material during the peak of arc migration that is partially, but not completely, overprinted by *in situ* crustal anatectic processes.

Subduction erosion

Subduction erosion, or the tectonic removal and transport of forearc crust and mantle lithosphere (von Huene and Scholl, 1991; von Huene et al., 2004), has been proposed as a mechanism to generate adakitic magmas in arc regions with old (> 5 Ma) subducting slabs and/or where upper plate crustal thicknesses are too thin (< 40 km) to stabilize garnet (Kay et al., 2005; Goss and Kay, 2006a). This process is favored along non-accreting margins worldwide with fast convergence rates (> 6 cm/yr) and thin sedimentary cover (< 1 km) on the subducting plate (von Huene and Scholl, 1991; Clift and Vannucchi, 2004). Along these margins, overpressurized fluid rising from the lower plate hydrofractures the overriding forearc crust causing collapse of weakened forearc material into flexure-induced grabens in the subducting slab (von Huene and Ranero, 2003; von Huene et al., 2004). Evidence for subduction erosion at non-accreting margins include broad forearc normal faulting and subsidence (von

Huene et al., 1997; Ranero and von Huene, 2000; Vannucchi et al., 2001; Laursen et al., 2002), over-steepened forearc prism sediments (Lallemand, 1995; Laursen et al., 2002; von Huene and Ranero, 2003), scars from subducted seamounts (Ranero and von Huene, 2000), and imaged "megalenses" of detached upper-plate crustal material at the plate interface (Ranero and von Huene, 2000). In addition to margin subsidence, the ubiquitous tectonic-scale changes associated with an actively eroding margin include trench retreat and in response, migration of the volcanic arc (e.g., Lallemand, 1995).

Estimates for the global subduction erosion flux range from ~ 0.6 km³/yr (von Huene and Scholl, 1991) to 2 km³/yr (Lallemand et al., 1992). Combined with another ~ 0.7 km³/yr of subducting terrigeneous and pelagic sediments (Plank and Langmuir, 1998), the minimum total flux of recycled crust at subduction zones worldwide is ~ 1.3 km³/yr. For the central Andes, the establishment of a hyper-arid climate in the Atacama desert between 19-16 Ma (Rech et al., 2006) and the development of internally drained basins within the southern Puna by 15 Ma (Vandervoort et al., 1995) cut off the supply of continentally-derived sediment to the Chile trench resulting in a lack of modern terrigeneous trench sediments north of the Juan Fernandez Ridge at ~ 33° S (Schweller et al., 1981). Given a constant flux of pelagic sediment, the principle source of continental material delivered to the Andean sub-arc mantle since the late Miocene was likely derived from forearc crust removed via subduction erosion (Stern, 1991; Stern and Skewes, 1995) or through lower crustal delamination (Kay and Kay, 1993; Kay et al., 1994a).

The concept of subduction erosion was first proposed for the Central Andes by Rutland (1971) and Ziegler (1971) who noted (1) Jurassic arc volcanics and plutons compose the majority of the modern Coastal Cordillera, (2) a missing Mesozoic paired metamorphic belt associated with this Mesozoic arc, (3) the seaward truncation of late Paleozoic metamorphic units with the coast at ~ 34° S, and (4) the stepwise migration of the volcanic arc ~ 250 km to the east since the Jurassic. These authors proposed as much as 200 km of continental crust had been removed from the Andean forearc since the Mesozoic via forearc subduction erosion. Assuming a constant arc trench gap during the Miocene, Kay et al. (2005) proposed a minimum of ~ 85 km of forearc loss due to subduction erosion along the northern SVZ forearc at ~ 34° S based on the eastward migration of arc volcanism and estimates of backarc shortening.

Long-term average rates for active subduction erosion along the coast of northern Chile since the Jurassic range from 35-50 km³/m.y./km (von Huene and Scholl, 1991; Scheuber, 1994). Since the middle Miocene, episodic periods of accelerated forearc subduction erosion have been related to changes in convergence parameters or by increased subduction of lower-plate bathymetric features (von Huene and Scholl, 1991). Faster "short-term" erosion rates for northern Chile range from 72 to 135 km³/m.y./km (von Huene et al., 1999; von Huene and Ranero, 2003; Clift and Vannucchi, 2004). North of the Juan Fernandez ridge, rapid average forearc retreat during the last 10 Ma has been estimated at 3-4 km/m.y. (Laursen et al., 2002). However, by 2 Ma, the net rate of subduction erosion along the northern Chilean coast may have slowed as tectonically-eroded forearc material began to underplate and uplift forearc units (Figure 2.20; Clift and Hartley, 2007).

The forearc of northern Chile between 30° and 22° S contains abundant mafic lavas and plutons from the Jurassic arc that intruded ensialic low-grade turbidite and mélange sediments of the Paleozoic Chañaral Epimetamorphic Complex (SERNAGEOMIN, 2003). Mafic rocks from mid-crustal depths within the Jurassic arc are exposed along the Mejiones peninsula and within the Coastal Cordillera as far south as 36° S (Pichowiak et al., 1990; Lucassen et al., 2002). The chemistry of these units are typical for an island arc that developed over a thin (< 30 km) post-rift crust (Pichowiak et al., 1990; Lucassen and Thirlwall, 1998; Lucassen et al., 2002). Zircons collected from mafic Jurassic (La Negra Formation) lava flows with ages ~ 1760 Ma suggest the possibility of a Proterozoic forearc crustal basement below Paleozoic and Jurassic units (Gelcich et al., 2005).



Figure 2.20 Sea-level-corrected depth-to-basement reconstructions from Clift and Hartley (2007) for two Chilean forearc basins from the northernmost flatslab region (upper = Caldera Basin ~ 27° S; lower = Carrizalillo Basin ~ 29° S). Vertical bars show the uncertainty in paleowater depth estimates at time of deposition. Shaded vertical region (< 2 Ma) shows period of net tectonic uplift and underplating of eroded forearc material. Horizontal bar shows temporal extent of Dos Hermanos and Pircas Negras adakitic volcanism along the arc inboard of the two sedimentary basins.

Various lines of geophysical evidence agree with surficial observations and suggest the forearc below the northern Chilean Coastal Cordillera is principally composed of mafic Mesozoic intrusives and cumulates with sialic Paleozoic units comprising only a volumetrically minor fraction (< 15 %) (Scheuber, 1994). Between 21-26° S, the uniformly fast (Vp 6.7-7.7 km/s) and dense (2.9-3.05 g/cm³) Chilean forearc has been explained as the preserved lower crustal sections of the Jurassic arc (Scheuber and Geise, 1999; Schmitz et al., 1999; Lucassen et al., 2001; Prezzi et al., 2005) potentially underlain by slivers of Paleozoic basement (Wigger et al., 1994; Scheuber and Geise, 1999). Though there is little published geophysical data along the forearc between 26-30° S, trench-parallel gravity data suggest that anomalously dense crustal material dominates the forearc structure as far south as 33° S (Götze et al., 1994; Tassara et al., 2006). In this sense, the forearc of northern Chile behaves as a rigid crystalline block similar to the mafic ophiolitic forearc of southern Central America (Christeson et al., 1999; Sallarès et al., 1999) that has experienced heightened subduction erosion over the last ~ 5 Ma due in part to the collision of the Cocos Ridge (Vannucchi et al., 2003). Forearc material removed from the Andean margin since the middle Miocene would likely reflect the lithologies of the modern forearc prism and be largely composed of mafic Mesozoic arc intrusives and cumulates with smaller percentages of Paleozoic sialic crust.

Contamination of the Andean mantle wedge with eroded mafic forearc can explain the spatial and temporal geochemical patterns seen in Neogene andesitic lavas of the northern flatslab-CVZ transition zone between 27-29° S. The *transient* increase in the La/Yb and Sm/Yb ratios in Pircas Negras lavas associated with the peak of frontal arc migration compared to lower ratios in compositionally-similar andesites that erupted before (21-18 Ma Escabroso and 18-13 Ma southern Maricunga andesites) and following (Quaternary CVZ andesites) arc migration suggest an *ephemeral* high-P

mafic crustal source. Accelerated subduction erosion along the northern margin of the Chilean flatslab after 8 Ma resulted in the migration of the 24-6 Ma Maricunga arc \sim 50 km to the east and flooded the sub-arc mantle with mafic crustal material derived Melting of this eclogitized forearc crust within the from the Chilean forearc. asthenospheric mantle wedge and reaction of these melts with surrounding mantle peridotite can explain the Cr- and Ni-rich high-Mg adakitic signatures characteristic of the 5-3 Ma Pircas Negras and esites and is entirely consistent with experimental models of mantle-hybridized adakite genesis (Rapp et al., 1999). These magmas subsequently mixed with lower-Mg adakitic melts generated from *in situ* lower crustal melting. Stored within the middle to lower Andean crust, high pressures (> 0.8 GPa) and H₂O contents (> 5 wt %) inhibited plagioclase fractionation and facilitated crystallization of high-Mg amphibole. Elsewhere along the Pacific rim, melting of tectonically-transported mafic forearc crust during discrete periods of arc migration and heightened subduction erosion have been proposed as a mechanism to generate transient adakitic signatures in lavas from the Andean SVZ (Stern, 1991; Kay et al., 2005), southern Central America (Clift et al., 2005; Goss and Kay, 2006a), and the Aleutians (Kay, 2006).

Isotopic mixing model

In order to test the hypothesis that mafic crust from the Andean forearc has contaminated the mantle during periods of heightened frontal arc migration along the northern margin of the Chilean flatslab, we present a multi-stage three component isotopic mixing model. The first stage involves determining the isotopic composition of a potential forearc contaminant by varying the proportions of Mesozoic and Paleozoic crust eroded from the forearc. The second stage mixes these potential source contaminants with sub-arc mantle to generate the isotopic variability seen in mantle-derived basalts from the southernmost Puna.

To determine an appropriate forearc contaminant, the average composition of La Negra Jurassic gabbros (SiO₂ = 52.6; Sr = 319 ppm; Nd = 2.1 ppm; Pb = 1.2 ppm; ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.703309; \ \epsilon\text{Nd} = 6.57; \ {}^{206}\text{Pb}/{}^{204}\text{Pb} = 18.23; \ {}^{207}\text{Pb}/{}^{204}\text{Pb} = 15.59; \ {}^{208}\text{Pb}/{}^{204}\text{Pb} = 15.59;$ = 38.08) from the Coastal Cordillera (Lucassen et al., 2002) are used to represent the mafic forearc endmember. Intrusive (gabbroic) units were chosen instead of La Negra lavas because (1) gabbros are exposed throughout the Jurassic units in the Coastal Cordillera, (2) the roots of the Mesozoic arc are likely dominated by intrusive mafic bodies analogous to the Sarangar gabbros near the base of the Kohistan arc (Garrido et al., 2006), and (3) gravity data suggest densities at the base of the Chilean forearc are greater than basalt. The sialic endmember composition is taken from the average of central Andean Paleozoic crust (SiO₂ = 68.3; Sr = 189 ppm; Nd = 24.3 ppm; Pb = 16ppm; ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.732000$; $\epsilon \text{Nd} = -8.72$; ${}^{206}\text{Pb}/{}^{204}\text{Pb} = 18.95$; ${}^{207}\text{Pb}/{}^{204}\text{Pb} = 15.69$; 208 Pb/ 204 Pb = 38.90; Lucassen et al., 2001). These values are similar to those used for Paleozoic upper crust by Stern (1991) and Kay et al. (2005) in mixing models for SVZ lavas and are comparable to the composition of average upper continental crust. No subducted terrigeneous or pelagic sediment is used in the model nor is any Proterozoic crust considered.

Mixing between Jurassic gabbros and Paleozoic crust generates a forearc source contaminant with isotopic ratios that fall along the solid mixing lines shown in Figure 2.14. Partial melting of this subducted and eclogitized forearc crust will generate low-Mg adakitic lavas with isotopic compositions also along the mixing line. Results from this model show that the Pircas Negras adakites plot along the ⁸⁷Sr/⁸⁶Sr and εNd mixing line (Figure 2.14a) and that melting a forearc crustal source comprised of 80–90 % Jurassic gabbros with 10-20 % Paleozoic silicic rocks can

explain their isotopic variability. These modeled proportions are consistent with geological and geophysical interpretations that indicate the northern Chilean forearc is dominantly composed (> 85 %) of dense mafic intrusives or cumulates from the Mesozoic arc lower crust.

Hybridization of low-Mg adakitic-melts of subducted forearc with mantle peridotite will similarly contaminate the isotopic composition of the sub-arc mantle. The second stage of this model involves mixing between pre-arc migration mantle with adakitic melts derived from the mixed forearc contaminants. The 24 Ma Segerstrom basalt is used to model the pre-migration sub-arc mantle $({}^{87}Sr/{}^{86}Sr =$ 0.703309; ϵ Nd = +6.57; 206 Pb/ 204 Pb = 18.23; 207 Pb/ 204 Pb = 15.59; 208 Pb/ 204 Pb = 38.08). Mantle trace element concentrations (Sr = 50 ppm; Nd = 3 ppm) used in the model are from the average of metasomatized spinel peridotites from southern Patagonia (Gorring and Kay, 2000). Though high compared to estimates of Sr and Nd in both depleted mantle (Salters and Stracke, 2004) and primitive mantle (Hofmann, 1988), these values maintain the constant Sr/Nd ratio of the primitive mantle (~ 16). Mantle Pb values are estimated at 0.175 ppm (Hofmann, 1988) and are similar to average values for Patagonian mantle xenoliths (0.13 ppm). Three forearc crustal sources with Jurassic: Paleozoic ratios of 9:1, 8.5:1.5; and 8:2 are mixed with the late Oligocene Segerstrom mantle. Figure 2.14a shows that 70-95 % of the mantle Sr and Nd could have been derived from a forearc source comprised of 80-90 % Jurassic gabbros. Therefore, contamination of the Andean mantle with a dominantly basic crustal composition (SiO₂ = 54-55 wt %) with only 10-20 % Paleozoic by mass can explain this isotopic shift towards a more radiogenic mantle. The source contributions to adakitic magmatism reported here are similar to those suggested for Costa Rican and Panamanian adakites from a multi-component isotope mixing model of enriched mantle, subducted sediment, and mafic forearc ophiolite (Goss and Kay, 2006a).

Applying the same multi-stage mixing model to the Pb-isotopic data reveal that the Pircas Negras and Dos Hermanos fall on the Pb-Pb mixing lines (Figure 2.14b and c) predicted by Sr-Nd modeling. However, the Pb model only requires mixing < 10 % forearc Pb into the pre-migration mantle, significantly less forearc mass required by Sr-Nd modeling. This discrepancy can be explained by the fact that Pb signatures in the Central Andes lavas are generally controlled by the *in situ* crustal basement (e.g., Woerner et al., 1992; Aitcheson et al., 1995) and that buffering of the Pb isotopic signature by Permo-Triassic Choiyoi basement (Figure 2.13; Moscoso et al., 1993) would push the Pb isotopic signature toward lower ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios and higher ²⁰⁸Pb/²⁰⁴Pb ratios, exactly the trends evident from the Pb isotopic modeling in Figure 2.14. The Choiyoi grano-rhyolite is a realistic crustal contaminant for these lavas as it underlies the entire region (Mpodozis and Kay, 1992) and is intruded by Pircas Negras andesites (Figure 2.3a). Unlike the Pircas Negras and esites from the northern flatslab transition zone, the < 2 Ma Incahuasi and San Francisco basalts from the southernmost CVZ do not fall on any forearc-mantle Pb-Pb mixing lines (Figure 2.14b and c) which may be due to a compositionally different crustal basement.

Since the Pircas Negras andesites fall very near the mixing line between Paleozoic and Jurassic forearc crust, they only require up to 10 % of their Sr and Nd to have originated from the pre-migration uncontaminated mantle. As evidenced by the Pb isotope trends, some degree of this Sr and Nd enrichment could have occurred in these melts through assimilation of *in situ* mafic lower and sialic upper crust. However, the (1) high Cr and Ni concentrations in some 5-3 Ma Pircas Negras, (2) elevated Mg #s, (3) transient association of HREE depletion with periods of frontal arc migration, and (4) contemporaneous contamination of the sub-arc mantle with

radiogenic crustal material all suggest some component of these melts must have originated from high-P melting of a crustal source *within* the Andean mantle wedge.

Subduction erosion flux

To examine the relationship between crustal mass balance, forearc subduction erosion, and frontal arc migration, a trench to backarc cross section based on available geophysical data through the region of Pircas Negras volcanism at 28° S is shown in Figure 2.21a. However, the current lack of seismic studies of the Andean crust between 26°S and 30°S limits the geophysical constraints on this schematic crosssection.

The geometry of the subducting slab used for the cross-sectional profile is the $\sim 28^{\circ}$ S transect from Pardo et al. (2002) that passes through the region of Pircas Negras volcanism. Though oblique to Nazca plate convergence, the profile of the Wadati-Benioff zone is broadly similar to the margin parallel geometries of Cahill and Isacks (1992) and Comte et al. (2002). Moho topography follows that defined for the flatslab region ~ 200 km south (Fromm et al., 2004), however crustal thicknesses below the frontal arc at 28° S were set to 70 km as calculated by McGlashan et al. (2007). Mantle geometry, including the westward extent of the forearc mantle, is consistent with gravity and seismic studies of the north Chilean forearc.

In unstable tectonic settings, both slab shallowing and forearc subduction erosion can produce frontal arc migration. However, as proposed for the southern margin of the Chilean flatslab (Kay et al., 2005), we suggest that the migration of the volcanic front along the northern margin of the flatslab was largely driven by erosional processes operating along the forearc. This is because the geometry of the slab between the trench and arc is generally constant along the entire Central Andean margin with the bulk of shallowing occurring in the backarc (Cahill and Isacks, 1992). Figure 2.21 Schematic cross section of the northern flatslab transition zone (28.5° to 27° S) showing major tectonomagmatic features. In both cross sections, the arc trench gap is held constant at 300 km. Lower crust is delineated at ~ 45 km, marking the 1.5 GPa the stability field of eclogitic garnet. Pre- and syn-migration volcanism is shown by yellow and blue triangles respectively

(A) Syn-arc migration cross section between 7-3 Ma. Shape of the subducted Nazca plate is based on crustal transect S1 from Pardo et al. (2002) for modern plate geometries. Topography is exaggerated by Crustal thicknesses are based on those from Fromm et al. ~ 10x. (2004), McGlashan et al. (2007), Yuan et al. (2002), and Tassara et al.(2006). Extent of dense Mesozoic arc crust is extrapolated from outcrop field mapping (SERNAGEOMIN, 2003) and from regional geophysical studies of the northern Chilean forearc (Wigger et al., 1994; Schmitz et al., 1999; Lucassen et al., 2001; Prezzi et al., 2005; Tassara et al., 2006). Position of magmatic units showing the progressive landward migration of the volcanic arc from the Mesozoic late Miocene are from the geological map of Chile to (SERNAGEOMIN, 2003). J = Jurassic; K = Cretaceous, P = Paleocene, O = Oligocene, M = Miocene; subscripts refer to early (E), middle (M) and late (L). Thick horizontal arrow shows the ~ 50 km of frontal arc migration from the early to late Miocene Maricunga belt (21-6 Ma) stratovolcanoes to the late Miocene-Pliocene arc front centers (7-3 Ma; Bonete Chico, Pissis, Veladero). Contemporaneous with this migration, slivers of forearc material comprised of 80-90 % mafic Mesozoic crust and 10-20 % sialic Paleozoic crust are shown being actively removed from the base of the overriding crust, transported to the sub-arc mantle wedge, flux melted, and reacted with mantle peridotite to generate the 5-3 Ma high-Mg Pircas Negras adakites. Storage and assimilation in the lower crust is followed by rapid eruption to the surface.

(B) *Pre-arc migration* cross section at 9-7 Ma showing the position of paleo-coastline and trench at 8 Ma as extrapolated using the ~ 50 km of frontal arc migration. Also shown is the restored ~ 124 km³/m.y./km of crustal material removed from the forearc via subduction erosion in the last 8 Ma. Transparent triangles mark the location of the 7-3 Ma Pircas Negras showing the late Miocene migration within the Pircas Negras suite. Pre-migration andesites (Dos Hermanos, Redonda, and Comecaballos Pircas Negras) lack a strong mantle signature and largely represent melts of lower crustal eclogite immediately preceding arc instability and migration.



Considering the ~ 50 km of eastward arc migration between 7 and 3 Ma and the relatively constant arc-trench gap along the modern CVZ between $23^{\circ}-28^{\circ}$ (~ 300 km), the position of the late Miocene (8-6 Ma) trench likely extended ~ 50 km further to the west. The result of this trench retreat is up to 50 km of forearc material, composed of Mesozoic basic and Paleozoic sialic rocks, removed through subduction erosion processes acting on the margin since the late Miocene. Restoring the Chile Trench to its pre-migration/pre-erosion position generates a maximum of ~ 992 km³ per kilometer of arc length of material eroded over this period, or a rate of ~ 124 km³/m.y./km over the last 8 Ma. This estimated erosion rate is similar to the short-term tectonic erosion rate calculated by Clift and Vannucchi (2004) for northern Chile.

Spatial and temporal model for the genesis of Pircas Negras adakites

In the waning stages of Maricunga arc volcanism between 10-6 Ma (Kay et al., 1994b; Mpodozis et al., 1995), melting of eclogitic Andean lower crust generated the 9-7 Ma Dos Hermanos, Redonda, and Comecaballos Pircas Negras adakitic andesites (Figure 2.21b). This likely resulted from crustal heating by ponded mantle-derived basalts, which erupted at \sim 9 Ma far in the backarc at Los Aparejos in the eastern Valle Ancho. An *in situ* lower crustal genesis explains the extreme depletion in HREE, lower concentrations of transition metals, and lower Mg #s characteristic of these andesites compared to younger (7-3 Ma) syn-migration Pircas Negras andesites.

Immediately following the subduction of the NE-trending arm of the Juan Fernandez ridge below the southernmost Puna at ~ 8 Ma (Yañez et al., 2001; Kay and Mpodozis, 2002), a period of arc instability commenced along the Andean margin manifest by ~ 50 km of eastward frontal arc migration from the Maricunga Belt to the late Miocene-Pliocene arc (Figures 2.2 and 2.21a) and backarc shallowing of the

subducting Nazca plate. Tectonic erosion may have been locally accelerated during this time by the subduction of the ridge as it collided with the forearc. Nonetheless, the eastward translation of the volcanic front represents the re-establishment of "arc equilibrium" following the rapid removal of forearc material via subduction erosion. The 7-3 Ma Pircas Negras adakitic lavas confined to this narrow spatial and temporal window likely formed from partial melting of a dominantly mafic (~ 80 %) forearc. Hydrous adakitic melts of subducted forearc crust would rise into and react with the overriding sub-arc mantle wedge thus acquiring their characteristic elevated Cr, Ni, Early crystallization of opx may record evidence of this mantleand Mg #s. metasomatism. Melt storage at crustal depths > 40 km permitted crystallization of pargasitic amphibole, suppressed plagioclase, and further assimilated Andean lower Rapid ascent from these depths inhibited plagioclase fractionation and crust. incorporated xenocrysts of quartz and plagioclase from upper-crustal magma conduits into the Pircas Negras magma.

The last pulse of Pircas Negras volcanism erupted in the northern Rio Salado between 3-2 Ma and is associated with the waning stage of the Pliocene arc at this latitude. These lavas are geochemically-similar to those immediately preceding frontal arc migration and correspondingly reflect a dominantly lower-crustal, as opposed to forearc-derived, eclogitic source.

Geodynamics of melting of subducted forearc crust

Various mechanisms have been proposed to induce fluid-saturated conductive heating of crustal material eroded from the base of the overriding plate forearc as it is transported via the subduction channel into the mantle wedge. At 3 GPa, the melting point of mafic eclogite is \sim 740° C (Hacker et al., 2003a), significantly lower than the melting temperature of the mantle but higher than isoviscous model-predicted slab-

mantle interface temperatures at 100 km depth (Peacock et al., 1994). Kelemen et al. (2003a) suggested that eroded forearc material may melt easier than subducted oceanic crust. Given its position at the base of the crust, the initial temperature of forearc crust is likely hotter than the top of the subducted oceanic crust and would thus require less heat to melt. These authors demonstrate that for a 1 km thick lens of eclogitized crust, small density differences (50-150 kg/m³) at low strain rates ($\sim 10^{-14}$) will generate eclogite diapirism into overlying mantle peridotite. For eroded Andean forearc, a mixture of 15 % eclogitic silicic crust with a density of 3.1 g/cm³ (Richardson and England, 1979) with 85 % eclogitic mafic crust with a density of 3.4 g/cm³ is neutrally buoyant with a peridotitic mantle with a density 3.35 g/cm³. Mantle corner flow and rising slab-derived fluids may sweep this eroded forearc into hotter regions of the mantle wedge away from the slab-mantle interface where fluid-saturated melting can occur. By this logic, density and kinematic forces alone acting within the Andean mantle could reasonably transport eclogitic forearc crust into hotter overlying regions of the mantle wedge.

IX CONCLUSIONS

The Pircas Negras and Dos Hermanos adakitic andesites from the northernmost margin of the Chilean flatslab between 27°-28.5° S are petrographically and chemically distinguishable from most arc lavas that characterize the Cenozoic magmatic history of the Andean arc. We summarize our results as follows:

(1) The main period of Pircas Negras volcanism between 7 and 3 Ma was contemporaneous with the late Miocene migration of the southernmost CVZ volcanic front and spatially limited to a \sim 50 km-wide N-S trending band between the Miocene Maricunga Belt and late Miocene to Pleistocene arc front centers. A general trend

from older Pircas Negras andesites in Chile (7-5.5 Ma) to younger Pircas Negras andesites to the east in Argentina (5-4 Ma) is apparent. The \sim 8 Ma Dos Hermanos and 8.8 Ma Pircas Negras predate the main pulse of arc migration. The youngest Pircas Negras andesites erupted between 3-2 Ma in the upper Rio Salado and are associated with the termination of arc volcanism in this region.

(2) The Pircas Negras andesites (Mg # 36-61) are glassy plagioclase-poor lavas dominated by oxidized high-Mg amphiboles (magnesiohastingite) with minor pyroxenes (cpx + rare opx) and olivine in glomeroporphyritc clusters. Ubiquitous quartz xenocrysts with reaction rims of cpx and relict plagioclase xenocrysts reflect upper crustal contamination of the Pircas Negras magmas. Two pyroxene geothermometry on two Pircas Negras andesites indicates pre-eruptive temperatures between 1060-1080 °C at 5 kb, though two oxide geothermometry yields cooler temperatures of ~ 800-900 °C in andesites with textural and geochemical evidence for storage at shallow crustal depths. The older Dos Hermanos lavas (Mg # 48-55) lack phenocrystic amphibole and contain only cpx as a phenocrystic phase.

(3) Adakitic trace element signatures (i.e., high La/Yb, Sm/Yb, Sr/Y or Sr/Yb) and high degrees of HFSE depletion relative to the LILE and LREE (high Ba/Ta and La/Ta ratios) are characteristic of the Dos Hermanos and Pircas Negras andesites. This adakitic signature is a transient geochemical feature observed only in lavas that are spatially and temporally associated with frontal arc migration and is absent in 21-18 Ma Escabroso, 18-13 Ma southern Maricunga, and Quaternary southernmost CVZ andesites associated with a more stable arc front. (4) Geochemical patterns and predicted temperatures from some 7-3 Ma Pircas Negras are similar to those from high-Mg andesitic melts generated in high-pressure (> 1.2 GPa) melting experiments of mafic crust that reacted with peridotite. Reaction with peridotite explains the high Cr and Ni concentrations, elevated Mg #s, and presence of opx in some of these magmas. The \sim 8 Ma Dos Hermanos and youngest 3-2 Ma Pircas Negras andesites exhibit the most extreme trace element patterns, however their lower Mg #s and transition metal concentrations suggest minimal interaction with mantle peridotite.

(5) Isotopic ratios for the Pircas Negras and Dos Hermanos andesites show more enriched values when compared to early-middle Miocene andesites. This trend is mirrored by a similar temporal change in the isotopic character of primitive basalts from the southernmost CVZ (Kay et al., 1999). Considering the barren nature of the Chile trench with respect to terrigeneous sediments, these trends are best explained by transient contamination of the sub-arc mantle with a radiogenic eroded forearc crustal component. Discrete increases in isotopic ratios are superimposed upon a broader scale *in situ* crustal contamination trend seen in the isotopic data of mafic to silicic magmas of the same age.

(6) Multi-stage isotopic modeling indicates that the Pircas Negras adakitic andesites can be explained by partial melting of Andean forearc material containing mixtures of 80-90 % mafic Jurassic gabbroic cumulates with 10-20 % radiogenic Paleozoic crust. These percentages are consistent with compositional estimates of the Chilean forearc from geophysical data. Primary adakitic lavas from partial melting of eroded forearc subsequently incorporated 0-20 % mantle Sr and Nd upon reaction with mantle peridotite. Similarly, the source contamination evident in < 2 Ma mantlederived melts from the CVZ can be modeled as 95-70 % Sr and Nd contamination of the sub-arc mantle by eroded forearc. Like most central Andean magmas, Pb isotopic ratios in the Pircas Negras are dominated by a crustal basement signature and trend toward the Permo-Triassic Choiyoi granite-rhyolite that underlies the region.

(7) Following the subduction of the NE-SW trending arm of the Juan Fernandez Ridge below the southernmost Puna at $\sim 10-8$ Ma, a period of arc instability characterized by rapid forearc subduction erosion commenced along the Andean margin between 27°-29° S. In response, the frontal arc migrated ~ 50 km to the east. Immediately preceding this arc migration, melting of back-arc lower crustal eclogite by ponding mantle-derived basalts generated the Dos Hermanos adakites. Material eroded from the forearc margin began to contaminate the mantle wedge around this time. Melting of this forearc crust at high-pressures within the subduction channel or the mantle wedge generated adakitic melts that later reacted with surrounding mantle peridotite. Stored in the thick Andean lower crust, these hydrous melts crystallized pargasitic amphibole before rapidly ascending to the surface.

(8) Assuming a constant arc-trench gap over the last 8 Ma, a schematic crosssection of the Andean arc based on available geophysical constraints indicates ~ 124 km³/m.y./km of crustal material must have been removed from the Andean forearc to account for the arc migration. These rates are consistent with other published short-term (~ 5-10 Ma) tectonic erosion rates for the Andes and Central America.

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CHAPTER 3

EXTREME HIGH FIELD STRENGTH ELEMENT (HFSE) DEPLETION AND NEAR-CHONDRITIC NB/TA RATIOS IN CENTRAL ANDEAN ADAKITE-LIKE LAVAS (~ 28° S, ~ 68° W)

ABSTRACT

The eruption of andesites with steep REE patterns and high Sr concentrations (adakite-like) in the northern Chilean flatslab region of the Central Andes spatially and temporally corresponds with the appearance of a marked HFSE (high field strength element) depletion in these lavas (La/Ta up to 100). Known as the Pircas Negras and Dos Hermanos andesites, these lavas erupted at the beginning (8-7 Ma), during (6-3 Ma), and immediately following (3-2 Ma) a period of tectonic instability characterized by rapid eastward migration of the frontal arc. ICP-MS analyses of the HFSE reveal a range of chondritic (20-18) to subchondritic (18-11) Nb/Ta ratios in these lavas. These data support a change from a rutile-bearing eclogite to a garnet-bearing amphibolite residual assemblage in equilibrium with these lavas that is contemporaneous with the onset of arc migration and slab shallowing. Experimentally determined partition coefficients for the HFSE rule out melting of eclogitized oceanic crust as a viable source for these adakites and show that a high pressure arc-like source with higher Nb and Nb/Ta ratios is required. Potential sources for the Pircas Negras and Dos Hermanos andesites include mafic Andean lower crust and/or forearc crust transported to the mantle via subduction erosion.

I INTRODUCTION

The characteristic depletion of the high field strength elements (HFSE; Nb, Ta, Zr, Hf, and Ti) with respect to the large ionic lithophile elements (LILE) and the light

rare earth elements (LREE) is a diagnostic feature of subduction-related volcanism. This "arc signature" is evident in the negative Nb and Ta anomalies ubiquitous in normalized incompatible element spider diagrams of arc magmas. Although the source of the HFSE arc signature is debated, its importance as a tectonic tracer has led to the proposal that the continental crust, which has a high-Mg andesitic bulk composition with a strong depletion in Nb and Ta, formed largely through subduction-related processes (Taylor and McLennan, 1985; Rudnick and Fountain, 1995). However, a paradox remains that the vast majority of arc lavas originate from flux melting of the mantle wedge via the addition of slab-derived fluids (e.g., Stolper and Newman, 1992; Grove et al., 2002) and partial melts of mantle peridotite invariably produce magmas with basaltic compositions. Lower crustal delamination of fractionated ultramafic cumulates (Kay and Kay, 1991; Jull and Kelemen, 2001) or genesis of primary high-Mg andesites from the interaction of slab melts with depleted sub-arc mantle (Kelemen et al., 2003a) have been proposed as potential mechanisms responsible for the largely andesitic bulk composition of the continental crust. The refractory and fluid-immobile nature of the HFSE enables the use of these elements in deciphering the sources and physical conditions necessary for the genesis of mafic arcderived lavas.

Two models have been proposed to explain negative HFSE anomalies in arc lavas. The first is based on the general immobility of the HFSE in fluid transfer from the subducting oceanic slab to the overlying mantle wedge. In this model, negative HFSE anomalies in arc magmas reflect the composition of the mantle wedge, which is itself depleted in the HFSE due to preferential enrichment of highly fluid-mobile LILE and LREE (e.g., McCulloch and Gamble, 1991; Pearce and Peate, 1995). However, experimental data at pressures relevant to slab dehydration (2-3 GPa) suggest partial mobility of the HFSE in aqueous fluids in the presence of residual titanite (Brenan et al., 1995b; Stalder et al., 1998) or amphibole (Ionov and Hofmann, 1995; Tiepolo et al., 2000). The second model involves a residual Ti-rich phase, such as rutile or amphibole, which retains the HFSE during partial melting of subducted oceanic crust or mantle peridotite. The stability of rutile at pressures > 1.4 GPa in residual eclogites in equilibrium with basaltic melt is well constrained by experimental work (Green and Pearson, 1986; Foley et al., 2000; Schmidt et al., 2004; Xiong et al., 2005). However, a problem remains as rutile is highly soluble in basaltic melts of peridotite and is therefore unstable as a residual phase within the mantle wedge (Ryerson and Watson, 1987). Alternatively, HFSE could be retained in an ilmenite-geikeilite [MgTiO₃] phase that is stabilized in mantle peridotite at lower temperatures near the wet mantle solidus (Grove et al., 2006).

Despite a common valence state (+5) and virtually-identical atomic radii ($r_{Nb} = r_{Ta} = 0.064$ nm; Shannon, 1976), fractionation between Nb and Ta is observed in both experimental (Schmidt et al., 2004) and natural systems (Münker, 1998; Münker et al., 2004a; 2004b) where rutile or amphibole are present in the source or mineral residue. With respect to this fractionation, a global mass imbalance exists with regard to the Nb/Ta ratio as virtually all terrestrial chemical reservoirs have subchondritic ratios (<19.9 ± 0.6; Münker et al., 2003). Possible complimentary reservoirs, such as depleted mantle and MORB, both have subchondritic Nb/Ta ratios of 15.5 ± 1 (Jochum, 1997; Rudnick et al., 2000) and 11-16 (Jochum and Hofmann, 1998; Büchl et al., 2002; Münker et al., 2003) respectively. Nb/Ta ratios for bulk upper and lower continental crust are even lower ranging from 9-14 (Taylor and McLennan, 1985; Rudnick and Fountain, 1995; Barth et al., 2000). Primitive mantle has an average Nb/Ta ratio of 17.5 (Hofmann, 1988) and Nb/Ta ratios of OIB lavas generally range from 15-17 (Pfänder et al., 2002). These ratios suggest that either: (1) the earth is not chondritic with respect to the HFSE, (2) depleted mantle and MORB are not

complimentary reservoirs to the continental crust, or (3) an additional reservoir with superchondritic Nb/Ta (as well as Nb/La and Ti/Zr) exists to satisfy global mass balance. Assuming that the HFSE are perfectly lithophile and that their concentrations in bulk silicate earth are chondritic, rutile-bearing eclogite trapped in oceanic crust subducted deep into the mantle has been proposed as a sink for the missing terrestrial Nb (Rudnick et al., 2000). Alternatively, the similar partitioning behavior of Nb and the strongly siderophile element V between liquid metal and silicate liquid suggests excess Nb may be stored in the Earth's core (Wade and Wood, 2001; Schmidt et al., 2004).

In this paper, we present HFSE data on a suite of late Miocene to Pliocene "adakitic" andesites from the northernmost Chilean flatslab region (27.5°-28.5° S) whose petrogenesis is attributed to melting of eclogitic and/or garnet amphibolitic crust (Kay et al., 1991; 1994b; Goss et al., Chapter 2). These lavas, known as the Pircas Negras and Dos Hermanos andesites, exhibit steep REE patterns and high Sr concentrations along with some of the most extreme HFSE depletions on Earth (La/Ta ratios up to 100). The temporal and spatial relationship between ephemeral tectonic processes acting on the Andean margin during the latest Miocene, adakitic geochemical signatures resulting from high-P crustal melting in the presence of garnet, and the concurrent appearance of pronounced HFSE anomalies provided the motivation for this investigation. Inter-HFSE systematics are used to evaluate the origin of this HFSE depletion and to assess potential residual assemblages in equilibrium with these melts. Unlike many other arc lavas worldwide that have Nb/Ta ratios ranging between primitive mantle and continental crust (10-17; Plank and White, 1995; Stolz et al., 1996), these adakitic andesites exhibit near-chondritic Nb/Ta ratios ranging from 16 to 20. We evaluate these distinct ratios with respect to

experimental data on hydrous eclogitic systems and present a model for their genesis within a cooling Andean frontal arc.

II ADAKITES FROM THE NORTHERN TRANSITION OF THE CHILEAN FLATSLAB

The Pircas Negras andesites define a suite of mafic andesites that erupted in a \sim 50 km wide E-W band between 27°-28.5° S latitude within the northern transition zone of the Chilean flatslab (Figure 3.1). In the field, these mafic lavas are identified as glassy plagioclase-poor andesites dominated by acicular pargasitic oxyhornblende phenocrysts with minor ultramafic crystal clots and resorbed xenocrysts of quartz and plagioclase. They erupted during a period of relative tectonic instability between 8-2 Ma as the frontal arc, defined by > 6500 m high dacitic and rhyodacitic stratovolcanoes, migrated ~ 50 km eastward from the Maricunga belt (Kay et al., 1994b; Mpodozis et al., 1995) to the southernmost extent of the late Miocene-Pleistocene central Andean arc (Figure 3.1). This migration occurred during the peak of Nazca plate shallowing that formed the Chilean flatslab (28°-33° S) between 10-4 Ma (Kay et al., 1987; 1991; Kay and Mpodozis, 2002). The ~ 8 Ma Dos Hermanos andesites preceded the migration and erupted from an isolated center some 20 km east of the Maricunga belt arc front at the northwestern end of the Valle Ancho (Figure 3.1). Like the Pircas Negras, these andesites are glassy and plagioclase-phenocryst free, however amphibole is entirely absent as diopside is the only phenocrystic phase.

The geochemistry of the Pircas Negras and Dos Hermanos andesites has been described by various authors (Kay et al., 1991; 1994b; Goss et al., Chapter 2). High Mg #s (35-61; average = 54; n = 26) and elevated NaO₂ contents (3.7-5.3 wt %) distinguish them from 21-18 Ma Escabroso (Doña Ana Group), 18-13 Maricunga belt, and Quaternary Central Volcanic Zone (CVZ) andesites. These high-Mg andesites

have an adakitic signature exhibited by strong depletion of the HREE elements (Sm/Yb = 4-9) and high Sr concentrations (Pircas Negras = 460-1050 ppm; Dos Hermanos = 1220-1430 ppm). This extreme high-pressure chemical signature is a transient feature that is evident only in lavas that erupted at the time of arc migration (Kay and Mpodozis, 2002; Goss et al., Chapter 2). Comparison with experimental work (Rapp et al., 1999; 2007) indicates that these adakites likely formed by melting of mafic eclogite or garnet amphibolite in (1) the thickened Andean lower crust or (2) in mafic forearc rocks transported to the mantle wedge via forearc subduction erosion. Isotopic modeling and temporal changes in trace element concentrations suggest that lower crustal melting best explains the ~ 8 Ma Dos Hermanos and 3-2 Ma Pircas Negras andesites (Figure 3.1) and that a transient pulse of forearc material delivered to the mantle during the peak of arc migration provided an additional crustal component that contributed to the genesis of the 6-3 Ma high-Mg Pircas Negras andesites (Goss et al., Chapter 2). The effect of secondary *in situ* crustal contamination in these lavas is evident from the ubiquitous presence of quartz and feldspar xenocrysts and by an isotopic enrichment trend of increasing ⁸⁷Sr/⁸⁶Sr ratios with increasing SiO₂ content.

The transient adakitic signature in the high-Mg andesites is accompanied by strong depletion in the HFSE with respect to both the LILE and LREE (Goss et al., Chapter 2). The bulk of the Pircas Negras andesites exhibit high La/Ta ratios (50-75), whereas extreme La/Ta ratios occur in the 8 Ma Dos Hermanos (92-101), 8.8 Ma Comecaballos Pircas Negras (99), and 3-2 Ma Pircas Negras lavas (77-81) (Figure 3.2). Similarly, extreme depletion in the HFSE is a transient feature confined to the 8-2 Ma period of arc instability as 21-18 Ma Escabroso, 18-13 Maricunga belt, and Quaternary CVZ andesites have lower La/Ta ratios (25-55; Figure 3.2).

Figure 3.1 (A) Map of the west coast of South America and the Andes Mountains showing the main tectonomorphic features (modified from Lamb and Davis, 2003). Dashed lines outline national borders. Black arrows with numbers indicate average convergence rate from DeMets et al. (1990). The geometry of the subducting plate is shown by dark contour lines with depths in kilometers (Cahill and Isacks, 1992). Regions with average elevations > 2000 m are outlined in orange. Triangles mark zones of active volcanism. NVZ = Northern Volcanic Zone; CVZ = Central Volcanic Zone; SVZ = Southern Volcanic Zone; AVZ = Austral Volcanic Zone. Yellow box identifies the northern flatslab transition zone (27°-28.5° S).

(B) Inset of the northern flatslab transition zone showing the eruptive extent of Pircas Negras and Dos Hermanos adakites relative to the location of the modern CVZ arc, the early-late Miocene Maricunga Belt volcanic arc, and the Mesozoic arc. Relative elevations indicated by shades of green to white are from the 90m SRTM Digital elevation model. Dark and light grey fields show the outcrop extent of Jurassic and Cretaceous magmatic units respectively (SERNAGEOMIN, 2003). The dashed yellow line marks the position of the Maricunga Belt arc front with some of the principal centers indicated (Kay et al., 1994b; Mpodozis et al., 1995). Solid yellow line marks the southern extent of the modern CVZ. Sites of Neogene basaltic volcanism in the CVZ are shown by white stars. The dashed yellow line to the south marks the late Miocene-Pleistocene arc identified by the Bonete/Incapillo stratovolcano complex. Yellow arrows show ~ 50 km of late Miocene frontal arc migration. Regions of adakitic volcanism include 8-6 Ma Pircas Negras and ~ 8 Ma Dos Hermanos lavas (red), 6-3 Ma Pircas Negras (yellow), and 3-2 Ma upper Rio Salado Pircas Negras (green). Age ranges are in white font (Kay et al., 1994b; Mpodozis et al., 1995; Goss et al., Chapter 2). Black solid star shows the location of the crustally-contaminated Quebrada de Veladero Pircas Negras flow (sample CO-324).





Figure 2.2 Plot of La/Ta versus La/Yb ratios for Pircas Negras and Dos Hermanos adakitic lavas from the northernmost flatslab transition zone (27° S-28.5° S). Samples are grouped according to age and tectonic regime – see chart on the right. Pre-migration (red): ~ 8 Ma Dos Hermanos, 8.8 Ma Pircas Negras, and 7.0-5.5 Ma Pircas Negras lavas from the southern end of the Maricunga belt in Chile. Syn-migration (yellow): 6.0-3 Ma Pircas Negras in Argentina associated with the eastward displacement of the main frontal arc. Post-migration (green): final pulse of Pircas Negras volcanism at 3-2 Ma associated with the siliceous Incapillo Caldera and Dome Complex. Dark grey fields identify the Segerstrom (24 Ma), < 2 Ma Incahuasi and San Francisco basaltic lavas. Fields for late Oligocene/early Miocene Escabroso (21-18 Ma), middle Miocene (18-13 Ma) Maricunga, and Quaternary (< 2 Ma) andesites from the southernmost CVZ are also shown. INAA geochemical data and K-Ar ages are from Kay et al. (1987; 1991; 1994b; 1999; in prep.), Mpodozis et al. (1995), Kay and Mpodozis (2000), and Goss et al. (Chapter 2).</p>

III METHODS

To test these hypotheses, we obtained HFSE concentrations on a subset of well characterized Pircas Negras and Dos Hermanos samples using Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) at Cornell University. Analytical methods are outlined in Appendix 1. USGS standard BCR-2 and an internal standard (PAL-Palisades Sill) were treated as unknowns and run as independent secondary standards. Accuracy for the HFSE and REE for these standards is shown in Table 3.1. All HFSE are well within the error estimates for BCR-2 obtained by isotope dilution MC-ICP-MS (Willbold and Jochum, 2005) with the exception of Ta which is high compared to the BCR-2 standard. Accuracy is estimated on repeated digestions and analyses of BCR-2 and is applied to unknown Pircas Negras and Dos Hermanos samples. Precision is based on relative standard deviation (RSD = SD/mean), which is generally < 3 % for replicate analyses of the BEN standard during each run. RSDs for unknowns are generally higher with average inter-run RSD values of < 4 % for all HFSE. A repeat digestion and analysis of BCR-2 gives a reproducibility error of < 3% for all HFSE.

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Replicate ICP-M	IS HFSE and	REE analyses	for USGS a	nd Cornell rock	standards		
	8/9/2004	8/10/2005	rep	orted	8/10/2005	kay	white
element (ppm)	BCR-2	BCR-2	BCR-2	error (2σ)	PAL	PAL	PAL
Zr	180	185	184	8.5	93.9	88.8	-
Nb	12.3	12.6	12.5	0.4	7.3	6.6	-
Hf	4.66	4.80	4.74	0.1	2.58	2.56	-
Та	0.78	0.79	0.740	0.019	0.61	0.65	-
La	26.3	24.3	25.0	1.0	10.2	10.5	11.41
Sm	6.8	6.6	6.7	0.3	3.4	3.4	3.67
Yb	3.3	3.3	3.5	0.2	2.0	2.2	2.32

Analyses for separate digestions and dilutions of the USGS BCR-2 and internal PAL (Palisades Sill) standards. Reported BCR-2 REE values are from (Govindaraju, 1989; 1994) and HFSE from isotope dilution (Willbold and Jochum, 2005). Reported PAL concentrations are working values from INAA (Kay) and thermal ionization isotope dilution REE (White). With respect to published values, error on elemental ratios for analyzed standards are Nb/Ta \pm 6.9 %, Nb/La \pm 2 %; Zr/Hf \pm 1.0 %; La/Ta \pm 5.0 % and Zr/Sm = \pm 2.5 %.

VI COMPARISON WITH NEUTRON ACTIVATION (INAA) DATA

Most analyzed samples had Ta and Hf concentrations that had previously been obtained by Neutron Activation (INAA). Methods are described by Kay et al. (1987) and internal standards (PAL, SIT, and WBD-2) run along with the unknown samples are reported in Appendix 2. Additionally, Nb and Zr atomic absorption (AA) data were determined by the Chilean Geological Survey (SERNAGEOMIN) on selected Pircas Negras samples. The data from the non-digestive INAA technique provide an independent check on the ICP-MS data with regard to the complete digestion of HFSE-bearing accessory phases and bulk yield of HFSE concentrations. No samples with $SiO_2 > 63$ wt % are reported here due to systematically low HFSE yields relative to INAA, which is interpreted to be due to incomplete digestion of accessory phases. Figure 3.3 shows the agreement between INAA and ICP-MS for various trace elements including Ta and Hf. Elements hosted in easily digestible phases with clean (no interferences) and strong (high peak to background) INAA peaks such as Cr, Co, Sc, Sm, Yb, U and Th exhibit excellent 1:1 correlation between analytical methods. This indicates complete digestion of all phases containing transition metals and REEs. Correlation of Ta to within analytical error is indicative of full digestion of titanite (Tiepolo et al., 2002), ilmenite, and other X^{4+} cation-bearing mineral phases.

In general, a 1:1 relationship between analytical methods exists for Hf concentrations except for the sub-set of Pircas Negras samples that have the highest Hf and SiO₂ concentrations (62-63 wt %; CO 145; CO 313; and CO 332) and evidence for the most significant upper crustal contamination as determined by high U, Th, and Rb concentrations (sample CO 324; Goss et al., Chapter 2). On average, these samples are ~ 15 % low in Hf concentration compared to the INAA analyses. Sample CO 145 has an independent AA analysis of Zr from the SERNAGEOMIN, which is also 15 % low. Therefore, we interpret low Zr and Hf yields on these samples as

incomplete digestion of microphenocrystic zircon. This analytical discrepancy is taken into consideration in the interpretation of the data. The low-yield samples do not exhibit any systematic difference in Zr/Hf ratios when compared to other Pircas Negras or Dos Hermanos lavas despite the fact that the two lowest Zr/Hf ratios are from low-yield samples (CO 145 and CO 324). For the majority of samples, the measured Zr/Hf ratio is reflective of the original ratio in the rock and digestion problems are not a major source of analytical error.



Figure 3.3 Comparison of INAA and ICP-MS data for various trace elements from northern flatslab transition zone basalts and andesites. Filled diamonds – $SiO_2 < 61$ wt %; Open diamonds – $SiO_2 > 61$ wt %. Best fit linear regressions through zero are shown by solid lines with slopes and R² values. Ideal correlations (1:1) are shown by dashed lines. Crustally-contaminated Rio Veladero Pircas Negras flow is identified (CO 324). The shaded field in the Hf INAA vs. ICP-MS graph shows samples with low ICP-MS yields reflective of incomplete digestion of X⁵⁺ bearing accessory phases.

The combination of digestive and non-digestive analytical methods provides a test of the quality of ICP-MS data even after accurate analyses of rock standards have been obtained. By using the well-characterized AGV-1 standard to generate calibration curves for the HFSE, we anticipated the Pircas Negras samples would digest like AGV-1 given their similar major element compositions. Without the secondary check from the INAA data, digestion problems in samples with higher SiO₂ concentrations would not have been apparent. ICP-MS Zr and Hf analyses on dissolved igneous rocks with SiO₂ > 62 wt % should be verified by: (1) an independent non-digestive analytical method (i.e., XRF or INAA) or by (2) digestion in weak HNO_3^- following fusion of a glass bead using an ultra-pure LiBO₄ flux.

V RESULTS

HFSE concentration data including Nb/Ta and Zr/Hf ratios obtained on the Pircas Negras and Dos Hermanos adakites are presented in Table 3.2. Nb and Zr concentrations range from 10-16 ppm and 101-313 ppm respectively and agree with Nb and Zr atomic absorption data from the Pircas Negras and Dos Hermanos lavas. All samples have Nb/Ta ratios of 16-20 that approach the chondritic value (19.9 \pm 0.6). Figure 3.4a shows that these Nb/Ta ratios are distinctly higher than those of average MORB, depleted mantle (DM), and continental crust and overlap the average Nb/Ta ratio of the primitive mantle (Nb/Ta ~ 17.5; McDonough and Sun, 1995). Near-chondritic ratios such as these are uncommon in arc lavas worldwide, consistent with the genesis of typical arc magmas from uniformly subchondritic sources (i.e., depleted mantle, subducted sediments, upper and lower crust; Stolz et al., 1996). Arc rocks with Nb/Ta ratios > 17 are found only in a few modern high-K lavas from the Marianas (Elliott et al., 1997) and Sunda arcs (Stolz et al., 1996), as well as some high-K arc lavas from the Cambrian Takaka terrane in New Zealand (Münker, 1998). The high Nb/Ta ratios in these lavas have been attributed to contamination of the sub-arc mantle by adakitic melts derived from slab melting.

HFSE data for mafic lavas from the northern flatslab transition zone of the Central Andes (~ 27°-28.5°)													
			ICP	-MS		INAA		ICP-	MS		INAA		
	SiO ₂	Nb	σ	Та	σ	Та	Zr	σ	Hf	σ	Hf	Nb/Ta	Zr/Hf
Dos Herma	anos												
CC 81	57.3	12.9	0.5	0.72	0.03	0.64	246	8	5.8	0.3	5.6	17.8	42.5
CC 82	56.1	12		-	-	0.63	237		-	-	5.6	19.1	42.3
CC 83	58.2	13		-	-	0.65	251		-	-	5.9	19.9	42.7
CO 428	59.0	12.9	0.5	0.66	0.03	0.66	229	4	5.3	0.2	5.4	19.4	43.0
7-6 Ma Pir	cas Negra	s											
CO 416	58.9	12.4	0.3	0.69	0.02	0.62	236	8	5.5	0.2	5.3	18.1	43.3
CO 416 ¹	58.9	12.0	0.2	0.73	0.03	0.62	231	4	5.5	0.2	5.3	16.4	42.0
CO 427	59.3	11.4	0.3	0.58	0.04	0.55	246	3	5.6	0.3	5.4	19.8	43.9
6-3 Ma Pir	cas Negra	S											
CC 94	63.4	9.9	0.2	0.58	0.03	0.61	223	4	5.6	0.2	5.6	17.0	40.1
CO 144	58.2	14.9	0.3	0.84	0.06	0.79	263	5	6.0	0.4	6.0	17.7	43.6
CO 145	62.7	12.4	0.2	0.73	0.03	0.63	243	6	6.0	0.3	6.7	16.9	40.3
CO 146	57.5	12.9	0.4	0.76	0.05	0.76	244	4	5.9	0.2	5.8	17.1	41.2
CO 163	62.8	11.7	0.2	-	-	0.62	-	-	-	-	6.7	-	-
CO 170	57.4	11.9	0.2	0.73	0.03	0.69	250	4	6.0	0.3	6.0	16.3	41.7
CO 309	61.7	12.1	0.6	0.73	0.02	0.69	254	10	5.8	0.2	5.8	16.5	44.0
CO 310	59.1	11.2	0.3	0.71	0.03	0.68	253	8	5.9	0.3	6.1	15.8	42.6
CO 324	59.1	15.7	0.4	1.24	0.05	1.21	239	5	6.0	0.2	7.0	12.6	39.9
CO 327	61.7	11.6	0.2	0.66	0.03	0.66	301	4	6.7	0.2	7.4	17.7	44.7
CO 329	59.0	11.9	0.3	0.67	0.02	0.66	270	5	6.2	0.2	6.6	17.8	43.8
CO 331	61.5	12.0	0.4	0.65	0.02	0.70	269	9	6.2	0.1	6.7	18.5	43.3
CO 332	59.3	12.7	0.4	0.70	0.02	0.70	284	13	6.4	0.2	6.5	18.2	44.3
CO 333	62.0	11.7	0.3	0.68	0.03	0.69	273	2	6.2	0.2	6.7	17.2	43.7
CO 412	57.4	11.2	0.2	0.64	0.03	0.64	229	3	5.3	0.3	5.3	17.5	43.3
CO 504	60.2	12.6	0.2	0.69	0.04	-	270	6	6.2	0.1	-	18.2	43.4
CO 296a	62.9	9.4	0.2	0.53	0.04	0.50	256	12	5.8	0.2	5.7	17.8	43.9
3-2 Ma Pir	cas Negra	S											
CO 312	60.9	11.1	0.3	0.60	0.04	0.59	313	9	7.3	0.2	7.2	18.5	42.6
CO 313	62.2	11.2	0.2	0.60	0.03	0.61	291	14	6.7	0.2	7.4	18.6	43.5
CO 179	63.3	11.0	0.3	0.65	0.03	0.60	304	8	6.8	0.2	6.5	17.0	44.8
CO 507	60.0	12.1	0.2	0.67	0.04	-	253	3	5.9	0.3	-	18.2	42.7
Basalt and	basaltic a	ndesite											
CC 262	55.0	10.3	0.2	0.60	0.03	0.65	192	3	4.8	0.2	4.8	17.1	40.4
CO 24	533	104	0.2	0.56	0.03	0.56	165	2	40	0.2	43	18.6	41.2

Table 3.2

Sigma values reflect RSD-error from ICP-MS analysis. Complete major and trace element analyses, K-Ar ages, and sample locations are from Goss et al. (Chapter 2) and references therein. INAA values are from Tittler (1995), Kay et al. (1991; 1994b; 1999), and Goss et al. (Chapter 2). SiO₂ and HFSE concentrations are reported as wt % oxide and ppm respectively. Italicized Nb and Nb/Ta data are from atomic absorption spectroscopy (AA) at the Chilean Geological Survey, Santiago. ¹Replicate digestion and analysis of sample CO 416. CO 296a is from V. Rodrigo (Mpodozis et al., 1996).



Figure 3.4 Graphs of La/Ta vs. (A) Nb/Ta and (B) Zr/Hf ratios for the Dos Hermanos and Pircas Negras adakites. Fields are as in Figure 3.2. Errors bars reflect accuracy of analyzed standards with respect to published values (Table 3.1). All data from ICP-MS (solid symbols). Dos Hermanos open squares are for Nb from atomic absorption and Ta from INAA. Chondritic ratios for Nb/Ta and Zr/Hf are shown by the grey bar (2003). Values for depleted mantle (DM, Jochum, 1997; Münker et al., 2003 - dark green box); primitive mantle (PM, Hofmann, 1988 - hatched box); MORB (Büchl et al., 2002; Münker et al., 2003 - light green box); upper and lower crust (Taylor and McLennan, 1985; Rudnick and Fountain, 1995 - yellow boxes; Barth et al., 2000 - orange box); and the missing eclogite reservoir (Rudnick et al., 2000 - grey box) are also plotted. Dashed lines show mixing between ~ 8 Ma Dos Hermanos (CO 428) and bulk upper crust.

A general age correlation is evident with ~ 8 Ma Dos Hermanos and 7-6 Ma Pircas Negras andesites from the Jotabeche region having the highest Nb/Ta ratios and 6-2 Ma Pircas Negras andesites having lower ratios closer to primitive mantle. This temporal progression towards lower Nb/Ta is accompanied by a decrease in the La/Yb, Sm/Yb, Sr/Yb ratios and a general increase in Cr and Ni concentrations (Goss et al., Chapter 2). Only one Pircas Negras sample exhibits a Nb/Ta ratio close to the bulk crustal value (CO 324; Nb/Ta = 12.6). The low Nb/Ta ratio in this sample is similar to the crust-like Nb/Ta ratios (10-12) common in Central Andean dacitic ignimbrites (Kay and Coira, in prep.) and is consistent with the high concentrations of upper-crust-like trace elements in this sample (Rb = 138 ppm; Cs = 7.38 ppm; Th =16.8 ppm; and U = 5.6 ppm; Goss et al., Chapter 2).

Like most arc rocks, the Pircas Negras and Dos Hermanos adakites exhibit super-chondritic Zr/Hf ratios (> 34.3; Münker et al., 2003) that range from 39.9 to 44.7 (Figure 3.4b). These ratios are higher than those in MORB ($DM_{Zr/Hf} = 35.0$; Hofmann, 1988; Büchl et al., 2002), primitive mantle ($PM_{Zr/Hf} = 36.3$; Hofmann, 1988), and bulk upper and lower continental crust ($UC_{Zr/Hf} = 32.8$ and $LC_{Zr/Hf} = 33.3$; Taylor and McLennan, 1985; Rudnick and Fountain, 1995). Unlike Nb/Ta ratios in the Pircas Negras and Dos Hermanos adakites, there is no systematic correlation between Zr/Hf ratios and eruption age.

A weak correlation exists between Nb/Ta and the anomalously high La/Ta ratios characteristic of the adakitic andesites that erupted in association with arc migration and slab shallowing between 27.5° and 28.5° S (Figure 3.4a). The \sim 8 Ma Dos Hermanos andesites display near-chondritic to chondritic Nb/Ta ratios (17.8-20) and show the most extreme HFSE depletion. The 7-6 Ma Pircas Negras lavas from near Cerro Jotabeche in Chile have similarly high Nb/Ta ratios (18.1-19.9) with somewhat lower La/Ta ratios than the Dos Hermanos. During the main pulse of Pircas

Negras volcanism at the height of arc migration from 6-3 Ma, Pircas Negras andesites exhibit lower Nb/Ta ratios (18.2-15.8) than the earlier lavas. The 3-2 Ma Pircas Negras andesites have nearly-chondritic Nb/Ta ratios (17.0-18.6) and higher La/Ta ratios than main suite of Pircas Negras. In general, there is no correlation between Zr/Hf and La/Ta (Figure 3.4b).

VI DISCUSSION

The weak correlation between Nb/Ta and La/Ta ratios and the temporal shift towards lower Nb/Ta ratios in Pircas Negras lavas erupting over the course of late Miocene to Pliocene frontal arc migration is evaluated with respect to (1) varying extents of *in situ* upper crustal contamination, (2) progressive depletion of an enriched primitive mantle source, and (3) a change in the HFSE-bearing phase in response to changing tectonic parameters.

Despite xenocrystic and isotopic evidence for *in situ* crustal contamination of the Pircas Negras and Dos Hermanos precursor melts (Goss et al., Chapter 2), it is unlikely that assimilation of Andean crust upon ascent controlled the temporal trends in the HFSE data. Support comes from HFSE ratio trends that are not inversely correlated with SiO₂ content or 87 Sr/ 86 Sr ratios as would be expected if a mantle-reacted adakitic melt was modified by assimilation of upper crust. Moreover, contamination with continental crust would result in both lower Nb/Ta and Zr/Hf ratios. Except for the crustally-contaminated Rio Veladero Pircas Negras flow (CO 324) with its lower Nb/Ta and Zr/Hf ratios (~ 12 and ~ 39; Figure 3.4), the HFSE ratios of the Pircas Negras do not reflect these crustal contamination trends. Mixing between the Dos Hermanos lavas, with their near-chondritic Nb/Ta and Zr/Hf ratios, and bulk upper crust will produce contaminated melts with Nb/Ta and Zr/Hf ratios significantly lower than those observed in the Pircas Negras lavas (Figure 3.4a).

We therefore rule out crustal contamination of the ~ 8 Ma Dos Hermanos lavas as an explanation for the HFSE ratios in the 6-2 Ma Pircas Negras andesites.

The low solubility of Nb and Ta in slab-derived fluids had led to the understanding that Nb/Ta ratios in non-crustally contaminated arc lavas are controlled by mantle composition. For some arc lavas with strong slab-fluid signatures as well as mid-ocean ridge basalts (Plank and White, 1995), a positive correlation between Nb/Ta ratios and Nb concentrations supports a general mantle-wedge control on the HFSE. Progressive depletion of the mantle wedge via non-modal clinopyroxene melting can explain this correlation since Ta is more compatible than Nb in clinopyroxene (D_{Nb}/D_{Ta} is ~ 0.3-0.8; e.g., Hart and Dunn, 1993; Johnson, 1998; Lundstrom et al., 1998; Green et al., 2000; Klein et al., 2000). However, Münker et al. (2004b) showed that progressive mantle depletion cannot exhibit a first-order control on the Nb/Ta ratios of Kamchatka arc front lavas. With the exception of a few backarc lavas associated with a more enriched mantle in Kamchatka (Sredinny Ridge), Nb/Ta in these lavas do not correlate with other trace element ratios indicative of mantle depletion (e.g., Zr/Nb and Zr/Hf; Figure 3.5). These authors conclude that the Nb and Ta systematics in Kamchatkan arc lavas must be controlled by a residual HFSE-bearing phase rather than progressive depletion of the mantle wedge.

The Pircas Negras and Dos Hermanos adakitic andesites exhibit substantially higher Nb concentrations (10-15 ppm) than the majority of Kamchatkan and Aleutian arc lavas (< 5 ppm) reported by Münker et al. (2004b). Only the enriched backarc Sredinny Ridge lavas and western Aleutian adakites have higher Nb concentrations (15-18 ppm). These samples also have Nb/Ta ratios that partially overlap the fields for the Pircas Negras andesites (Figure 3.5). As with Nb/Ta ratios from central Kamchatkan or western Aleutian lavas, the high Nb/Ta ratios of the Pircas Negras and Dos Hermanos andesites do not correlate with other trace element ratios indicative of

variable mantle depletion (e.g., Zr/Hf, Lu/Hf, or Zr/Nb). Therefore, it is unlikely that the range of Nb/Ta observed in the Andean adakites are related to progressive depletion of the sub-arc Andean mantle wedge.



Figure 3.5Plot of Zr/Hf versus Nb/Ta ratios for the Dos Hermanos and Pircas
Negras adakitic lavas. Colored fields are as in Figure 3.2. Depletion
trend is based on the compatibility partitioning order of Nb < Ta < Zr <
Hf < Lu in mantle minerals (Münker et al., 2004b and references
therein). Fields for central Kamchatka andesites, western Aleutian
adakites, and backarc Sredinny Ridge lavas (Kamchatka) are from
Münker et al. (2004b). MORB field is from Münker et al. (2003).

One possibility to explain the near-chondritic Nb/Ta ratios (> 18) of the Pircas Negras and Dos Hermanos andesites is that they reflect the Nb/Ta ratio of the central Andean mantle. Primitive mantle-derived basalts rarely penetrate through the \geq 60 km thick Andean crust without extensive crustal contamination or fractional crystallization. Episodes of delamination and subduction erosion have likely modified the chemical composition of the mantle with crustal material (Kay and Kay, 1993;

Kay et al., 1994a; Goss et al., Chapter 2). Despite this, the Quaternary southern CVZ Incahuasi and San Francisco primitive basalts near ~ 27° S, some ~ 100 km north of the Pircas Negras lavas, provide chemical information about the Andean mantle under the southernmost CVZ. As reported by Kay et al. (1999), these lavas have 9-10 wt % MgO, high Cr and Ni contents (Cr = 500-700 ppm; Ni ~ 200 ppm), and Fo₈₈₋₈₉ olivine phenocrysts in equilibrium with the melt. HFSE ICP-MS data for these most-mafic of Puna lavas reveal elevated Nb/Ta ratios of 19 to 21 (Kay et al., in prep.). The similarly primitive ~ 24 Ma Segerstrom basalt from the same region exhibits a lower Nb/Ta of 17. Further south within the Valle Ancho, a ~ 9 Ma backarc basalt from near Los Aparejos (sample CO 24) also has an elevated Nb/Ta ratio of 18.6 (Table 3.2). These data suggest (1) the mantle below the southernmost Puna has Nb/Ta ratios outside of the range of MORB (11-16; Büchl et al., 2002) and OIB (15-17; Pfänder et al., 2002) and (2) the Nb/Ta ratio of the mantle underneath the southernmost CVZ could have increased since the early Miocene.

High Nb/Ta ratios and elevated Nb contents in Sredinny Ridge lavas led Münker et al. (2004b) to propose a continental-lithospheric mantle below the Kamchatkan backarc. Beneath the southern Puna (25-28° S), the continental lithospheric mantle is considered to be thin with the asthenospheric mantle virtually in contact with the overlying MOHO (Whitman et al., 1996). Delamination during the latest Miocene and possible magmatic erosion of the lithospheric mantle lid may have contaminated the mantle below the Puna with continental lithospheric material resulting in higher Nb/Ta ratios in the Quaternary southern Puna primitive basalts. A similar processes cannot be ruled out as a cause for the near-chondritic Nb/Ta of the Pircas Negras and Dos Hermanos lavas that erupted further south within the northern flatslab transition zone. Moreover, temporal changes in mantle HFSE ratios are not likely due to a variable flux of sediments delivered to the mantle as the Chile trench north of 32° S is currently void of terrestrial detritus (Schweller et al., 1981) and has likely been sediment-starved since the middle Miocene (Cornejo et al., 1993; Vandervoort et al., 1995).

An alternative mechanism to generate the near-chondritic Nb/Ta ratios in the Pircas Negras and Dos Hermanos lavas is that these melts equilibrated with a residual HFSE-bearing phase capable of fractionating Nb from Ta. As proposed by Münker et al. (2004b) for Aleutian and Kamchatkan lavas with an adakitic signature, variable proportions of residual rutile and/or amphibole in the high-pressure crustal source of these melts may be responsible for the range of Nb/Ta ratios. Here, we apply the trace element tests used by Münker et al. (2004b) to the Pircas Negras and Dos Hermanos adakitic lavas that have been modeled as high-P melts of either garnet-bearing *in situ* lower crust or from crust eroded from the forearc via subduction erosion (Kay et al., 1991; Kay and Mpodozis, 2002; Goss et al., Chapter 2). Unlike the Kamchatkan adakites, where a proposed slab tear permits thermal conditions for slab melting (Yogodzinski et al., 2001), anatexis of the Eocene-age subducting Nazca plate is not likely to be the source of the Pircas Negras/Dos Hermanos adakites due to isotopic and thermal considerations (Kay and Mpodozis, 2002).

A compilation of HFSE partition coefficients for minerals in garnet amphibolite, eclogite, and mantle peridotite (Münker et al., 2004a) and HFSE concentrations in these minerals (Foley et al., 2000; Tiepolo et al., 2000; Foley et al., 2002; Zack et al., 2002) shows that rutile and to a lesser extent low-Mg amphibole are the principle phases capable of hosting Nb and Ta. These residual phases oppositely fractionate Nb from Ta in mafic to intermediate lavas (see Figure 3.6). Melts in equilibrium with rutile-bearing eclogite have higher Nb/Ta and lower Nb/La ratios than their source as Ta is more, and La is less compatible than Nb in rutile ($D_{Nb}/D_{Ta} <$ 1; $D_{Nb}/D_{La} >$ 1; Green and Pearson, 1987; Jenner et al., 1993). In contrast, melts in equilibrium with garnet amphibolite have lower Nb/Ta and Nb/La ratios than their source as Nb is more compatible than both Ta and La in low-Mg amphibole (D_{Nb}/D_{Ta} and $D_{Nb}/D_{La} > 1$; Tiepolo et al., 2000; Foley et al., 2002).



Figure 3.6 Plot of Zr/Sm versus (A) Nb/Ta and (B) Nb/La ratios for the Pircas Negras and Dos Hermanos adakitic andesites. Fields are the same as in Figure 3.5. Distribution coefficients and fractionation trends are from Münker et al. (2004b and references therein). Green box shows the compositional range for a potential eclogitic source (Rudnick et al., 2000). Thick dark arrows show expected crustal contamination trends based on bulk upper and lower crustal compositions (Taylor and McLennan, 1985; Barth et al., 2000). Dashed lines on (B) show linear trends in the data before (8-6 Ma) and during (6-2 Ma) arc migration.

Due to the greater compatibility of the MREE relative to the HFSE in low-Mg amphibole $(D_{Nb,Zr}/D_{Sm} < 1)$ compared to rutile $(D_{Nb,Zr}/D_{Sm} > 1)$, plots of Nb/Ta and Nb/La versus Zr/Sm ratios (Figure 3.6) can be used to discriminate which residual phase is controlling HFSE concentrations in melts of high-pressure mafic crust (Foley et al., 2002; Münker et al., 2004b). According to these authors, a negative correlation between Nb/Ta and Zr/Sm ratios indicates both residual rutile and low-Mg amphibole are controlling the HFSE budget in the co-existing melt. A weakly negative trend between Nb/Ta and Zr/Sm ratios for the Pircas Negras and Dos Hermanos adakites can be seen in Figure 3.6a. To discriminate *between* HFSE-bearing residual phases, these authors show that a positive correlation between Nb/La and Zr/Sm ratios indicates rutile as the dominant residual phase and a negative correlation indicates the dominance of low-Mg amphibole. This is because La is more incompatible than the HFSE in both amphibole and rutile $(D_{Nb,Zr}/D_{La} > 1)$. As is the case for both western Aleutian and central Kamchatkan lavas (Münker et al., 2004b), Figure 3.6b shows a positive trend between Nb/La and Zr/Sm for the 8 Ma Dos Hermanos and 7-6 Ma Pircas Negras adakites that is suggestive of rutile control of the HFSE during this period. In contrast, a weakly negative Nb/La – Zr/Sm trend for the 7-6 Ma, 6-3 Ma, and 3-2 Ma Pircas Negras adakites is indicative of a greater role for low-Mg residual amphibole (Figure 3.6b). We interpret these HFSE trends, in addition to the sharp increase in Zr/Sm ratios, as evidence for a temporal change towards greater amphibole control of the HFSE in the high-pressure residue in equilibrium with the 6-2 Ma Pircas Negras magmas.

HFSE response to Andean arc migration

The central Andean margin has experienced large-scale tectonic changes during the Neogene including rapid uplift and crustal thickening due to $\sim 100-300$ km

of crustal shortening and ductile flow of the lower crust (e.g., Isacks, 1988). At 8 Ma, the Dos Hermanos andesite erupted in the backarc of the waning Maricunga arc to the west and is best explained as a low percentage melt of underplated mafic magmas in the eclogite facies at the base of the thickened Andean crust (Goss et al., Chapter 2). This is consistent with the extreme adakitic signature and lower Mg #s, Cr, and Ni concentrations of the Dos Hermanos andesites compared to the 7-4 Ma Pircas Negras andesites. Rutile would likely be the stable titaniferous phase in eclogites at these P-T conditions as is consistent with the HFSE trends (see Figures 3.2-3.6). Lower crustal melts in equilibrium with residual rutile-bearing eclogite would generate the high Nb/Ta ratios with low Zr/Sm ratios in these lavas. Ponding of hot (> 1100 °C) mantle-derived back-arc magmas similar to the 9 Ma Los Aparejos basalts within the lower crust or at the MOHO is a potential mechanism to generate the Dos Hermanos adakitic melt. At P > 1.5 GPa, amphibole is unstable at temperatures > 1100 °C (Huang and Wyllie, 1986) and is unlikely to be an important residual HFSE-bearing phase in the Dos Hermanos source. Further, relatively dry conditions at the base of the backarc crust at 8 Ma is consistent with the lack of phenocrystic amphibole and the lower Ba/La ratios in the Dos Hermanos andesites compared to the younger Pircas Negras andesites. All of the geochemical and petrologic evidence point to melting of a rutile-bearing eclogitic lower crust by mantle-derived arc magmas as the petrogenetic process that formed the Dos Hermanos adakites.

A dominantly amphibole-poor rutile-bearing eclogitic source can also explain the high La/Ta ratios in the Dos Hermanos compared to the Pircas Negras andesites. These extreme ratios result not from differences in HFSE depletion ($Ta_{DH} = 0.63-0.72$ ppm vs. $Ta_{PN} = 0.53-0.84$ ppm), but in the degree of LREE enrichment ($La_{DH} = 58-66$ ppm vs. $La_{PN} = 29-47$ ppm) in these lavas. Higher LREE concentrations in adakitic melts derived from a purely eclogitic (cpx + garnet) as opposed to a garnet-bearing amphibolitic source are explained by the lower compatibility of the LREE in garnet or cpx compared to amphibole during high pressure melting of mafic crust (Klein et al., 1997; 2000; Klemme et al., 2002).

The HFSE systematics of the Pircas Negras high-Mg adakites reflect their genesis during a transient period of tectonic instability along the central Andean margin. The ~ 50 km of eastward frontal arc migration between 7-3 Ma has been related by Kay and Mpodozis (2002) to a period of margin-wide tectonic reorganization (Tebbens and Cande, 1997) and subduction of the NE-trending arm of the Juan Fernandez Ridge (Yañez et al., 2001), both of which may have resulted in a rapid increase in the rate of forearc subduction erosion (> $100 \text{ km}^3/\text{m.y./km}$). Alongstrike geophysical imaging (Wigger et al., 1994; Schmitz et al., 1999; Tassara et al., 2006) and isotopic modeling of the Pircas Negras lavas (Goss et al., Chapter 2) are consistent with a forearc contaminant dominantly composed of the mafic intrusive and cumulate sections of Mesozoic arc crust (> 80 %) with a minor component of the underlying Paleozoic sialic crust (< 20 %), both of which are exposed in the general region along the Chilean coast (Figure 3.1; Mpodozis and Ramos, 1989). Given the lack of direct information on composition of the Andean lower crust, HFSE-ratios alone are incapable of discriminating between *in situ* vs. eroded arc crust as a source for the Pircas Negras.

As proposed by Kay et al. (1987; 1991) and Kay and Mpodozis (2002), the ephemeral and dramatic increase in fluid-mobile element ratios (i.e., "slab-derived fluid signature"; Ba/Ta or Ba/La) that accompanied the shallowing of the Nazca plate could have resulted from higher slab-fluid concentrations in precursor mantle-hybridized adakitic melts. Dehydration of the subducting slab into a thinning and cooling asthenospheric mantle wedge can account for higher fluid-mobile element concentrations in syn-migration lavas. Moreover, high shear wave speeds (Vs)

obtained from seismic data across the Chilean flat slab are consistent with the partial eclogitization of the Andean lower crust catalyzed by a transient increase in hydrous fluids (Gilbert et al., 2006). These authors propose eroded forearc crust or subducted pelagic sediments as a source for the fluid needed to eclogitize the lower crust. Excess water from the dehydrating slab and from subduction erosion may have stabilized residual amphibole in the source of the Pircas Negras magmas as evidenced by (1) the abundance of oxidized pargasitic (high-Mg) amphibole phenocrysts in Pircas Negras andesites and (2) the sharp increase in the "slab-derived fluid signature" in the Pircas Negras andesites compared to both early-middle Miocene and modern CVZ andesites (Goss et al., Chapter 2). Experimental evidence shows that the variation in oxygen fugacity from \leq cobalt-cobalt oxide (CCO) to nickel-nickel oxide (NNO) that may accompany an increase in hydrous fluid concentrations would not result in major differences in the partitioning of Nb, Ta, and Ti between silicate melt and rutile (Schmidt et al., 2004). Thus, as suggested by temporal trends in Nb/Ta and Nb/La ratios, equilibration of these adakitic melts in a wetter transitional arc setting is consistent with a change to an amphibole-bearing residue controlling the HFSE.

It is unlikely that fractionation of phenocrystic pargasitic amphibole had significant control on either the extreme HFSE-depletion or the near-chondritic range of Nb/Ta ratios measured in the Pircas Negras adakitic andesites. HFSE partitioning experiments between pargasitic amphiboles and silicate melts have shown that D_{Nb}/D_{Ta} is close to unity and therefore high-Mg amphiboles cannot be responsible for inter- or intra-HFSE fractionation (Brenan et al., 1995a; Klein et al., 1997; Hilyard et al., 2000; Tiepolo et al., 2000). However, low-Mg amphiboles (Mg # 0.50-0.65) characteristic of amphibolites from subducted oceanic crust (Foley et al., 2002) or arc lower crust (Garrido et al., 2006), have $D_{Nb}/D_{Ta} > 1$ and are capable of producing lower Nb/Ta ratios in melts in equilibrium with these amphiboles. Within the hydrous

cooling conditions that existed during the 7-3 Ma period of arc instability, low-Mg amphiboles could have been present in either (1) eroded mafic forearc crust within the subduction channel or (2) *in situ* lower crust below the northern flatslab transition zone. Mafic forearc crust transported to the base of the mantle wedge would remain within the stability field of amphibole (< 1100 °C) due to refrigeration from the subducting Nazca plate before being swept into hotter regions of the mantle wedge and melted.

Comparison to results from HFSE modeling

HFSE modeling results show that melting of mafic crust at high-pressures (> 1.5 GPa) provides a mechanism to generate higher Nb/Ta ratios in adakitic lavas. A non-modal batch melting model of a rutile-bearing residual MORB eclogite (Nb/Ta = 15.5 ± 1.0) produces adakitic melts with Nb/Ta ratios between 16-18 (Figure 3.7; Schmidt et al., 2004). Correspondingly, eclogitic residues in equilibrium with these melts have Nb/Ta ratios lower than MORB (11.5-15.5) due to the preferential partitioning of Ta in rutile. Schmidt et al. (2004) show that for melting of MORB crust with average TiO₂ contents of 1.5 wt %, rutile is exhausted as a residual phase after ~ 30 % partial melting. At lower pressures, ilmenite and titanite replace rutile as the residual titaniferous phase in eclogites. The D_{Nb}/D_{Ta} for both these phases is less than unity and thus would also result in adakitic melts with high Nb/Ta (Green and Pearson, 1986; Schmidt et al., 2004). Also shown on Figure 3.7, modeled melts of garnet-free MORB in the amphibolite facies have lower Nb/Ta ratios (11-15) consistent with the preferential partitioning of Nb in amphibole. Therefore, a change in residual mineralogy from rutile to amphibole evident from high-pressure melting models is entirely consistent with the observed HFSE trends in the Pircas Negras and Dos Hermanos lavas.



Figure 3.7 Plot of Nb (ppm) vs. Nb/Ta ratios for the ~ 8 Ma Dos Hermanos and 7-2 Ma Pircas Negras. Also shown are values for depleted mantle (DM, Jochum, 1997; Münker et al., 2003); primitive mantle (PM, Hofmann, 1988); bulk upper crust (Taylor and McLennan, 1985; Barth et al., 2000); mean eclogite and the missing silicate reservoir (Rudnick et al., 2000). Thin dashed arrows show batch melt models (F = 0.05-0.40) from Schmidt et al. (2004) for: (1) rutile-bearing MORB eclogite (50:50, gt:cpx) and (2) garnet-free MORB amphibolite. Bulk TiO₂ contents in MORB vary from 1.6 to 3.0 wt %. Wider dashed arrow points towards lower Nb/Ta ratios for an eclogitic residue in equilibrium with modeled melts of eclogitic MORB with 3 wt % TiO₂. Solid arrows show extrapolated melt concentrations for a rutile-bearing eclogite and amphibolite from a mafic arc crustal source (grey box) with initial Nb concentrations and Nb/Ta ratios greater than MORB.

Although these slab-melting models generate Nb/Ta ratios greater than MORB, such models fail to produce the high Nb concentrations and near-chondritic Nb/Ta ratios (> 18-20) of the Dos Hermanos and Pircas Negras adakites (Figure 3.7). Moreover, the high Zr/Hf ratios of the Pircas Negras andesites (Zr/Hf = 40-45; Figure 3.4b) relative to MORB (Zr/Hf ~ 32-38; Münker et al., 2003) also require that

Zr must have fractionated from Hf (Figure 3.4b). As discussed by Münker et al. (2004b), slab-melting processes should not significantly fractionate Zr from Hf due to the opposite D_{Zr}/D_{Hf} partitioning of cpx and garnet in eclogite (50:50 modal ratio cpx:gt).

Given the geochemical and tectonic arguments against slab melting (Kay and Mpodozis, 2002; Goss et al., Chapter 2), anatexis of rutile-bearing eclogitic Nazca plate crust cannot be responsible for the near-chondritic Nb/Ta ratios, extreme HFSE-depletion, or the steep REE patterns in the Pircas Negras or Dos Hermanos adakitic lavas. However, if the Schmidt et al. (2004) melting model is applied to a basaltic arc crustal source, such as the ~ 9 Ma Los Aparejos (Table 2) or ~ 24 Ma Segerstrom basalt (Kay et al., in prep.) with Nb concentrations and Nb/Ta ratios greater than MORB (> 7 ppm and > 15 respectively; Figure 3.7), the result would be an adakitic melt with elevated Nb concentrations (> 10 ppm) and higher Nb/Ta ratios (17-19; solid arrow labeled "rutile" in Figure 3.7) similar to those of the Dos Hermanos adakitic andesites. *In situ* mafic lower crust derived from ponded mantle-derived basalts or gabbroic cumulates would likely have chemical characteristics similar to these Miocene mantle-derived basalts.

In response to the changing thermal and compositional conditions below the arc front during the peak of arc migration and slab shallowing, a switch to an amphibole-dominated high-pressure arc-crustal source shown in Figure 3.7 (solid arrow labeled "amphibole") can account for the lower Nb/Ta ratios in the 6-3 Ma Pircas Negras relative to the Dos Hermanos. Mixing of these mantle-hybridized adakitic melts derived from amphibolitized forearc with adakitic melts of the *in situ* crust explains the temporal HFSE trends and is consistent with petrogenetic models for these lavas based on trace element and isotopic data (Goss et al., Chapter 2).

VII CONCLUSIONS

The 8-2 Ma Dos Hermanos/Pircas Negras adakitic andesites from the northernmost Chilean flatslab region of the Central Andes (27.5°-28.5° S) record some of the most-pronounced HFSE-depletion of Phanerozoic arc lavas on Earth (La/Ta ratios up to 101). These lavas erupted before (8 Ma Dos Hermanos and 8-7 Ma Pircas Negras), during (6-3 Ma Pircas Negras), and following (3-2 Ma Pircas Negras) a period of arc instability characterized by ~ 50 km of eastward frontal arc migration and back-arc shallowing of the subducted Nazca plate. Compared to other arc lavas, pre-migration adakites exhibit anomalously-high Nb/Ta ratios (18-20) approaching the chondritic value of 19.9 ± 0.6 . Crustal contamination, progressive depletion of an enriched mantle, and slab melting cannot explain the HFSE trends in these adakitic lavas. Based on HFSE-partitioning in eclogitic and amphibolitic mineral phases, the oldest of these lavas can be explained as partial melts of rutile-bearing eclogites at the base of the thick Andean mafic lower crust. Syn-migration Pircas Negras with uniformly lower Nb/Ta ratios (16-18) are better explained by a change to melting of a more hydrous amphibolitic source of either subducted forearc or in situ lower crust. Comparison of HFSE trends in 8-2 Ma Central Andean adakites to HFSE-models for mafic eclogite supports a more hydrated residual source mineralogy during the peak of arc instability.

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CHAPTER 4

THE INCAPILLO CALDERA AND DOME COMPLEX (~ 28° S): A STRANDED MAGMA CHAMBER OVER A DYING ANDEAN ARC

ABSTRACT

The Pleistocene Incapillo Caldera and Dome Complex (5570 m) is situated at the southern termination of the Andean Central Volcanic Zone (~ 28° S), where the more steeply dipping segment of the subducting Nazca plate transitions into the Chilean "flatslab" to the south. The ~ 250 m high walls of the elliptical caldera (6 x 5 km) are dominantly composed of a homogeneous pumice-rich rhyodacitic ignimbrite that radiates up to 15 km from the caldera rim. Flanking the caldera to the east and west are ~ 40 steep-sided rhyodacitic domes that predate the main "caldera-forming" ignimbrite. The morphology of these domes reflects the non-explosive effusive eruption of a crystal-rich gas-poor rhyodacitic magma. A volumetrically-minor debris flow composed of abundant pumice, dacites, and lithic clasts is topographically confined to a glacial valley south of the caldera and unconformably overlies the ignimbrite. Rafts containing mixed pumice clasts at the distal end of the ignimbrite reflect the convective physical condition within the magma chamber immediately prior to the pyroclastic eruption. Including the domes and ignimbrite, the total estimated volume of erupted Incapillo magma is ~ 37 km^3 . New biotite ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ ages along with existing K-Ar ages reveal that the final eruption of the Incapillo Caldera at 0.51 ± 0.04 Ma marks the youngest volcanic activity within the ~ 700 km long amagmatic flatslab segment of the central Andes (27° to 33.5° S).

Distinctive and virtually identical chemical signatures of the domes and ignimbrites (SiO₂ = 67-71 wt %; La/Yb = 37-54; Ba/La 16-28; La/Ta 30-85; 87 Sr/ 86 Sr = 0.70638 to 0.70669; ϵ Nd = -4.2 to -4.6) indicate that all erupted lavas originated

from the same magma chamber and that differentiation effects between units were The strong HREE depletion (Sm/Yb = 6-8) that distinguishes Incapillo minor. magmas from the large ignimbrites of the Altiplano-Puna plateau can be explained by the extent and degree of partial melting at lower crustal depths (> 40 km) in the This high-pressure geochemical signature was partially presence of garnet. overprinted by shallow-level assimilation and fractional crystallization processes. Energy-constrained AFC modeling of Sr, Nd, and Pb isotopic ratios suggests that incorporation of anatectic upper crustal melts into a fractionated dacitic host best explains the petrogenesis of the Incapillo magmas. The diminution of the sub-arc asthenospheric wedge during Nazca plate shallowing left the Incapillo magma chamber unreplenished by both mafic mantle-derived and lower crustal melts and thus stranded at shallow depths within the thick Andean crust. Based on its small size, effusive eruptive style, and distinctive high-pressure chemical signature, the Incapillo Caldera and Dome Complex provides an endmember model for an Andean caldera erupting within a waning magmatic arc over a shallowing subduction zone.

I. INTRODUCTION

The Central Andes (15°-28° S) is recognized as the type example of a continental-margin volcanic arc associated with non-collisional convergent tectonics. The eruptive style, size, and composition of explosive silicic volcanism varies along the margin and these differences can to a first order be explained by spatial and temporal differences in the tectonic setting and crustal composition (Kay et al., 1999). During the late Miocene to Pliocene, explosive silicic volcanism has been localized within the amalgamated 11 to 4 Ma Altiplano-Puna Volcanic Complex (APVC - Figure 4.1; de Silva, 1989b; Coira et al., 1993; Kay et al., 1999; de Silva and Gosnold, 2007) that straddles the border between Argentina, Chile, and Bolivia. Additionally,

the massive ~ 6.4 to 2.2 Ma Cerro Galán caldera of northwest Argentina erupted in the backarc near 26° S east of the southern Central Volcanic Zone (CVZ) (Sparks et al., 1985; Francis et al., 1989). Large-scale (> 1000 km³) silicic volcanism within the Puna has been attributed to an ignimbrite flare up caused by a rapidly steepening Nazca slab, expanding asthenospheric wedge, and massive crustal melting by intruded mantle-derived basalt (Kay et al., 1999). In contrast, smaller (< 50 km³) mid-late Miocene ignimbrites exposed near the Salar de Antofalla (SAF - Figure 4.1) at 25°-26° S have been explained as fractionated andesitic melts that subsequently assimilated upper crust (Siebel et al., 2001; Schnurr et al., 2007)

Approximately 100 km along the frontal arc further to the south, the Incapillo Caldera and Dome Complex is the southernmost ignimbritic caldera of the Central Andes (Figure 4.1). Its small size, high-pressure geochemical signature, characteristic eruption of steep-sided rhyodacitic domes, and position along the volcanic front of a waning magmatic arc testify to the different processes responsible for siliceous magmatism at this latitude compared to the larger centers to the north. In this paper, we investigate the volcanology, geochronology, and petrology of Incapillo magmatic units with respect to other siliceous volcanic centers of the Central Andes. We calculate erupted volumes of the Incapillo ignimbrite and dome material, present a series of new ⁴⁰Ar/³⁹Ar fusion ages that compliment existing K-Ar ages (Kay and Mpodozis, 2000), and outline an eruption model for the volcanic complex. The petrogenesis of Incapillo magmas is considered using more than 40 major and trace element analyses along with Sr, Nd, Pb and O isotopic analyses from the Incapillo Caldera and Dome Complex.

Figure 4.1 SRTM digital elevation model of the Central Andes showing main morphotectonic features. Nazca plate convergence direction is the long-term integrated NUVEL-1 rate from DeMets et al (1990). Dark solid lines show contours of the subducting Nazca plate (Cahill and Isacks, 1992) with depths (kms) to the Wadati-Benioff zone. Solid vellow lines show extents of the Central (CVZ) and Southern (SVZ) Volcanic Zone volcanic fronts and a black open box gives the position of the early to late Miocene Maricunga Belt volcanic arc (Kay et al., 1994b; Mpodozis et al., 1995). Tan box shows the study area of the Incapillo Caldera and Dome Complex shown in detail in Figure 4.2. Shaded area shows the position of the Altiplano-Puna Volcanic Complex (APVC; de Silva, 1989b; de Silva and Gosnold, 2007) with inset of silicic major centers. APVC volcanic center abbreviations and eruptive ages are: Pu = Purico; Pz = Panizos (7.9-6.7 Ma; Ort, 1993); PG = Pastos Grandes; G = Guacha (4.2 Ma; Francis and Baker, 1978;de Silva and Francis, 1991); V = Vilama-Coruto (8.5-7.0 Ma; Coira et al., 1996; Soler et al., 2007); C = Coranzuli (6.7-6.4 Ma; Seggiaro, 1994); Pr = Pairique (11 Ma; Coira et al., 1996); P = La Pacana (5.5-4 Ma; Gardeweg and Ramírez, 1987; Lindsav et al., 2001). Other centers mentioned in the text include Cerro Galán, Ojos del Salado (OS), Tres Cruces (T), the ignimbrites from the Salar de Antofalla region (SAF; Siebel et al., 2001; Schnurr et al., 2007), Cerro Tupungatito (T), 11-8 Ma Volcán Copiapó (Cp), the 16-9 Ma Cerro de los Tórtolas-Tambo (CdT), and the 6-5 Ma Vallecito-Vacas Heladas (V-VH) ignimbrite. The location of the Cordillera Blanca batholith in central Peru is shown in the inset map by a star.



II. REGIONAL TECTONICS

The Incapillo Caldera and Dome Complex (28° S, 68.8° W) is situated at the northernmost margin of the Chilean flatslab where the steeply dipping segment of the Nazca plate north of 28° S gradually shallows to near-horizontal at 100 km depths near 30° S (Figure 4.1; Cahill and Isacks, 1992). Along the margin, nearly-orthogonal subduction of the Nazca plate below South America (075° N) at an average velocity of 84 mm/a is responsible for the continuous chain of active arc volcanism spanning from southern Peru (15° S) to Ojos del Salado in Chile (26° S). South of Ojos del Salado, the Chilean flatslab region is characterized by a 500 km wide zone of increased intracrustal seismicity (Smalley and Isacks, 1990; Pardo et al., 2002), Laramide-style thick skinned deformation (Jordan et al., 1983), and an amagmatic gap that extends \sim 700 km to the south to Volcán Tupungatito (33.5° S), the northernmost active volcano in the Southern Volcanic Zone (SVZ). This gap in active volcanism has been explained by Barazangi and Isacks (1976) to have resulted from the loss asthenospheric wedge volume due to shallowing of the Nazca slab that began after \sim 18 Ma and reached a maximum between 10 and 5 Ma (Kay et al., 1987; 1991).

Crustal thicknesses below the Incapillo Caldera and Dome Complex are amongst the thickest for any volcanic margin on Earth. Using depth phase precursors, McGlashan et al (2007) reported a 70 km MOHO depth directly below the Incapillo Caldera at 28° S. This crustal thickness is similar to the 65-75 km thick crust estimated for the Altiplano (Figure 4.1; Beck et al., 1996; Beck and Zandt, 2002; Yuan et al., 2002) and somewhat thicker than the 42-67 km thick crust of the Puna (Figure 4.1; Yuan et al., 2002) and central flatslab regions (Fromm et al., 2004; McGlashan et al., 2007).
III. RELATION OF INCAPILLO TO MIOCENE ARC-FRONT CENTERS

The late Miocene to Pliocene magmatic history of the northern flatslab transition zone is characterized by regional tectonic instability and frontal arc migration in tandem with an increased rate of forearc subduction erosion and backarc slab shallowing along the margin (Kay and Mpodozis, 2000; 2002). Late Oligocene to late Miocene silicic magmatic activity was concentrated within the Maricunga belt \sim 50 km west of the Incapillo complex (Figure 4.1; Kay et al., 1994b; Mpodozis et al., 1995; Goss et al., Chapter 2). Major silicic centers of the Maricunga belt include the 27-23 Ma dacitic to rhyodacitic Tilito Formation ignimbrites (Doña Ana Group), the 15-14 Ma Valle Ancho ignimbrite, the 11-7 Ma Copiapó dacite complex, and the ~ 6 Ma Nevado de Jotabeche dacitic domes and flows. The final ignimbritic eruption of Nevado de Jotabeche (Kay et al., 1994b; McKee et al., 1994; Mpodozis et al., 1995) marked the termination of Maricunga belt volcanism and was contemporaneous with the migration of the volcanic front ~ 50 km to the east. The 6-2 Ma dacitic eruptions of Volcán Pissis, Sierras de Veladero, and Bonete Chico define the main axis of the latest Miocene-Pliocene arc that largely predates the eruption of the Incapillo complex (Figures 4.1 and 4.2, Kay and Mpodozis, 2000).

By the late Pliocene, siliceous magmatism persisted to the north near Ojos del Salado (Mpodozis et al., 1996; Gardeweg et al., 2000) while at 28° S, large-scale dacitic volcanism waned. The Incapillo Caldera and Dome Complex erupted during this post-migration period between 3-0.5 Ma as the last volcanic event for ~ 700 km within the currently amagmatic segment along the arc (Kay and Mpodozis, 2000). Most of the Incapillo domes and all of the ignimbrites are contained within a topographic low between the high peaks of Pissis (6793 m) to the north, Bonete Chico (6759 m) to the east, and the Sierras de Veladero (6335 m) to the west (Figures 4.2b and 4.3).



Figure 4.2 (A) Composite ASTER digital image (15 m resolution) of the 3-0.5 Ma Incapillo Caldera and Dome Complex and latest Miocene/Pliocene dacitic centers of the northern flatslab transition zone (Bonete Chico, Pissis, Sierras de Veladero, and Bonete Grande).

(B) Geological map of the Incapillo Caldera and Dome Complex adapted from Mpodozis (unpublished), Rubiolo et al. (2002), Caminos and Fauqué (2000), and Fauqué (2000). Principle late Miocene to Pleistocene volcanic units as well as exposures of the Permo-Triassic Choiyoi granite-rhyolite province and quartzite metamorphic basement are shown. Sample locations (Appendix 11) are shown with available K-Ar (Table 4.1) and 40 Ar/ 39 Ar ages (Table 4.2). Dome numbers correspond to domes used in volume calculations (Table 4.3).









Figure 4.3 Top: Photograph of the north wall of the 6 x 5 km Incapillo caldera showing principle volcano-structural units. Dashed yellow line marks the stratigraphic contact between the 0.87 ± 0.03 Ma pre-caldera dacite (sample CO 516) and the overlying 0.51 ± 0.04 Ma Incapillo ignimbrite. *Bottom*: Photograph looking west across the Quebrada de Veladero from Cerro Bonete Chico showing main pyroclastic deposits associated with the Incapillo caldera. Dashed yellow line shows the contact between the Incapillo ignimbrite and the lithic-rich overlying Veladero debris flow. Dashed arrows show flow directions of the caldera-forming Incapillo pyroclastic flow.

IV. CALDERA MORPHOLOGY

With a rim altitude of 5500 m, the Incapillo caldera (translated from Quechua as "Crown of the Inca") is the highest explosive caldera in the world (Figures 4.2 and 4.3) and was first described by Baker (1981) and later by de Silva and Francis (1991) from satellite photos as Cerro Bonete. The well exposed 200-350 meter high walls of the 6 x 5 km elliptical caldera are dominantly composed of a homogeneous pumicerich layered outflow ignimbrite called the Incapillo ignimbrite. This ignimbrite unconformably overlies a series of altered dacitic lava flows that are exposed along the north wall of the caldera (Figure 4.3). Based on their lower stratigraphic position and general northward slope, these flows likely reflect the edifice of a pre-caldera stratocone or dome. Isolated rhyodacitic domes on the north and south rims of the caldera show evidence for erosional collapse of the caldera walls. Based on early remote sensing studies, these lava domes were originally thought to be flat topped "mesetas" formed by eroded ignimbrite (Baker, 1981; de Silva and Francis, 1991). A similar post-caldera extrusive lava dome within the center of the caldera exhibits extensive hydrothermal alteration (Figure 4.3). Adjacent to this resurgent magmatic dome is the Laguna del Corona del Inca, a 2 x 1 km crater lake that is likely the source of lacustrine and evaporite deposits that blanket the caldera floor. Based on thermal infrared imaging, the temperature of the crater lake is estimated at ~ 13 °C and thought to be fed by a weakly active hydrothermal system (Markham and Barker, 1986).

V. PRINICIPLE INCAPILLO CALDERA AND DOME COMPLEX ERUPTIVE UNITS

The major eruptive units associated with the Incapillo Caldera and Dome Complex include: (1) the caldera-forming Incapillo outflow ignimbrite, (2) the stratigraphically younger and topographically-confined Veladero debris flow, (3) more than 40 flat-topped rhyodacitic domes and associated cumulitic xenoliths, and (4) a series of older oxidized domes.

Incapillo Ignimbrite

Composing the cliff-like walls of (Figure 4.3) and radiating up to 15 km in all directions from the rim of the Incapillo caldera is the Incapillo ignimbrite: a homogeneous layered ignimbrite that is the most striking and obvious Incapillo unit visible on satellite imagery (Figure 4.2). The ignimbrite is generally topographically-confined to the Quebrada de Veladero (Figures 4.2 and 4.3) to the south and the valley of an E-W flowing ephemeral river on the southern flank of Monte Pissis. However, a pumice-rich unit from near the headwaters of the Rio Salado may also be part of the Incapillo ignimbrite (sample CO 183; Figure 4.2). Ignimbrite thicknesses range from a maximum of ~ 250 m within the center of the caldera and taper to ~ 10 m at the distal end within the Quebrada de Veladero. The lowermost unit of the ignimbrite is composed of a 5 cm thick welded basal surge. This surge deposit is seen where the ignimbrite is undercut by fluvial erosion and unconformably caps late Miocene dacitic flows from the Sierras de Veladero (Figure 4.4a).

The extremely lithic-poor Incapillo ignimbrite is composed of 0.5-1.0 meter thick bands of crystal-rich (quartz and plagioclase) and ash-dominated pyroclastic flow deposits that alternate with uniform matrix-supported layers of white pumice (Figure 4.4c). Pumice clasts are generally 5-20 cm in diameter, dominated by 50-60 % translucent devitrified glass, and contain approximately 15-40 % vesicles. Pumices contain phenocrysts (< 1 mm crystals) of plagioclase (25-30 %), quartz (20-25 %), sanidine (20-25 %), biotite (10-15 %), and hornblende (10-15 %) with minor Fe-Ti oxides (~ 5 %), apatite, and titanite. Within 1 km of the caldera, the ignimbrite becomes completely massive and matrix dominated (Figure 4.4a and c). With the exception of the thin basal surge unit, all of the Incapillo ignimbrite flows within the Quebrada de Veladero and along the caldera rim are completely unwelded.

The largest pumice clasts in the Incapillo ignimbrite occur at the far distal end of the flow in the Quebrada de Veladero. Here, ~ 2 m thick rafts composed of mixed pumices that are 5-30 cm in diameter, are interlayered with 1-2 m thick laminated white ash flows (Figure 4.4e). At least 3 separate pumice raft sequences are apparent at the distal toe of the ignimbrite. These pumices are distinct from the white homogenous pumices that dominate the Incapillo ignimbrite as they are clearly mixtures of two magmas: a fluidized biotite-bearing rhyodacite and a more viscous and crystal-rich (sanidine and quartz) rhyolite (Figure 4.4f).

Veladero debris flow

The Veladero debris flow, which conformably overlies the Incapillo ignimbrite, is spatially confined to the Quebrada de Veladero (Figures 4.2, 4.3a, 4.4a and b) and is not exposed at the rim or within the walls of the Incapillo caldera. Its northernmost extent is ~ 5 km south of the caldera rim. Here, the deposit is 15-25 m thick and thins to 10-15 m at its southernmost extent within the Quebrada de Veladero. In the field and on satellite imagery (ASTER and Landsat TM), the Veladero debris flow is clearly identifiable from the underlying and larger Incapillo ignimbrite by its oxidized yellow-orange color, marginal levees, and highly-indurated hummocky topography (Figure 4.2).

The composition and texture of the Veladero flow is clearly distinct from the Incapillo ignimbrite (Figure 4.4d). It is comprised of clasts of red and grey biotitebearing dacite (15-20 %), glassy brown pumice (10-15 %), a highly vesiculated white pumice similar to the Incapillo ignimbrite pumice (\sim 5-10 %), abundant angular and rounded lithic fragments (5-10 %), and euhedral crystals of quartz (1-5 mm; 5-10 %), biotite (0.1-1mm; ~ 5 %), and plagioclase (1-5mm; ~ 5 %). All clasts are supported by a light to moderately cemented ash- and clay-rich matrix (~ 25-30 %). Matrix cementation accommodates the near-vertical erosional cliffs of the Veladero debris flow in comparison to the more-shallowly sloping erosional edges of the Incapillo ignimbrite (Figure 4.4a). Except for near the basal contact at the far distal end of the flow, where larger pumices and dacites (10-20 cm) form a weakly laminated and sheared stratigraphy, the Veladero debris flow is massive, poorly-sorted, and non-graded. Based on its restricted spatial extent, cemented texture, heterogeneous lithic-rich composition, and massive bedding, the Veladero unit likely formed from an unconsolidated debris flow or lahar.

Eastern and Western Domes

Surrounding the Incapillo caldera are ~ 40 steep-sided rhyodacitic domes that are locally referred to as "tortas" (cake-shaped domes). They erupted in two main clusters (see Figures 4.2 and 4.5): a western group within the Sierras de Veladero along the upper Rio Salado and an eastern group bounded by Bonete Chico and Volcán Pissis. The western domes unconformably cap Pircas Negras adakitic andesites along the length of the Rio Salado (Goss et al., Chapter 2). A few smaller domes erupted on the western and northern rims of the Incapillo caldera.

Vertical relief of the domes ranges from 100 to 600 m and many have a multilobate morphology with a \sim 1 km wide apron of eroded dome material. No basal ash layer is evident. Field observation and ASTER imagery reveal numerous water-filled pit craters 20 m in diameter on the summits of the largest of the western domes (Figure 4.5b and c). These explosion craters are surrounded by 10 m high lava spires composed of blocky dacite.



Figure 4.4 Photographs of pyroclastic deposits associated with the Incapillo caldera. (A and B) Contacts between the Incapillo ignimbrite and the overlying Veladero debris flow within the Quebrada de Veladero, (C) Non-welded and homogeneous pumice-rich Incapillo ignimbrite, (D) Cemented lithic- and dacite-rich Veladero debris flow, (E) 2 m thick pumice rafts at the distal end of the Incapillo ignimbrite within the Quebrada de Veladero, (F) Mixed pumice clast from the upper pumice raft shown in Figure 4.4e.



Figure 4.5 Images of rhyodacitic domes from the Incapillo Caldera and Dome Complex. (A) ASTER satellite image of the caldera and eastern dome field. 5-2 Ma oxidized domes associated with the Pliocene dacitic centers (i.e., Bonete, Pissis, and Veladero) are overlain by the younger steep-sided Incapillo domes. (B) Western dome field along the upper Rio Salado on the west side of the Sierras de Veladero. Explosion craters/pits dot the summit of the largest and southernmost dome. (C) Photograph of an explosion crater surrounded by ~ 10 m high rhyodacitic lava spines.

Incapillo dome lavas are extremely crystal rich (> 60 %) with large plagioclase (0.5-12 mm; 40-50 %), quartz (1-8 mm; 30-40 %), biotite (1-3 mm; 10-15 %), amphibole (0.2-3 mm; 5-10 %), and titanite (0.2-0.5 mm; 1-3 %) with minor abundances of oxides, apatite, and zircon suspended in a translucent cryptocrystalline groundmass. Some alkali feldspar is present (< 5 %) in a few dome lavas. This

phenocrystic assemblage is ubiquitous in the dome lavas associated with the Incapillo magmatic system, including those that are 20-25 km west of the caldera along the upper Rio Salado (Figures 4.2 and 4.5).

Biotite-bearing amphibolite xenoliths that are 0.5-4 cm in diameter occur within the western Incapillo dome lavas at sample site CO 512 (Figure 4.6a). The xenoliths have a magmatic texture with prismatic amphiboles (0.5-2 mm) poikilitically suspended in large (1-5 mm) optically-continuous plagioclase host crystals (Figure 4.6b and c). Many of the amphiboles have a skeletal texture with their cores replaced by a cryptocrystalline glassy matrix. Secondary biotite phenocrysts (0.2-0.8 mm) are intergrown and enclosed within the amphiboles. Point counting indicates phenocryst abundances of 70 % (amphibole), 17 % (plagioclase), 7 % (biotite), 3 % glass, 2 % magnetite, and 1 % apatite.

Oxidized Domes

A suite of older domes erupted on the flanks of Bonete Chico and Sierras de Veladero and within the Quebrada de Veladero (Figures 4.2 and 4.5a). These domes, which are identifiable in satellite imagery by their reddish oxidized color, also occur north and east of the Incapillo caldera. Many of the oxidized domes are partially covered by younger Incapillo domes.

The petrographic features of the older dome lavas are generally similar to the Incapillo domes (plag, qz, bio, amp, titanite, oxides). In detail, they contain more amphibole (25-50 %) and less quartz (0-25 %) with similar abundances of plagioclase (40-70 %). Despite an oxidized appearance in the field and in satellite imagery, only negligible oxidation is observed in thin section.



Figure 4.6 (A) Photograph of biotite-bearing amphibolite xenoliths hosted in Incapillo dacitic dome lava from the upper Rio Salado region (from sample CO 512b within the western dome field). A bulk major element analyses of the xenolith is given in Table 4.4 (sample CO 512b); (B+C) Photomicrographs of an amphibolite xenolith showing major crystalline phases (hb = hornblende; pl = plagioclase, bio = biotite). Note secondary intergrowths of biotite within hornblende and a poikilitic magmatic texture. Major element mineral chemistry on representative phases are given in Appendix 12.

VI. GEOCHRONOLOGY (K-Ar AND ⁴⁰Ar/³⁹Ar DATING)

Whole rock and biotite K-Ar ages for Incapillo ignimbrite pumices, rhyodacitic dome lavas, and dacitic stratovolcanoes were obtained by the Chilean Geological Survey (SERNAGEOMIN). These ages were discussed by Kay and Mpodozis (2000) and are presented here with full analytical data in Table 4.1. K-Ar analytical methods

and data reduction procedures are discussed in Mpodozis (1995). In addition, 40 Ar/ 39 Ar single-crystal fusion ages from selected ignimbrite and dome lava biotites were measured at the University of Wisconsin-Madison Rare Gas Chronology Laboratory following methods outlined in Singer et al. (2004), Hora et al. (2007), and discussed in Appendix 1. These new 40 Ar/ 39 Ar ages provide a tighter control on the eruptive chronology of the Incapillo Caldera and Dome Complex and refine the magmatic evolution of the southernmost CVZ arc.

Table 4.	L						
K-Ar ages	for < 7 Ma eve	olved lavas	from th	e northern fla	tslab trans	ition zone	e (~ 27°-28.5° S)
sample	type	% K	Ar ⁴⁰	% Ar atm	age	±	type
	Incapillo calo	dera dome	S				
CO 136	rhyodacite	7.139	0.808	84	2.9 ±	0.4	biotite
CO 137	dacite	7.096	0.312	92	1.1 ±	0.4	biotite
	Incapillo Ign	<u>imbrite</u>					
CO 141	pumice	7.049	0.437	91	1.6 ±	0.5	biotite
	<u>Older Incapi</u>	llo oxidize	d domes				
CO 140	dacite	2.296	0.16	98	-	-	WR
CO 140	dacite	2.296	0.166	96	1.9 ±	0.7	WR^*
CO 142	dacite	2.686	0.477	45	4.6 ±	0.2	WR
CO 151	dacite	2.569	0.466	81	4.7 ±	0.5	WR
CO 157	dacite	2.614	0.370	84	3.6 ±	0.5	WR
	L. Miocene a	<u>irc</u>					
Pissis							
CO 37	dacite	7.240	1.155	73	4.1 ±	0.4	biotite
CO 38	andesite	7.011	1.833	71	6.2 ±	0.5	biotite
CO 39	andesite	2.961	0.487	36	4.2 ±	0.2	WR
CO 180	dacite	2.440	0.307	76	3.2 ±	0.3	WR
CO 182	dacite	2.466	0.444	87	4.6 ±	0.7	WR
Sierras de	Veladero						
CO 152	dacite	7.255	1.072	93	3.8 ±	1.0	biotite
CO 153	dacite	2.189	0.476	89	5.6 ±	1.0	WR
Bonete Chi	ico						
CO 147	dacite	2.615	0.259	83	2.5 ±	0.4	WR
CO 148	dacite	2.789	0.377	35	3.5 ±	0.1	WR
CO 149	dacite	2.055	0.334	51	4.2 ±	0.3	WR

Table 4.1

Ages obtained at the SERNAGEOMIN geochronology lab (Santiago, Chile); WR= whole rock analysis

*Average of two repeat analyses

Results

The results of 94 single-crystal laser fusion ⁴⁰Ar/³⁹Ar analyses from five Incapillo samples are reported in Table 4.2 with age spectra and inverse isochrons shown in Figure 4.7. Dated minerals include (1) biotite from rhyodacitic domes in both the eastern (CO 323) and western (CO 508) dome fields, (2) hornblende from a Pircas Negras adakitic andesite from the upper Rio Salado (CO 507; Goss et al., Chapter 2) that is directly overlain by Incapillo domes, (3) biotite from two Incapillo ignimbritic pumices (CO 514 and CO 524) and, (4) biotite from the pre-caldera dacitic flow from the north wall of the Incapillo caldera (CO 515). Final ⁴⁰Ar/³⁹Ar fusion ages are calculated using both a weighted mean average and isochron analysis of 8 to 26 individual single-crystal laser fusions (see Figure 4.7). The nearly-identical isochron and weighted mean apparent ages suggest minimal to zero excess Ar present in the analyzed mineral separates.

Incapillo domes and Pircas Negras adakitic andesite

A 40 Ar/ 39 Ar age of 1.337 ± 0.129 Ma for the eastern Incapillo dome (CO 323; Table 4.2) is consistent with biotite K-Ar ages of 2.9 ± 0.4 Ma to 1.1 ± 0.4 Ma for similar domes along and just south of the Incapillo caldera (Table 4.1). The western Incapillo dome has an age of 2.551 ± 0.033 Ma (CO 508) and is younger than the Pircas Negras andesite (CO 507) directly below that was dated at 3.968 ± 0.192 Ma. These ages show that Incapillo dome eruptions began at ~ 2.5-3.0 Ma on both the eastern and western flanks of the Sierras de Veladero and that silicic dome-forming eruptions along the upper Rio Salado commenced during the waning stages of Pircas Negras magmatism between 4 and 2 Ma (Goss et al., Chapter 2).

⁴⁰ Ar/ ³⁹ Ar	single-crystal lase	r fusion and	alyses on mine	eral separates from]	Incapillo do	ome lavas ai	nd ignimbritic pumices		
			_	Weighted N	/lean ages			Isochron ages	
Sample	Туре	Mineral	N^1	Age (Ma) $\pm 2 \sigma$	MSWD	K/Ca	${}^{40}\text{Ar}/{}^{36}\text{Ar}_i\pm 2\sigma$	MSWD	Age (Ma) $\pm 2\sigma$
CO-323	Eastern dome	bio	8 of 8	1.355 ± 0.022	0.08	10.264	297.7 ± 15.7	0.08	1.337 ± 0.129
CO-508*	Western dome	bio	22 of 26	2.554 ± 0.029	0.86	10.492	296.1 ± 2.9	0.90	2.551 ± 0.033
CO-514*	Incapillo Ign.	bio	21 of 21	0.511 ± 0.018	0.65	12.205	296.2 ± 1.0	0.57	0.505 ± 0.020
CO-524*	Incapillo Ign.	bio	10 of 11	0.515 ± 0.022	0.32	11.999	296.2 ± 3.4	0.34	0.509 ± 0.037
C0-516*	Pre-caldera flow	bio	14 of 19	0.881 ± 0.019	0.18	18.991	297.2 ± 3.2	0.10	0.873 ± 0.025
CO-507	Pircas Negras	hbde	12 of 12	3.898 ± 0.085	0.41	0.101	$292.8~\pm~6.8$	0.38	3.968 ± 0.192

Complete ⁴⁰Ar/³⁹Ar methods are outlined in Appendix 1. MSWD - mean square of weighted deviations All ages calculated using the decay constants of Steiger and Jäger (1977) (λ^{40} K = 5.543 x 10⁻¹⁰ yr⁻¹) J-value calculated relative to 28.34 Ma for the Taylor Creek rhyolite sanidine

* Indicates sample that has been subjected to a clean-up step prior to fusion ¹Number of single-crystal fusions included in the age statistics

Table 4.2

Figure 4.7 ⁴⁰Ar^{/39}Ar age spectra (left column) and inverse isochron (right column) diagrams for selected Incapillo dome and pyroclastic units. Complete 40 Ar^{/39}Ar data is shown in Table 4.2. Grey squares show each laser fusion analysis with 2σ error ellipse. n = number of analyses of the total analyses used in the weighted mean average and isochron age.



Incapillo ignimbrite and caldera units

With respect to the formation of the Incapillo caldera, the older pre-caldera lava flow exposed at the base of the north caldera wall yielded a 40 Ar/ 39 Ar age of 0.873 ± 0.025 Ma (CO 515; Table 4.2). This is 0.35-0.40 m.y. older than the two Incapillo ignimbrite pumices that are dated at 0.505 ± 0.020 Ma (CO 514) and 0.509 ± 0.037 Ma (CO 524). These 40 Ar/ 39 Ar ages are significantly younger than the imprecise 1.6 ± 0.5 Ma K-Ar biotite age given in Table 4.1 for the Incapillo ignimbrite (CO 141) and reveal that the Incapillo Caldera and Dome Complex erupted nearly contemporaneous with the Ojos del Salado (1.53 ± 0.13 to 0.34 ± 0.19 Ma; Mpodozis et al., 1996; Gardeweg et al., 1998) and Tres Cruces (2.1 ± 0.3 to 0.028 ± 0.011 Ma; Gardeweg et al., 2000) complexes in the southernmost CVZ (~ 27° S). Based on these ages, the ~ 0.51 Ma Incapillo caldera-forming eruption is the youngest volcanic eruption between 27.5° and 33° S in the Central Andes.

Older domes and late Miocene dacitic stratovolcanoes

Whole rock and biotite K-Ar ages from oxidized domes on the flanks of Bonete Chico and Sierras de Veladero range from 4.7 ± 0.5 Ma to 1.9 ± 0.5 Ma (Table 4.1) and mainly pre-date the dome eruptions associated with the Incapillo magmatic system. These domes erupted simultaneously with the larger dacitic volcanic centers including Pissis (6.2 ± 0.5 to 3.2 ± 0.3 Ma), Sierras de Veladero (5.6 ± 1.0 to $4.2 \pm$ 0.4), and Bonete Chico (4.2 ± 0.6 to 2.5 ± 0.4 Ma) that reestablished the frontal arc ~ 50 km to the east during the latest Miocene and Pliocene.

VII CALCULATION OF ERUPTED VOLUME

In order to constrain the magnitude of the Incapillo eruptive event, surfaceintegrated volumes of eruptive units were calculated using the 90 m resolution SRTM

digital elevation model (DEM) for the Central Andes imported into the terrain and surface-modeling Surfer[®] program. With a known upper and/or lower surface elevation, topographically-integrated volumes can be calculated. This technique is more accurate than binning units into perfect geometric shapes (i.e., approximating a dome as a cylinder). For example, the volume of a typical Incapillo dome (e.g., dome #10; Figure 4.2b) is substantially overestimated by geometric-binning [where volume = basal area $(km^2)^*$ height (m)] compared to topographic-integration (3.68 km³ vs. 2.42 km³). Table 4.3 gives calculated volumes and masses for Incapillo domes, ignimbrites, and the post-eruptive Veladero debris flow.

Table 4.3					
Estimates of erupted vo	lume for the Inca	pillo Caldera and	Dome complex		
	Volume (km ³)	Density (kg/m ³)	$DRE^{1}(km^{3})$	Mass (kg)	Method
Caldera	4.3	-	-	-	Topo-integrated
Pyroclastic Deposits					
Incapillo Ignimbrite					
Outflow ¹	21.9	1675	14.1	3.7E+13	Geometric binning
Inflow ¹	9.8	1675	6.3	1.1E+13	Geometric binning
Total	31.7	1675	20.4	4.7E+13	Geometric binning
Veladero Debris Flow ²	0.7	1950	0.5	1.3E+12	Topo-integrated
Dome #	Volume (km ³)	Density (kg/m ³)	$DRE^{1}(km^{3})$	Mass (kg)	Method
Domes					
1	2.16	-	-	-	Topo-integrated
2-3	0.58	-	-	-	Topo-integrated
5	1.77	-	-	-	Topo-integrated
10	2.42	-	-	-	Topo-integrated
22	0.73	-	-	-	Topo-integrated
24-27	0.11	-	-	-	Topo-integrated
28-29	0.11	-	-	-	Topo-integrated
30	0.06	-	-	-	Topo-integrated
31	0.02	-	-	-	Topo-integrated
32-34	0.20	-	-	-	Topo-integrated
36	0.08	-	-	-	Topo-integrated
40	7.80	-	-		Topo-integrated
Total	16.03	2650	-	4.2E+13	Topo-integrated

¹Average density reflects an ignimbrite composition of 60 % pumice with an averaged measured density (δ) of 1022 kg/m³ and 40 % crystalline matrix comprised of quartz (67 %; δ = 2620 kg/m³), albite (20 %; $\delta = 2620 \text{ kg/m}^3$), sanidine (5 %; $\delta = 2520 \text{ kg/m}^3$), biotite (5 %; $\delta = 3090 \text{ kg/m}^3$), and hornblende (3 %; $\delta = 3270 \text{ kg/m}^3$) consistent with the observed mineral abundances in the ignimbrite. ²Density of the Veladero debris flow is calculated from cut and weighed blocks of cemented debris flow material.

Erupted volumes for the largest < 3 Ma Incapillo domes were calculated by defining a lower surface specific to each dome and using the digital topography as the upper surface. No correction was made for sloping lower surfaces or for dense rock equivalent (DRE). The largest domes have volumes that range from $1.2 - 7.0 \text{ km}^3$ with a total volume of erupted material of ~ 16 km³. Converting this volume into mass using an average density for rhyodacite (2650 kg/m³) yields 4.2 x 10¹³ kg of erupted Incapillo dome lava.

The topographically-integrated volume of the Incapillo caldera was calculated by defining the upper surface as the average caldera rim elevation (5400 m) and the lower surface as the DEM topography of the caldera floor. The resultant volume of the caldera is 4.3 km³ and is similar to other intermediate-sized collapse calderas such as Katmai in Alaska ($\sim 5 \text{ km}^3$; Hildreth, 1991). This is a maximum estimate of the initial caldera volume as post-eruptive erosion has likely widened the caldera over the last 0.5 Ma.

Due to its gradually tapering thickness and unknown basal topography, the topographically-integrated volume of the Incapillo ignimbrite could not be effectively calculated using the DEM. Instead, the ignimbrite outflow volume was calculated by approximating the unit as a 250 m high cone of siliceous material that progressively thins to 10 m at a radial distance of 10 km. This approach gives a total volume of 26.2 km³. After subtracting out 4.3 km³ of missing caldera material and correcting for vesicularity, the total outflow volume of the Incapillo ignimbrite is ~ 14.1 km³ (DRE). Dense rock equivalent (DRE) is based on a calculated density of 1675 kg/m³ for the Incapillo ignimbrite, which corresponds to a rhyolitic magma with 35 % vesicularity and is consistent with estimated density and vesicularity for the Atana ignimbrite from La Pacana caldera in the APVC (Lindsay et al., 2001).

For the Incapillo caldera, the volume of intracaldera tuff (i.e., inflow) is difficult to estimate because of the lack of clearly exposed caldera ring faults or exposures of sub-caldera floor basement that could help to constrain the basement topography and subsidence depth. Assuming a realistic subsidence depth of 0.5 km³, the total ignimbrite inflow volume is estimated at 6.3 km³ DRE. Combined with the outflow, the total volume of the Incapillo ignimbrite is ~ 20 km³ DRE and is a minimum estimate as co-ignimbrite ash is not included in the volume total.

Lastly, the lithic-rich Veladero debris flow has a topographically-integrated volume of $\sim 0.7 \text{ km}^3$ or $\sim 0.5 \text{ km}^3$ DRE and a mass of $0.13 \times 10^{13} \text{ kg}$ (average density = 1959 kg/m³ measured from cemented debris flow blocks). This is an order of magnitude smaller than the caldera-forming Incapillo ignimbrite and is consistent with its origin as a topographically-confined debris flow.

The total erupted volume in DRE for all Incapillo ignimbrites (~ 20 km³) is comparable to the 1912 eruption of Katmai, which produced a total of 12 km³ of ignimbrite (Hildreth, 1991). Including the rhyodacitic domes, the total calculated volume of all erupted magmas at Incapillo is ~ 37 km³. Incapillo is far smaller than other Central Andean calderas (Figure 4.1) such as Vilama (1400 km³; Soler et al., 2007), Coranzuli (650 km³; Seggiaro, 1994); Panizos (~ 650 km³; Ort, 1993), La Pacana (2500 km³; Lindsay et al., 2001) and Cerro Galán (~ 2000 km³; Sparks et al., 1985). However, the Incapillo ignimbrite is similar in size to numerous ignimbrites in the Salar de Antofalla (SAF) region of the southern Puna with volumes ranging from 5-50 km³ (Siebel et al., 2001).

VIII. GEOCHEMISTRY OF INCAPILLO UNITS

Incapillo dome lavas and ignimbrite pumices were analyzed for major and trace elements following the methods outlined in Kay et al. (1987) and Goss et al.

(Chapter 2). A complete description of analytical methods is given in Appendix 1. Juvenile clasts and pumices from the Veladero block and ash flow were not analyzed due to oxidation and lithic contamination. Major elements were obtained by electron microprobe at Cornell University. Error for major elements is 2-5 % for elements with concentrations > 1 wt % and \pm 10-20 % for elements with < 1 wt %. *In situ* major element microprobe analyses on xenolith mineral phases were analyzed relative to Smithsonian mineral standards. Trace element data were obtained by Instrumental Neutron Activation Analysis (INAA) at Cornell University. Long term averages for internal standards are given in Appendix 2. For selected samples, non-activating elements in INAA or those with either a low signal/noise ratio or peak interference (i.e., Rb, Nb, Zr, Y, Pb) were determined by atomic absorption (AA) at the Chilean Geological Survey (SERNAGEOMIN).

Selected Incapillo dome lavas were analyzed for Sr and Nd isotopes using a VG Sector 54 Thermal Ionization Mass Spectrometer (TIMS) in the Keck Isotope Lab at Cornell University based on the analytical methods of White and Duncan (1996). Pb separations were done at Cornell University using the technique outlined by White and Dupré (1986) and analyzed at the University of Florida on a "Nu-Plasma" multi collector (MC) ICP-MS (Kamenov et al., 2004). Nd isotopes on Incapillo ignimbrite pumices were analyzed by MC-ICPMS at the University of Florida following methods outlined in Kamenov et al. (2007). Oxygen isotopes were analyzed by ArF laser fluorination on selected quartz grains at the Universität Göttingen based on the procedures by Fiebig et al. (1999) and were corrected to the average measured value of the Gore Mountain garnet (UWG-2; $\delta^{18}O = 5.7$).

Major elements

Major element compositions for Incapillo dome lava and ignimbrite pumices are given in Tables 4.4 and 4.5 and plotted in Figure 4.8. All Incapillo lavas are high-K rhyodacites (SiO₂ 67-70 wt %) and rhyolites (SiO₂ > 70 wt %) based on the classification of Le Maitre (1989). The 4.7-1.9 Ma oxidized domes south of the Incapillo caldera are dacites and represent the least evolved of all sampled dome lavas.

Incapillo dome lavas and ignimbritic pumices are compositionally similar and largely plot in overlapping fields on most major element variation diagrams (Figure 4.8). In detail, Incapillo dome lavas have higher MgO contents (0.5-2.0 wt %) than ignimbrite pumices (< 1.3 wt %) at constant SiO₂ concentrations due to greater crystallinity (> 60 %). The 0.87 ± 0.03 Ma pre-caldera rhyodacitic flow from the north caldera wall is similar to the Incapillo domes. Major element concentrations are generally like those of evolved lavas and pumices from the Puna with Al₂O₃ = 14-17 wt %, CaO = 2-5 wt %, and K₂O > 2.5 wt %. TiO₂ concentrations range from 0.28-0.72 wt % in Incapillo units and 0.61-0.83 wt % in the less evolved older domes (Tables 4.4 and 4.5). FeO_T, Al₂O₃, MgO, and CaO concentrations decrease with increasing SiO₂ content defining linear differentiation trends within all units. These trends become more subdued (FeO_T, MgO, and CaO) to non-apparent (Al₂O₃) when only Incapillo domes and ignimbrite pumices are considered.

Incapillo domes and ignimbrite pumices are distinct from siliceous magmas from the APVC, Cerro Galán, and Salar de Antofalla regions based on Na₂O concentrations (Figure 4.9a) and the aluminum saturation index (Al/CNK = molar Al₂O₃/(CaO+Na₂O+K₂O; Figure 4.9b). Incapillo Na₂O contents range from 3.8-5.4 wt % and are significantly higher than in APVC and Galán ignimbrites at similar SiO₂ and K₂O concentrations (geochemical data compilation in Kay and Coira (in prep.)). High Na₂O contents result in metaluminous magmas (Al/CNK = 0.70-1.05) with

Al/CNK ratios that increase with SiO₂ content. Incapillo magmas are more Na-rich and metaluminous than virtually all other siliceous magmas from the Central Andes (Figure 4.9).



Figure 4.8 Harker diagrams for Incapillo dome lavas (solid symbols) and pyroclastic pumices (open symbols - grouped by dashed line). Data is given in Tables 4.4 and 4.5 respectively. Also shown is the pre-caldera flow from the north rim of the Incapillo caldera (large open square). K₂O classification from Le Maitre et al. (1989).



Figure 4.9 Graphs of (A) K₂O wt % vs. Na₂O wt % and (B) SiO₂ wt % vs. aluminum saturation index $[Al/CNK = molar Al_2O_3/(CaO+NaO+K_2O)]$ (lower) for Incapillo dome lavas and ignimbrite pumices. Data is in Tables 4.4 and 4.5. Sample markers are the same as in Figure 4.8. APVC field includes data from Panizos, Vilama, Sifón, Atana-La Pacana, Pairique, Granada, Purico, and Coranzulí centers. Data compilation is from Kay and Coira (in prep.) and from references discussed in Figure 4.1. The field for Cerro Galán represents only the 2.2 Ma eruption with data from Francis et al (1989) and unpublished compilations. Data for small- to medium-sized ignimbrites from the Salar de Antofalla region (SAF) are from Siebel et al. (2001) and include < 6 Ma pumices and matrix analyses with SiO₂ > 66 wt %. Jotabeche data is from Kay et al. (1994b) and Tittler (1995). Large crosses are average compositions of Cordillera Blanca (Peru) ignimbrites and granites (Atherton and Petford, 1993).

	Pre-caldera	Xenolith	Incapillo Caldera Domes							Eastern Domes		
sample	CO 516	CO 512b	CO136	CO137	CO317	CO318	CO319	CO139	CO 323	CO 517		
SiO ₂	69.97	48.45	70.00	68.09	67.00	68.27	64.70	67.83	71.03	71.93		
TiO ₂	0.40	1.519	0.30	0.41	0.60	0.66	0.72	0.43	0.41	0.34		
Al_2O_3	14.99	9.32	15.37	14.51	14.85	14.00	14.68	15.40	15.25	14.78		
Fe ₂ O ₃												
FeO	2.14	15.09	1.89	2.54	3.24	3.53	3.93	2.44	2.09	1.87		
FeOt	2.14		1.89	2.54	3.24	3.53	3.93	2.44	2.09	1.87		
MnO	0.05	0.322	0.04	0.05	0.05	0.06	0.09	0.05	0.03	0.05		
MgO	0.89	11.58	0.66	1.19	1.39	1.75	2.13	1.26	0.96	0.62		
CaO	2.95	9.63	2.28	2.87	3.06	3.26	4.38	2.76	1.78	2.03		
Na ₂ O	4.70	1.82	4.38	4.06	5.31	4.30	5.12	4.09	4.02	4.04		
K ₂ O	3.77	1.99	4.25	4.14	4.28	3.97	3.99	3.77	4.06	4.23		
P_2O_5	0.14	0.280	0.13	0.17	0.24	0.22	0.26	0.14	0.14	0.11		
Total	100.00	100.00	99.30	98.03	100.03	100.01	100.00	98.17	99.77	100.00		
Al/K+Na+Ca	0.87	0.41	0.96	0.89	0.78	0.81	0.71	0.97	1.07	0.99		
La			33.0	39.1	60.0	55.7	51.8	40.2	34.4			
Ce			65.5	78.1	112.2	106.6	106.6	76.0	73.4			
Nd			33.1	32.9	51.3	35.1	48.1	28.8	28.9			
Sm			5.09	5.7	8.46	7.85	8.46	5.2	5.37			
Eu			0.83	1.0	1.28	1.35	1.50	0.9	0.95			
Tb			0.318	0.3	0.485	0.376	0.410	0.3	0.323			
Yb			0.62	0.8	1.10	1.24	1.25	0.8	0.80			
Lu			0.048	0.098	0.125	0.146	0.132	0.068	0.092			
Y			8	10				10				
Rb			160	147				141				
Sr			483	521	797	674	849	553	528			
Sr*			525	553				581				
Ba			819	801	1426	1171	1366	802	910			
Ba*			809	772				850				
Pb			23	19				21				
Cs			7.69	6.08	11.34	7.43	8.53	7.80	6.71			

 Table 4.4

 Major and trace element analyses for Incapillo domes and lava flows

	Pre-caldera	Xenolith		Incapillo Caldera Domes						
sample	CO 516	CO 512b	CO136	CO137	CO317	CO318	CO319	CO139	CO 323	CO 517
J			8.6	6.7	14.5	8.9	9.9	7.4	7.1	
Гh			16.5	16.3	26.3	21.3	22.7	15.8	17.4	
Zr			176	199				184		
Nb			11	13				11		
Hf			4.6	4.7	7.3	6.7	6.9	4.4	4.6	
Га			0.97	0.8	1.40	1.12	1.22	1.0	0.84	
Sc*			3	5				5		
se			3.0	4.5	5.4	6.6	7.1	4.9	3.6	
Cr			1	16	5	22	26	23	5	
Cr*			7	22				31		
Ni			1	5	0	0	4	8	1	
Ni*			2	6				4		
Co			3	5.2	5	7	8	5.5	4	
Co*			3	7				5		
Cu			8	11				9		
Zn –			60	70				61		
/			33	49				49		
Rb/Sr			0.33	0.28				0.25	0.00	
Ba/La			24.8	20.5	23.8	21.0	26.4	20.0	26.4	
.a/Sm			6.5	6.8	7.1	7.1	6.1	7.7	6.4	
.a/Yb			52.9	48.4	54.4	44.7	41.5	51.5	43.1	
Eu/Eu*			0.69	0.73	0.66	0.80	0.82	0.81	0.76	
Sm/Yb			8.2	7.1	7.7	6.3	6.8	6.7	6.7	
Ba/Th			50	49	54	55	60	51	52	
Ba/Ta			842	967	1015	1047	1117	767	1080	
La/Ta			34	47	43	50	42	38	41	
Гh/U			1.9	2.4	1.8	2.4	2.3	2.1	2.4	
Sr/Yh			775	645	722	542	670	708	662	

 Table 4.4 (continued)

Major and trace element analyses for Incapillo domes and lava flows

				Wester	rn (Rio Salado) I	Domes						
sample	CO184	CO314	CO316	CO 505	CO 506	CO 508	CO 509	CO 510	CO 511	CO 513		
SiO ₂	68.31	69.72	68.79	67.79	70.16	70.41	69.08	68.90	66.36	71.74		
TiO ₂	0.49	0.58	0.53	0.58	0.49	0.43	0.53	0.49	0.68	0.41		
Al_2O_3	15.62	13.93	14.35	15.29	14.34	14.83	14.95	15.22	15.65	14.25		
Fe ₂ O ₃	1.92											
FeO	0.91	3.00	2.96	3.45	2.56	2.40	2.57	2.38	3.39	2.23		
FeOt	2.64	3.00	2.96	3.45	2.56	2.40	2.57	2.38	3.39	2.23		
MnO	0.05	0.06	0.05	0.07	0.05	0.04	0.03	0.06	0.06	0.05		
MgO	1.03	1.59	1.48	1.54	1.25	1.00	1.53	1.38	2.00	0.93		
CaO	2.92	2.46	3.11	3.36	2.76	2.53	2.76	3.56	3.59	2.07		
Na ₂ O	4.70	4.76	5.39	4.06	3.87	4.05	4.31	4.19	4.27	3.78		
K ₂ O	3.22	4.47	4.18	3.65	4.33	4.21	4.04	3.66	3.78	4.42		
P_2O_5	0.13	0.16	0.20	0.20	0.19	0.11	0.20	0.17	0.24	0.12		
Total	99.12	100.72	101.05	100.00	100.00	100.00	100.00	100.00	100.00	100.00		
Al/K+Na+Ca	0.95	0.81	0.75	0.91	0.89	0.94	0.91	0.88	0.89	0.97		
La	36.2	46.9	42.1									
Ce	73.8	92.5	86.2									
Nd	30.4	26.0	38.7									
Sm	5.22	6.45	6.98									
Eu	1.13	1.08	1.13									
Tb	0.339	0.481	0.257									
Yb	0.77	0.99	1.02									
Lu	0.072	0.145	0.113									
Y	9											
Rb	131											
Sr	623	551	616									
Sr*	644											
Ва	931	888	1165									
Ba*	897											
Pb	17											
Cs	5.6	9.29	8.70									

 Table 4.4 (continued)

 Major and trace element analyses for Incapillo domes and lava flows

				Wester	rn (Rio Salado) I	Domes				
sample	CO184	CO314	CO316	CO 505	CO 506	CO 508	CO 509	CO 510	CO 511	CO 513
U	5.4	10.0	10.8							
Th	13.9	24.6	22.8							
Zr	220									
Nb	10									
Hf	5.6	5.5	6.2							
Та	0.78	1.09	1.06							
Sc*	4	0	0							
Sc	4.5	5.2	4.9							
Cr	8	16	14							
Cr*	14	0	0							
Ni	3	0	0							
Ni*	< 2	0	0							
Co	5	6	5							
Co*	4									
Cu	9									
Zn	61									
V	48									
Rb/Sr	0.21	0.00	0.00							
Ba/La	25.7	18.9	27.7							
La/Sm	6.9	7.3	6.0							
La/Yb	47.3	47.4	41.3							
Eu/Eu*	0.91	0.67	0.82							
Sm/Yb	6.8	6.5	6.8							
Ba/Th	67	36	51							
Ba/Ta	1194	813	1103							
La/Ta	46	43	40							
Th/U	2.6	2.5	2.1							
Sr/Yb	813	556	604							

 Table 4.4 (continued)

 Major and trace element analyses for Incapillo domes and lava flows

				Ol	der Oxidized D	omes			
sample	CO 322	CO140	CO 518	CO135	CO 525	CO 522	CO142	CO151	CO 157
SiO ₂	67.94	63.00	67.67	63.50	65.49	68.42	65.50	63.97	64.16
TiO ₂	0.61	0.70	0.66	0.83	0.74	0.63	0.73	0.74	0.74
Al_2O_3	15.64	16.40	15.79	16.10	15.96	15.15	16.37	16.31	16.60
Fe ₂ O ₃							2.01	3.05	2.43
FeO	3.15	3.86	3.12	3.79	3.92	3.07	1.61	1.23	1.79
FeOt	3.15	3.86	3.12	3.79	3.92	3.07	3.42	3.97	3.97
MnO	0.08	0.06	0.05	0.06	0.07	0.04	0.05	0.06	0.06
MgO	1.58	2.21	1.58	2.17	2.02	1.08	1.51	2.08	1.86
CaO	2.49	4.27	3.36	4.20	4.24	3.14	3.61	4.09	3.90
Na ₂ O	4.80	4.50	4.10	4.36	4.14	4.04	4.63	4.46	4.27
K ₂ O	3.65	3.46	3.44	3.45	3.12	4.20	3.37	3.02	3.06
P_2O_5	0.21	0.26	0.23	0.25	0.30	0.24	0.25	0.20	0.21
Total	100.14	98.72	100.00	98.71	100.00	100.00	99.44	98.90	98.83
Al/K+Na+Ca	0.95	0.87	0.95	0.87	0.89	0.90	0.92	0.91	1.27
La	47.2	41.0		45.3			44.9	41.2	47.7
Ce	97.8	81.9		98.4			93.7	84.5	78.4
Nd	33.8	40.9		40.3			33.8	33.2	43.1
Sm	6.42	5.72		7.6			5.8	5.9	6.81
Eu	1.25	1.29		1.5			1.5	1.5	1.32
Гb	0.303	0.425		0.6			0.5	0.5	0.6
Yb	1.02	0.84		1.2			0.5	0.7	1.03
Lu	0.117	0.120		0.177			0.064	0.095	0.137
Y	10	10		14			9	10	13
Rb	106.9	85		114			96	98	92
Sr	694	759		646			739	765	703
Sr*	665	810		672			723	690	670
Ва	1040	1122		875			1042	937	1120
Ba*	1031	1000		855			1070	871	1070
Pb	14.7	13		13			14	14	13
Cs	4.46	1.44		4.2			1.6	3.1	2.3

 Table 4.4 (continued)

 Major and trace element analyses for Incapillo domes and lava flows

				Ol	der Oxidized D	omes			
sample	CO 322	CO140	CO 518	CO135	CO 525	CO 522	CO142	CO151	CO 157
U	5.3	1.7		5.5			2.2	2.2	2.0
Th	14.9	8.0		15.3			11.9	8.8	7.9
Zr	164	261		283			270	253	270
Nb	12.1	12		15.5			9	11	10
Hf	5.9	5.9		7.0			6.0	5.9	4.3
Та	0.72	0.58		1.1			0.54	0.67	0.68
Sc*		8		8			5	7	7
Sc	5.4	7.4		8.1			5.2	7.5	7.7
Cr	15	43		65			24	51	33
Cr*	24	47		63			27	53	41
Ni	1	15		21			10	15	14
Ni*	4.4	12		15			4	12	8
Со	6	10		11.2			8.0	10.3	10
Co*	6	12		11			7	9	8
Cu		14		28			15	15	17
Zn		91		<i>93</i>			90	81	79
V	60	83		93			68	33	81
Rb/Sr	0.15	0.11		0.18			0.13	0.13	0.13
Ba/La	22.0	27.4		19.3			23.2	22.7	23.5
La/Sm	7.4	7.2		6.0			7.7	7.0	7.0
La/Yb	46.1	48.8		38.6			83.7	55.3	46.3
Eu/Eu*	0.91	0.90		0.82			0.99	0.96	0.74
Sm/Yb	6.3	6.8		6.5			10.9	7.9	6.6
Ba/Th	70	139		57			88	106	142
Ba/Ta	1446	1927		811			1944	1398	1646
La/Ta	66	70		42			84	61	70
Th/U	2.8	4.8		2.8			5.5	4.0	3.9
Sr/Yb	678	904		550			1377	1027	682

 Table 4.4 (continued)

Major and trace element analyses for Incapillo domes and lava flows

					Incapil	lo Ignimbrite p	oumices				
sample	CO138	CO320	CO 514	CO141	CO 325	CO 524	CO143	CO 527b	CO 527m	CO 527f	CO183
SiO ₂	69.50	70.17	69.91	67.03	69.58	71.51	69.14	70.84	67.23	71.11	69.29
TiO ₂	0.28	0.44	0.40	0.37	0.40	0.38	0.30	0.38	0.52	0.39	0.28
Al_2O_3	15.10	16.20	14.66	15.32	15.01	14.79	15.36	15.16	16.14	15.02	14.37
Fe ₂ O ₃							1.75				1.65
FeO	2.17	2.64	2.03	2.06	2.36	2.00	0.18	2.00	3.88	2.05	0.70
FeOt	2.17	2.64	2.03	2.06	2.36	2.00	1.75	2.00	3.88	2.05	2.18
MnO	0.04	0.02	0.04	0.04	0.06	0.08	0.04	0.04	0.07	0.04	0.04
MgO	0.63	0.82	0.79	0.81	0.87	0.70	0.66	0.73	1.29	0.70	0.66
CaO	2.46	2.47	4.42	2.98	2.99	2.55	2.34	2.53	3.74	2.46	2.10
Na ₂ O	4.25	4.81	3.79	4.29	4.79	4.08	4.44	4.25	3.82	4.21	4.27
K ₂ O	3.66	2.93	3.77	3.90	3.81	3.80	4.13	3.96	3.08	3.90	4.43
P_2O_5	0.13	0.19	0.18	0.16	0.15	0.11	0.15	0.13	0.21	0.12	0.15
Total	98.22	100.67	100.00	96.96	100.00	100.00	98.32	100.00	100.00	100.00	97.77
Al/K+Na+Ca	0.98	1.04	0.80	0.92	0.86	0.96	0.96	0.96	0.98	0.96	0.92
La	44.5	43.5		36.8	40.2		37.4				27.8
Ce	93.5	90.3		74.2	87.2		79.2				65.2
Nd	36.0	34.7		31.9	41.9		31.5				31.0
Sm	6.6	6.25		5.5	6.94		5.4				5.2
Eu	0.9	1.19		0.9	1.18		0.9				0.8
Tb	0.4	0.693		0.3	0.318		0.3				0.4
Yh	0.9	0.95		0.8	0.99		0.7				0.7
Iu	0.048	0.106		0.058	0.122		0.074				0.176
V	8	0.100		8	0.122		0.074				0.170
I Dh	164			142			162				180
KU Sr	104	607		545	601		505				180
51	427	607		543	001		505				4/9
Sr [*]	520	0.50		594	000		347				481
Ва	/14	879		/38	890		842				810
Ba*	618			765			786				749
Pb	11			19			20				20
Cs	10.1	8.48		6.4	8.06		7.3				7.8

 Table 4.5

 Major and trace element analyses for Incapillo ignimbritic pumices

	Incapillo Ignimbrite pumices											
sample	CO138	CO320	CO 514	CO141	CO 325	CO 524	CO143	CO 527b	CO 527m	CO 527f	CO183	
U	10.9	6.7		6.7	10.0		7.9				8.8	
Th	21.3	19.5		14.1	17.0		16.2				16.4	
Zr	170			212			214				187	
Nb	11			14			15				15	
Hf	5.2	5.6		4.8	5.9		4.8				5.0	
Та	1.1	1.01		0.8	1.05		0.8				0.9	
Sc*	3			4			3				3	
Sc	3.7	4.6		3.4	4.0		3.1				3.0	
Cr	2.5	8		4.1	3		1.8				2.6	
Cr*	11			10			6				8	
Ni	<1	1.69		2.04	0		2.35				1.55	
Ni*	8			2			<2				< 2	
Со	3.4	4		3.6	4		2.9				2.8	
Co*	2			6			4				4	
Cu	16			7			11				11	
Zn	56			70			63				65	
V	27			38			31				30	
DL/C-	0.29	0.00		0.26	0.00		0.22				0.29	
K0/Sr	0.38	0.00		0.26	0.00		0.32				0.38	
Da/La	10.0	20.2		20.0	22.2 5 0		22.3				29.2	
La/Sili La/Vh	0.7 50.6	15.6		0.7	J.0 40.9		7.0				3.4 27.2	
La/ I U	50.0	43.0		40.0	40.8		35.8				57.5	
Eu/Eu*	0.05	0.67		0.77	0.80		0.73				0.63	
Sm/YD	7.5	0.0		7.2	7.0		7.7				7.0	
Ba/In	34	45		52	52		52				49	
Ba/Ta	665	8/1		952	851		1002				8/6	
La/Ta	41	43		48	38		45				30	
Th/U	2.0	2.9		2.1	1.7		2.0				1.9	
Sr/Yb	486	636		722	610		725				644	

 Table 4.5 (continued)

Major and trace element analyses for Incapillo ignimbritic pumices

Trace elements

Trace element concentrations and ratios for Incapillo magmas are given in Tables 4.4 and 4.5. Despite their eruption up to ~ 30 km distance from the caldera, all Incapillo dome lavas and ignimbritic pumices exhibit remarkably similar trace element patterns characterized by steep REE patterns that are extreme for evolved arc lavas from the Central Andes. Like most arc lavas however, Incapillo lavas exhibit strong enrichments in the large ionic lithophile elements (LILE) that contrast with large negative high field strength element (HFSE) anomalies (Figure 4.10). Unlike the 6 Ma Jotabeche lavas, Incapillo ignimbrite pumices and domes have negative Eu anomalies (Eu/Eu^{*}) that range from 0.63-0.80 and 0.66-0.91 respectively. Also shown on Figure 4.10, the older oxidized domes (CO 142) have similar trace element patterns to the Incapillo lavas although they have lower concentrations of U and Ta, greater LREE enrichment, and more subdued Eu/Eu^{*} anomalies (0.74-0.99). In sum, Incapillo magmas are distinct from other large Neogene ignimbrites of the central Andes primarily by their strong arc signature, steep REE patterns, and adakitic Sr/Yb ratios.

The pronounced arc signature observed in Incapillo magmas is evident in their high La/Ta (30-50; Kay and Mpodozis, 2000), Ba/La (16-30), and Ba/Ta (650-1200) ratios compared to APVC, Salar de Antofalla region, or Galán ignimbrites (Figure 4.11). These elevated ratios are principally controlled by high concentrations of LILE (e.g., Ba = 700-1430 ppm) and LREE (La = 27-60 ppm) relative to the HFSE (Ta = 0.78-1.4 ppm). Exceptionally low HFSE concentrations in the older oxidized domes (Ta = 0.54-1.07 ppm) yield high La/Ta (42-84) and Ba/Ta (811-1944) ratios. As shown in Figure 4.11, these ratios are like those from other evolved lavas that erupted during the height of arc migration including the ~ 6 Ma Jotabeche rhyodacites (Ba/Ta = 1500-2000; La/Ta = 40-70; Kay et al., 1994b) and the 5-2 Ma Pircas Negras andesites (Ba/Ta = ~ 1500-2250; La/Ta = ~ 50-80; Goss et al., Chapter 2).



Figure 4.10 Chondrite-normalized (Masuda et al., 1973) spider diagrams for (A) representative Incapillo ignimbrite pumices and dome lavas and (B) ~ 6 Ma Jotabeche and 2.2 Ma Cerro Galán pumices. Jotabeche and Cerro Galán trace element data are from Tittler (1995) and Francis et al. (1989) respectively. Age for Cerro Galán is from Sparks et al. (1985). Chemical range for all Incapillo ignimbrite pumices (grey stippled) and domes (tan) are shown in B. Note: negative Lu anomalies in Incapillo and Jotabeche lavas are due to higher analytical error.



Figure 4.11 Plot of La/Ta vs. Ba/Ta for Incapillo dome lavas (Table 4.4) and ignimbritic pumices (Table 4.5). Symbols are the same as in Figure 4.8. Also plotted are ~ 6 Ma Jotabeche ignimbrites and rhyodacitic lava flows (Tittler, 1995) and 5-2 Ma Pircas Negras adakitic andesites from the Rio Salado (Goss et al., Chapter 2). Data for APVC, Cerro Galán, and southern Puna (SAF) ignimbrites are from the same sources as in Figure 4.9.

The steep REE patterns characteristic of Incapillo magmas were discussed by Kay and Mpodozis (2000) and are a ubiquitous feature of syn-migration andesites and dacites from the northern flatslab region (Kay and Mpodozis, 2002; Goss et al., Chapter 2). Figure 4.12 shows that all Incapillo domes and ignimbritic pumices have high La/Yb ratios (37-54) compared to most APVC and SAF magmas, though similarly elevated La/Yb ratios have been reported in backarc rhyolitic pumices from
the Cerro Galán and Coranzulí ignimbritic centers (see Kay et al., 1999) as well as in rhyodacitic domes from the Tres Cruces Massif in the southernmost CVZ (Mpodozis et al., 1996; Kay and Mpodozis, 2000). Even higher La/Yb ratios are reported for the \sim 6 Ma Jotabeche rhyodacitic domes and ignimbrites (\sim 50-75; Kay et al., 1994b). As with the Jotabeche lavas, the steep REE patterns in the Incapillo units are largely controlled by HREE depletion, not LREE enrichment (Figures 4.10b and 4.12b). Uniformly high Sm/Yb ratios in Incapillo lavas (\sim 6-8) are distinct from all APVC ignimbrites and trend towards the higher Sm/Yb ratios in Jotabeche (6-10) and Pircas Negras (7-9) lavas.

Lastly, elevated Sr/Yb ratios (500-850; or Sr/Y = 55-73) in all Incapillo domes and ignimbrite pumices contrast with lower ratios in ignimbrites from siliceous centers of the Puna-Altiplano plateau (~ 50-400; Figure 4.12c). These high Sr/Yb ratios are a function of *both* elevated Sr concentration (~ 500-850 ppm) and Yb depletion (< 1.25 ppm). Older oxidized domes exhibit even higher Sr/Yb ratios (550-1350) that are similar to Sr/Yb ratios in Jotabeche rhyodacites (~ 950-1850; Kay et al., 1994b) and Pircas Negras andesites (~ 850-1050; Goss et al., Chapter 2). High Sr/Yb ratios and low Yb (and Y) concentrations like these are characteristic of Archean and Proterozoic tonalite-trondhjemite-dacites (TTD) and modern adakites defined by Defant and Drummond (1990). Within the Central Andes, ignimbrites and granodiorites from the Cordillera Blanca above the Peruvian flatslab exhibit TTD-like chemical signature (Petford and Atherton, 1996) as do middle to late Miocene andesites and dacites from the Main Cordillera above the Chilean flatslab (Figure 4.1; Kay et al., 1987; 1991; Kay and Mpodozis, 2002).



Figure 4.12 Plots of (A) SiO₂ vs. La/Yb (B) Sm/Yb vs. La/Sm and (C) Yb (ppm) vs. Sr/Yb for Incapillo pumices and domes. Symbols and references are the same as in Figures 4.8-4.11.

Isotopic ratios

Sr, Nd, Pb, and O isotopic ratios for Incapillo and older oxidized dome lavas are given in Table 4.6 and shown in Figure 4.13. Isotopic data for 6-2 Ma dacitic centers that surround the Incapillo Caldera (i.e., Bonete Chico, Sierras de Veladero, and Pissis) are also presented (see Figure 4.2b and Appendix 11 for sample locations) as are new isotopic data for rhyodacitic pumices from the \sim 6 Ma Jotabeche ignimbrite and early Miocene Tilito ignimbrites from the Doña Ana formation.

Incapillo domes and ignimbrites

Incapillo rhyodacitic domes, including those ~ 30 km to the west along the upper Rio Salado basin, exhibit generally similar Sr, Nd, and Pb isotopic ratios (87 Sr/ 86 Sr = 0.70658 to 0.70669; ϵ Nd = -4.19 to -4.73; 206 Pb/ 204 Pb = 18.73 to 18.75; 207 Pb/ 204 Pb = 15.62 to 15.63; and 208 Pb/ 204 Pb = 38.77 to 38.79). One dome lava (CO 137) has especially radiogenic Pb isotope ratios (206 Pb/ 204 Pb = 18.95 and 208 Pb/ 204 Pb = 38.83) compared to the other analyzed domes. Isotopic ratios from Incapillo ignimbritic pumices are more homogeneous and overlap the fields for the Incapillo domes (87 Sr/ 86 Sr = 0.70658-0.70659; ϵ Nd = -4.31 to -4.56; 206 Pb/ 204 Pb = 18.74 to 18.75; 207 Pb/ 204 Pb = 15.63; and 208 Pb/ 204 Pb = 38.79 to 38.80). Quartz phenocrysts from a rhyodacitic Incapillo dome yield a crustal δ 18 O value of 9.12 ± 0.2. A 4.7 Ma oxidized dome from the Quebrada Veladero has a somewhat less radiogenic 87 Sr/ 86 Sr ratio (0.70639) and a similar ϵ Nd value (-4.50) compared to Incapillo dome and ignimbrite lavas.

Miocene-Pliocene centers

As shown in Figure 4.13, isotopic ratios for the 6-2 Ma dacitic arc centers are generally less enriched than those from Incapillo (87 Sr/ 86 Sr = 0.70592 to 0.70654; ϵ Nd

= -3.53 to -4.04; ²⁰⁶Pb/²⁰⁴Pb = 18.66 to 18.72; ²⁰⁷Pb/²⁰⁴Pb = 15.62; and ²⁰⁸Pb/²⁰⁴Pb = 38.73 to 38.76). However, a 2.5 Ma Bonete Chico dacitic flow (CO 147) has more radiogenic ⁸⁷Sr/⁸⁶Sr (0.70732) than any Incapillo or 6-2 Ma dacitic flow. Rhyodacitic pumices from the ~ 6 Ma Jotabeche ignimbrite exhibit lower ⁸⁷Sr/⁸⁶Sr isotopic ratios and higher ε Nd values than other late Miocene siliceous lavas in the region (⁸⁷Sr/⁸⁶Sr = 0.70539 to 0.70562; ε Nd = -2.47 to -2.55; ²⁰⁶Pb/²⁰⁴Pb = 18.68; ²⁰⁷Pb/²⁰⁴Pb = 15.62; and ²⁰⁸Pb/²⁰⁴Pb = 38.70 to 38.77). The early Miocene Tilito pumices are the least enriched all analyzed samples (⁸⁷Sr/⁸⁶Sr = 0.70539 to 0.70557; ε Nd = -0.65 to -1.42). Quartz phenocrysts from Bonete Chico dacite and Jotabeche rhyodacitic ignimbrite both have crustal δ^{18} O values of 8.93 ± 0.2 and 8.23 ± 0.2 respectively.

APVC and southern Puna ignimbrites

Isotopic data for < 10 Ma Puna ignimbrites (Kay et al., 1999 and references therein) are significantly more enriched than the Incapillo magmas (87 Sr/ 86 Sr = 0.708 to 0.717; ϵ Nd = -8.54 to -12.45; 206 Pb/ 204 Pb = 18.8 to 19.05; 207 Pb/ 204 Pb = 15.65 to 15.69; and 208 Pb/ 204 Pb = 38.7 to 39.2). Previous authors have related this isotopic signature to contamination by Precambrian basement rocks and Paleozoic juvenile and sedimentary crustal units (e.g., Macfarlane et al., 1990; Coira et al., 1993; Aitcheson et al., 1995; Tosdal, 1996; Kay et al., 1999). In contrast to the APVC or Galán ignimbrites, small to medium volume ignimbrites from the Salar de Antofalla region (Figure 4.1) have less enriched isotopic ratios that are more similar to isotopic ratios from Incapillo magmas (87 Sr/ 86 Sr = 0.706 to 0.709; ϵ Nd = -2.4 to -5.1; 206 Pb/ 204 Pb = 18.7 to 19.0; 207 Pb/ 204 Pb = 15.62 to 15.67; and 208 Pb/ 204 Pb = 38.7 to 39.0; Siebel et al., 2001).

Sr, Nd, and Pb isotopic analyses for Neogene lavas from the northern flatslab transition zone (~ 27°-28.5°)											
sample	unit	age (Ma)	⁸⁷ Sr/ ⁸⁶ Sr	% S.E.	¹⁴³ Nd/ ¹⁴⁴ Nd	% S.E.	εNd	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	$\delta^{18}O_{qz}$
	Incapillo Caldera										
CO 136	Incapillo domes (caldera)	1.1 ± 0.4	0.7066930	0.0008	0.5124143	0.0011	-4.36	-	-	-	
CO 137	Incapillo domes (caldera)	2.9 ± 0.4	0.7065835	0.0013	0.5123983	0.0010	-4.68	18.950	15.631	38.830	
CO 317	Incapillo domes (caldera)	-	0.7066530	0.0007	0.5124231	0.0008	-4.19	18.751	15.626	38.797	+9.12
CO 316	Incapillo domes (west)	-	0.7066673	0.0006	0.5123955	0.0008	-4.73	18.745	15.625	38.785	
CO 508	Incapillo domes (west)	2.55 ± 0.03	-	-	-	-	-	18.742	15.623	38.777	
CO 323	Incapillo domes (east)	1.34 ± 0.13	-	-	-	-	-	18.733	15.623	38.772	
CO 514 ⁻	Incapillo ignimbrite	0.51 ± 0.02	0.7065894	0.0009	0.5124050	0.0006	-4.55	18.742	15.627	38.792	
CO 524 ⁻	Incapillo ignimbrite	0.51 ± 0.04	-	-	0.5124170	0.0010	-4.31	18.750	15.630	38.806	
CO 141 ⁻	Incapillo ignimbrite	1.6 ± 0.5	0.7065996	0.0009	0.5124040	0.0010	-4.56	-	-	-	
CO 142	Older oxidized dome	4.6 ± 0.2	0.7063884	0.0006	0.5124071	0.0008	-4.50	-	-	-	
	6-3 Ma southernmost CVZ										
CO 37	Pissis	4.1 ± 0.4	0.7063681	0.0005	0.5124568	0.0010	-3.53	18.683	15.617	38.742	
CO 38	Pissis	6.2 ± 0.5	0.7059168	0.0010	-	-	-	-	-	-	
CO 180	Pissis	3.2 ± 0.3	0.7062093	0.0007	0.5124452	0.0009	-3.76	-	-	-	
CO 182	Pissis	4.6 ± 0.7	0.7064560	0.0006	0.5124386	0.0009	-3.89	18.658	15.616	38.734	
CO 152	Veladero	3.8 ± 0.4	0.7056832	0.0008	0.5124660	0.0009	-3.36	-	-	-	
CO 147	Bonete Chico	2.5 ± 0.4	0.7073255	0.0007	0.5123832	0.0008	-4.97	-	-	-	
CO 148	Bonete Chico	4.0 ± 0.2	0.7065223	0.0006	-	-	-	18.709	15.617	38.744	
CO 149	Bonete Chico	4.2 ± 0.3	0.7062090	0.0007	0.5124492	0.0007	-3.68	-	-	-	
CO 321	Bonete Chico	-	0.7065435	0.0008	0.5124311	0.0009	-4.04	18.719	15.617	38.759	+8.93
	Southern Maricunga Belt										
CO 311	Jotabeche ignimbrite	-	0.7056180	0.0008	0.5125074	0.0008	-2.55	18.680	15.627	38.701	
CO 423	Jotabeche ignimbrite	6.7 ± 0.4	0.7053888	0.0006	0.5125112	0.0009	-2.47	-	-	-	+8.23
	E. Miocene										
CO 265	Tilito ignimbrite	21.9 ± 0.8	0.7055679	0.0009	0.5126048	0.0008	-0.65	-	-	-	
CO 303	Tilito ignimbrite	-	0.7053913	0.0009	0.5125651	0.0009	-1.42	-	-	-	
CO 328A	Tilito ignimbrite	-	0.7055477	0.0007	0.5125964	0.0012	-0.81	-	-	-	

Table 4.6

Isotopic ratios were obtained on a VG sector thermal mass spectrometer at Cornell University and reflect measured values. Sr isotopic ratios were normalized to an ⁸⁶Sr/⁸⁸Sr ratio of 0.1194. Cornell value for ⁸⁷Sr/⁸⁶Sr for NBS 987 is 0.7102957 \pm 0.00006 (2 sigma error; n = 40 from 6/2003 to 9/2004), ¹⁴³Nd/¹⁴⁴Nd for Ames is 0.5121436 \pm 0.000028 (2 sigma error; n = 28 from 2/2004 to 5/2004); and ¹⁴³Nd/¹⁴⁴Nd for La Jolla is 0.5118496 \pm 0.000015 (n = 13 from 2/2004 to 4/2004). Epsilon Nd is based on a CHUR value of 0.512614. Error for ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd analyses are reported as percent standard error. Nd isotope ratios on Incapillo ignimbrite pumices were measured at the University of Florida using MC-ICPMS. Reported Nd standard values are JNdI = 0.512094 \pm 0.000012 and La Jolla = 0.511850 \pm 0.00001 which is within analytical error to the long-term Cornell La Jolla value. Pb isotope ratios were obtained via MC-ICPMS at the University of Florida and are relative to reported NBS Pb standard values of ²⁰⁶Pb/²⁰⁴Pb = 16.937 (+/-0.004), ²⁰⁷Pb/2⁰⁴Pb = 15.491 (+/-0.004), and ²⁰⁸Pb/²⁰⁴Pb = 36.695 (+/-0.009). Uncertainty on NBS Pb isotopic ratios is 2x standard error. Oxygen isotope data is corrected to the average measured value of the Gore Mountain garnet (UWS-21 δ^{18} O = +5.7). In-run error (2 σ) is estimated at \pm 0.2 ‰ and external precision from repeat analyses is 0.2-0.5 ‰.

(A) Plot of 87 Sr/ 86 Sr vs. ϵ Nd, (B) 206 Pb/ 204 Pb vs. 207 Pb/ 204 Pb and (C) 206 Pb/ 204 Pb vs. 208 Pb/ 204 Pb for Incapillo ignimbritic pumices and domes. Figure 4.13 Symbols are the same as in Figures 4.8-4.12. Also plotted are ~ 6 Ma Jotabeche ignimbrites and lava flows (Kay et al., 1994b; Tittler, 1995), 6-2 Ma dacitic centers (Bonete Chico, Pissis, and Veladero), 5-2 Ma Pircas Negras adakitic andesites from the upper Rio Salado (Goss et al., Chapter 2), \sim 23 Ma Tilito (Doña Ana) ignimbritic pumices, and average isotopic values of central Andean Paleozoic granitoids (Becchio et al., 1999; Lucassen et al., 2001). Mixing lines on Figure 4.13a correspond to compositional trends defined by EC-AFC modeling (Bohrson and Spera, 2001; Spera and Bohrson, 2001) with trace element compositions, mixing percentages, r-values, and thermodynamic parameters given in Tables 4.7-4.8. Letters refer to average Paleozoic crust (white; A, B, and E) and bulk upper continental crust (grey; C, D, and F) used as potential assimilants in the models. Solid mixing lines show melt compositions modeled with the amphibolite xenoliths (Fig. 6) as the fractionating assemblage, whereas dashed lines show compositions modeled with a more plagioclase-rich assemblage. End-member compositions and bulk Kd values are given in Appendices 13 and 14 respectively. The tick marks on the Pb-Pb mixing line in Figures 4.13b and 4.13c are for bulk mixing with Paleozoic crust. The shaded fields along the bulk mixing lines labeled "EC-AFC" in Figs. 4.13b and 4.13c show the range of modeled Pb isotopic values predicted by EC-AFC modeling. Grey dashed arrow is the best fit mixing line produced by a hypothetical crustal assimilant. Pb-isotopic fields for Chilean flatslab & southern CVZ and Sierras Pampeanas lavas are shown (Kay and Abbruzzi, 1996; Kay et al., 1999) and references therein). Choiyoi fields are from Moscoso et al. (1993).



IX. DISCUSSION

The Incapillo Caldera and Dome Complex is an example of a < 3 Ma Andean siliceous center that erupted during a period of waning arc magmatism following a late Miocene episode of localized tectonic disturbance. As discussed by Goss et al. (Chapter 2), this episode was characterized by rapid frontal arc migration, enhanced forearc subduction erosion, and shallowing of the subducting slab beneath the backarc. These spatial and temporal changes in tectonic setting controlled the eruptive style, volume, and geochemical evolution of Incapillo lavas that strongly contrast with the large ignimbritic megacalderas of the Central Andes associated with the inception of magmatism along the arc front and across the backarc between 11 and 4 Ma (Kay et al., 1999).

Here, we refine the eruptive sequence of the Incapillo Caldera and Dome Complex using the K-Ar and ⁴⁰Ar/³⁹Ar ages and present a comprehensive eruption model based on petrography and mapping from both litho-stratigraphy and digital imagery. Lastly, a petrogenetic model based on the geochemical characteristics of Incapillo magmas is presented and is consistent with the temporal and spatial position of Incapillo within a dying Andean magmatic arc.

Eruptive Sequence and Model

The 40 Ar/ 39 Ar data in Table 2 clearly shows that the pumice-rich Incapillo ignimbrite was ejected in the final eruptive event associated with the Incapillo magmatic system at ~ 0.51 Ma. The Incapillo eruptive sequence is divided into the following three stages shown in Figure 4.14: (1) an initial period of regional effusive eruptions of rhyodacitic domes; (2) an episode of intense boiling-over pyroclastic eruptions followed by caldera collapse; and (3) a terminal period of post-eruptive localized debris flows and resurgent dome eruptions.



Figure 4.14 Three stage eruptive model for the formation of the Incapillo Caldera and Dome Complex. *Stage one* (3-1 Ma) is characterized by effusive eruption of compositionally homogeneous rhyodacitic domes. *Stage 2* $(0.51 \pm 0.2 \text{ Ma})$ represents the pyroclastic eruption of the Incapillo magma chamber contemporaneous with caldera subsidence and deposition of the Incapillo ignimbrite. *Stage 3* (< 0.51 Ma) is characterized by a resurgence of residual dome material, deposition of the Veladero debris flow, and erosional widening of the caldera.

Stage 1- Effusive dome eruptions

Siliceous magmatism associated with the Incapillo complex began at ~ 3 Ma with the effusive eruption of steep-sided domes and coulées along the slopes of Bonete Chico and the Sierras de Veladero and persisted until after the pyroclastic eruption that formed the Incapillo caldera. The chemical and petrographic similarity of the domes (Figures 4.11-4.13) irrespective of their distance from the Incapillo caldera suggests that they were generated in a common magma chamber either directly below the caldera or as multiple shallow-chambers fed by a larger and deeper primary chamber. This gas-poor viscous rhyodacitic magma likely migrated to the surface laterally via now-obscured northwest and northeast trending faults that parallel larger regional structural features like the Valle Ancho and Laguna Verde faults to the north (Figure 4.1; Mpodozis et al., 1997) or through a preexisting network of magma conduits formed during the older eruptions of Veladero and Bonete Chico. Similarly, Baldwin and Marrett (2004) proposed that the emplacement of non-explosive dacitic domes within the Cordillera de San Buenaventura (27° S; Figure 4.1) was controlled by the opening of a releasing bend between regional-scale strike-slip faults.

With regard to eruption dynamics of these early domes, degassing and lava extrusion occurred contemporaneously via gas-permeable conduits that resulted in the characteristic pit craters and lava spines observed on the summits of the largest domes (Figure 4.5b and c). Eichelberger et al. (1986) modeled similar tephra-filled "vent funnels" within the Mono-Inyo domes (California, USA) as a means to rapidly devolatilize and effusively erupt a highly siliceous magma. The initial "open-system" ash layer reported for Mono-Inyo domes and observed at Cerro Chao and Tocopuri at $\sim 22^{\circ}$ S in the Central Andes (de Silva et al., 1994) is not apparent at the base of the Incapillo domes. Instead, the Incapillo domes directly overlay andesitic Pircas Negras and dacitic Veladero and Bonete Chico lavas flows. This observation is further

evidence for the purely non-explosive initial magmatic stage of the Incapillo Caldera and Dome Complex.

Stage 2 – *Pyroclastic eruption and edifice collapse*

The Incapillo ignimbrite was deposited during the $\sim 0.51 \pm 0.02$ Ma pyroclastic eruption that formed the Incapillo caldera and ended the ~ 2 m.y. period of effusive Incapillo volcanism. Exposed along the north wall of the caldera (Figure 4.3a), the 0.87 ± 0.03 Ma rhyodacitic lava flow provides evidence for the existence of a dome or volcanic center at the location of the Incapillo caldera before the explosive eruption. Given the general lack of lithics in the Incapillo ignimbrite, this pre-caldera edifice must have been small and may have been morphologically similar to the < 3 Ma Incapillo domes that surround the caldera. Proximal finely-laminated deposits at the base of the ignimbrite indicate that the initial blast generated a basal surge that was immediately followed by a series of pumice-rich pyroclastic flows. The Incapillo ignimbrite shares many of the physical characteristics of high-grade peralkaline ignimbrites (Freundt, 1998) that have thickness of 10-30 m, volumes of \sim 5-20 km³, extend \sim 10-40 km from calderas 3-10 km in diameter, and generally lack air fall deposits (Schmincke, 1974; Mahood, 1984). These type of ignimbrites are thought to originate within extensional tectonic settings from caldera subsidence-related pyroclastic eruptions that could not support high Plinian eruption columns. Like these ignimbrites, the lack of associated ash fall deposits covering the 6-2 Ma dacitic centers or any of the < 3 Ma Incapillo domes suggests that the explosive ~ 0.51 Ma Incapillo eruption produced a "boiling over cauldron" series of pyroclastic flows (e.g., Freundt, 1999) rather than a Plinian cloud that reached stratospheric altitudes (> 10 km). Ground-hugging pyroclastic flows traveled around these older centers via topographic lows and built-up the ignimbrite to > 200 m thick

around the central vent. This eruption model is consistent with the presence of faultbounded grabens to the north (Figure 4.2; Mpodozis et al., 1997) that suggest Incapillo may have erupted within a localized extensional setting.

The virtually identical trace element and isotopic characteristics between the ignimbrite pumices and 3-1 Ma dome lavas strongly suggest that all Incapillo eruptive units originated from the same source. The reasons as to why the Incapillo magma chamber suddenly exploded at ~ 0.51 Ma rather than forming another non-explosive dome may lie in the basal pumice rafts at the distal end of the ignimbrite. These earliest and most energetic pyroclastic flows reflect the physical condition of the magma at the start of the eruption. The clear mixing textures evident in the distal pumice rafts suggest that the explosive eruption that generated the Incapillo ignimbrite was likely catalyzed by the mixing of a rhyodacitic magma like the dome lavas (SiO_2) = 67 %; FeO = 3.88 %) with a crystal-rich rhyolitic cap (SiO₂ = 71.11 %; FeO = 2.05 %) (Figure 4.4f; Table 4.5). Intrusion of a hotter more-basic magma into the base of a cooling partially-crystalline acidic magma chamber would lead to vigorous thermal convection and super-saturation of volatiles that may ultimately trigger an explosive eruption (Sparks et al., 1977; Folch and Marti, 1998). Alternatively, contractive closure (e.g., McNulty et al., 1998; Schmitt, 2001) of the magmatic conduits that permitted effusive eruption and passive degassing of Incapillo dome lava could also potentially explain the change to explosive volcanism. However, this model cannot explain the clear mixing textures evident in the pumices nor does evidence exist to support a post-1 Ma change to a more-compressive tectonic regime.

Caldera collapse probably occurred during the terminal stages of the pyroclastic eruption exposing the pre-caldera dacite and the 200 m thick ignimbritic outflow units that now comprise the walls of the caldera. Though no clear ring-faults are exposed within the interior of the caldera, its symmetrical shape, uniform depth,

and steeply sloped walls suggest a "plate-type" (or piston) subsidence mechanism as defined by Lipman (1997). The ring fault associated with caldera subsidence has been eroded back into a collapse collar by mass wasting induced scarp-retreat and by intracaldera fill burial.

Stage 3-Post-eruptive debris flows and dome resurgence

The third and final eruptive stage of the Incapillo Caldera and Dome Complex (Figure 4.14) is marked by deposition of the Veladero debris flow and eruption of resurgent domes. The geographical extent of the debris flow is enigmatic as it is only found within the Quebrada de Veladero south of the caldera. Moderate matrix cementation of the deposit with clay-sized ash ($< 5 \mu m$) suggests the involvement of water and transport of the debris flow as a fluidized slurry (e.g., Rodine and Johnson, 1976). The source of this water is unknown but could have originated by melting of a Pleistocene glacial cap or from a paleo-crater lake. The non-conformable contact between the Incapillo ignimbrite and Veladero debris flow (Figure 4.4a and b) indicates this depositional event likely occurred after the pyroclastic eruption terminated.

Continued resurgent dome activity within the Incapillo caldera followed the ~ 0.51 Ma pyroclastic eruption. As no radiometric ages exist for the resurgent domes, the lag time between caldera collapse and the final dome eruption is unknown. Given that no post-ignimbrite domes exist outside of the caldera walls, these magmas may only have ascended to the surface via the main explosive conduit that expulsed the Incapillo ignimbrite. The potentially elevated temperatures of the Incapillo crater lake waters (Markham and Barker, 1986) may indicate the presence of an active hydrothermal system below Incapillo. These observations preclude its classification as an extinct Andean volcanic center.

Sources of Incapillo Magmas

The strong geochemical differences between Incapillo and the larger APVC and Galán ignimbritic calderas support a fundamentally different model for Incapillo petrogenesis with regard to source composition and depth of magma equilibration. Central to this model is the initial generation of a high-pressure "adakitic" melt of mafic crust, derived from anatexis of either underplated lower-crustal basalt by ponded mantle-derived basalts or mafic forearc crust transported to mantle depths via forearc subduction erosion. Unlike the APVC or Galán ignimbrites, which represent melts of sialic radiogenic crust that mixed with mantle-derived basalt (e.g., Francis et al., 1989; Ort, 1993; Kay et al., 1999; Lindsay et al., 2001), Incapillo domes and ignimbrites originated from melting of hydrous mafic crust in equilibrium with a plagioclase-poor garnet-bearing residue.

The high-pressure origin of the Incapillo magmas is evidenced by their anomalously steep REE patterns (i.e., La/Yb > 30), in particular the strong depletion in the HREE (Sm/Yb > 5), relative to flatter patterns in APVC and southernmost Puna siliceous magmas (Figures 4.10 and 4.12a and b). These steep REE patterns are broadly similar to those of the Archean tonalite-trondjhemite-dacite suite (TTDs; Martin, 1987; Drummond and Defant, 1990; Martin, 1999). Though accessory phases such as xenotime can significantly fractionate the HREE from co-existing silicate melts (e.g., Miller and Mittlefehldt, 1982; Gromet and Silver, 1983; Bea, 1996), the strong HREE depletion seen in 8-2 Ma northern flatslab transition zone mafic and siliceous magmas has mainly been attributed to garnet in a high-pressure residual assemblage (Kay et al., 1994b; Mpodozis et al., 1995; Kay et al., 1999; Kay and Mpodozis, 2000; Goss et al., Chapter 2). Furthermore, the very high Na₂O contents, low Al/CNK ratios, high Sr concentrations (> 450-800 ppm), and elevated Sr/Yb ratios in Incapillo magmas compared to other central Andean ignimbrites indicate the lack of plagioclase as a major residual or early phenocrystic phase. Plagioclase is readily suppressed in hydrous andesitic and tonalitic melts at pressures in excess of 1.5 GPa (Huang and Wyllie, 1986; Moore and Carmichael, 1998). These chemical signatures are consistent with experimental data that suggest Na-rich adakitic granitoids as well as their Archean TTD analogues can be produced by 20-40 % partial melting of hydrous olivine-normative metabasalt at 1050-1100 °C and 1.2-3.2 GPa in equilibrium with eclogitic and/or garnet granulitic residues (Sen and Dunn, 1994; Rapp and Watson, 1995). Elsewhere in the central Andes, strong HREE depletion and elevated Sr and Na₂O contents in middle to late Miocene Volcán Copiapó and Jotabeche dacites from the southern Maricunga Belt (Kay et al., 1994b; Mpodozis et al., 1995), middle Miocene Cerro de las Tórtolas dacites from the Chilean flatslab region (Kay et al., 1987; 1991; Kay and Mpodozis, 2002), and granites and rhyolites from the Cordillera Blanca batholith in Peru (8°-10° S, Figure 4.1; Atherton and Petford, 1993; Petford and Atherton, 1996) have been similarly attributed to melt equilibration with residual garnet in the absence of plagioclase.

Two potential petrogenetic models to produce the Incapillo evolved lavas are evaluated with respect to the geochemical data: (1) low degree partial melting of eclogitic or amphibolitic mafic lower crust and (2) assimilation and fractional crystallization (AFC) of sialic upper crust into a parental Pircas Negras adakitic magma.

Partial melting of lower crust

The possibility that Incapillo lavas may have originated solely from an uncontaminated low-degree partial melt of *in situ* mafic crust at depths > 45 km is supported by previous trace element modeling by Petford and Atherton (1996) on compositionally similar Cordillera Blanca (Peru) tonalitic ignimbrites and granitoids.

Like the Incapillo magmas, these siliceous magmas have steep REE patterns (La/Yb = 34-60; Sm/Yb = 7.6-9.0), high Sr (< 600 ppm), and elevated Na-contents (3.0-5.5 wt %) and are modeled by these authors as 35 % batch melts of a lower crustal garnet amphibolite with a basaltic composition. Furthermore, ~ 2.5 Ma Incapillo domes from the upper Rio Salado directly overlay 3-2 Ma Pircas Negras adakitic dacites that have been explained by Goss et al. (Chapter 2) as partial melts of *in situ* garnet-bearing mafic lower crust. The tectonic changes occurring between 7-3 Ma may have led to cooler mantle conditions that facilitated a lower degree of lower crustal partial melting immediately before the regional termination of magmatism at ~ 0.5 Ma. In light of these thermal changes, Incapillo magmas could have formed as an *even lower* degree partial melt of the same garnet-bearing lower crustal source as the 3-2 Ma Pircas Negras.

A number of factors however preclude lower crustal melting as the *only* mechanism responsible for generating Incapillo magmas. First, a smaller percentage of partial melting of the same plagioclase-poor eclogitic lower crust modeled for the 3-2 Ma Pircas Negras andesites would produce siliceous melts with even *steeper* REE patterns, *higher* Sr and Ba concentrations, and negligible Eu/Eu* anomalies. These geochemical characteristics are seen in ~ 6 Ma Jotabeche and 6-5 Ma Vacas Heladas rhyodacitic ignimbrites (Figure 4.1) that have been explained as low degree partial melts of mafic lower crust (Kay et al., 1991; 1994b; Mpodozis et al., 1995; Kay and Mpodozis, 2002). However, they are opposite the observed trends from Incapillo magmas that have flatter REE patterns, lower Sr and Ba concentrations, and prominently negative Eu/Eu* anomalies compared to older Pircas Negras andesites and 5-2 Ma oxidized domes. The shift toward more enriched Sr, Nd, and particularly Pb isotopic values compared to late Miocene dacites signify some degree of assimilation of isotopically enriched crust. Lastly, the presence of quartz phenocrysts

in Incapillo dome rhyodacites with $\delta^{18}O = 8.9-9.1$ ‰ indicates assimilation of upper crustal material that once interacted with low temperature meteoric waters. This claim is based on the fact that $\delta^{18}O$ values in quartz > 7.5 ‰ cannot be attained solely by mineral fractionation from a mantle-derived magma (Taylor and Sheppard, 1986). We conclude that although Incapillo precursor magmas initially equilibrated at lower crustal depths, geochemical considerations strongly suggest that shallow-level processes, such as fractional crystallization and upper crustal assimilation, later modified the trace element and isotopic nature of these magmas.

Assimilation and fractional crystallization (AFC)

Mixing of fractionated Pircas Negras adakitic andesite with anatectic melts of older sialic upper crust is an attractive and plausible mechanism to form the Incapillo rhyodacites based on a number of qualitative arguments. First, a suite of Pircas Negras andesites erupted just to the south and west of the Incapillo center (Goss et al., Chapter 2) and are capped by Incapillo domes and ignimbrites. Second, the main pulse of Pircas Negras volcanism terminated at ~ 2 Ma just as volcanic activity at Incapillo commenced. With respect to the crustal assimilant, the presence of Carboniferous sediments and granites/rhyolites of the Paganzo Group exposed in the vicinity of Incapillo (Guerrero et al., 1993; Mpodozis et al., 1997; Rubiolo et al., 2002) supports the presence of a radiogenic Paleozoic basement directly below the northern flatslab transition zone. Moreover, all analyzed lavas from the northern flatslab transition zone including Incapillo units fall within Pb isotopic fields defined for central Andean Paleozoic basement (Macfarlane et al., 1990). This strongly supports the existence of a regional Paleozoic basement and the involvement of this basement in the genesis of Incapillo magmas.

In addition to crustal contamination, various lines of evidence support an important role for fractional crystallization in the genesis of Incapillo magmas. Trace element characteristics, namely the lower Sr concentrations and negative Eu/Eu* anomalies compared to late Miocene dacites, are strong indicators of shallow-level (< 30 km) plagioclase fractionation. The biotite-bearing amphibolite xenoliths with clear magmatic textures hosted in Incapillo dome lavas (Figure 4.6) most likely formed as mineral cumulates that fractionated from precursor magmas. Interstitial plagioclase and secondary growth of biotite within the amphiboles are best explained as an amphibole-dominated cumulitic mush was entrained by rising melt and rapidly crystallized at shallower depths within the upper crust. Compositionally, the pargasitic amphiboles present in the xenoliths (Mg #s 0.61-0.71; Appendix 12) are similar to amphiboles that dominate the mineral assemblage of the Pircas Negras adakitic andesites (Mg # 0.62-0.80; Goss et al., Chapter 2). This observation, combined with the more extreme adakitic signature in the Pircas Negras andesites compared to the Incapillo rhyodacites, suggests these lavas may be genetically related through fractionation processes.

Energy-Constrained Assimilation-Fractional Crystallization (EC-AFC) modeling

To test the hypothesis that Incapillo lavas are related to adakitic Pircas Negras andesites through AFC processes, <u>Energy-Constrained Assimilation Fractional</u> <u>Crystallization modeling calculations (EC-AFC; Bohrson and Spera, 2001; Spera and Bohrson, 2001) were performed with the results shown in Figure 4.13 and Tables 4.7-4.8. This quantitative model based on the classic DePaolo (1981) AFC equations, balances mass and heat while tracking compositional changes in the hybrid magmas caused by simultaneous crystal fractionation and addition of anatectic melt generated by wall rock assimilation. It has long been understood that for evolved magmatic</u>

systems, fractional crystallization and assimilation are not decoupled processes with regard to heat-balance and that the latent heat of crystallization released by fractionating phases largely contributes to the heat flux required for crustal anatexis. (Bowen, 1928; Taylor, 1980; DePaolo, 1981). The compositional heterogeneity in evolved Central Andean lavas has been shown to be the result of combined assimilation and fractional crystallization processes (e.g., DePaolo, 1981; Aitcheson and Forrest, 1994; Caffe et al., 2002). Simple bulk-mixing models that ignore the thermal and compositional effect of fractional crystallization are not thermodynamically sound (DePaolo, 1981; Spera and Bohrson, 2001) and thus were not considered in petrogenetic modeling of Incapillo magmas.

For the EC-AFC models, Sr and Nd isotopic ratios of the Incapillo magmas were best matched by mixing an intermediate source magma with a sialic assimilant and then evaluated by comparing the trace elements of the mixed product with average Incapillo compositions. Endmember compositions used in the models are given in Appendix 13. The initial precursor magma is $a \sim 4$ Ma Pircas Negras and esite from the upper Rio Salado (sample CO 309; 87 Sr/ 86 Sr = 0.705564, ϵ Nd = -2.6, 206 Pb/ 204 Pb = 18.63, ${}^{207}\text{Pb}/{}^{204}\text{Pb} = 15.61$; ${}^{208}\text{Pb}/{}^{204}\text{Pb} = 38.60$; Goss et al., Chapter 2). Both central Andean Paleozoic crust and average bulk upper crust were considered as crustal assimilants. Paleozoic upper crust was modeled using the average of late Paleozoic granitoids from northern Chile (${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.732064$, $\epsilon \text{Nd} = -8.72$, ${}^{206}\text{Pb}/{}^{204}\text{Pb} =$ 18.95, ${}^{207}Pb/{}^{204}Pb = 15.69$; ${}^{208}Pb/{}^{204}Pb = 38.90$; Lucassen et al., 2001) that are chemically similar to Paleozoic units in northwest Argentina (Becchio et al., 1999; Coira et al., 1999). Also considered were more enriched ENd values (-11.45) and ⁸⁷Sr/⁸⁶Sr ratios (0.744177) reported for southern Puna Paleozoic metamorphic rocks (Becchio et al., 1999). Trace element concentrations for average upper crust are from Rudnick and Fountain (1995) with isotopic ratios from average Paleozoic.

Initial thermal and chemcial parameters for EC-AFC modeling calculations									
EC-AFC									
	[A]	[B]	[C]	[D]	[E]	[F]			
Parent	PN (309)								
Assimilant	PzG	PzG-EP	UC	UC	PzG-EP	UC			
Frac. Assemblage (f)	xeno	xeno	xeno	xeno	pl-xeno	pl-xeno			
Ta ^o (^o C)	600	600	300	600	600	600			
F (remaining liquid)	0.62	0.67	0.60	0.69	0.69	0.71			
$r (M_a^*/M_c)$	0.81	0.67	0.40	0.63	0.63	0.58			
⁸⁷ Sr/ ⁸⁶ Sr parent	0.70556	0.70556	0.70556	0.70556	0.70556	0.70556			
Sr parent (ppm)	899	899	899	899	899	899			
⁸⁷ Sr/ ⁸⁶ Sr assimilant	0.73206	0.74418	0.73206	0.73206	0.74418	0.73206			
Sr assimilant (ppm)	189	189	350	350	189	350			
εNd parent	-2.6	-2.6	-2.6	-2.6	-2.6	-2.6			
Nd parent (ppm)	38.2	38.2	38.2	38.2	38.2	38.2			
εNd assimilant	-8.7	-11.5	-8.7	-8.7	-11.5	-8.7			
Nd assimilant (ppm)	20.1	20.1	26	26	20.1	26			
²⁰⁶ Pb/ ²⁰⁴ Pb parent	18.63	18.63	18.63	18.63	18.63	18.63			
Pb parent (ppm)	10.5	10.5	10.5	10.5	10.5	10.5			
²⁰⁶ Pb/ ²⁰⁴ Pb assimilant	18.95	18.95	18.95	18.95	18.95	18.95			
Pb assimilant (ppm)	16	16	20	20	16	20			

Table 4.7

Endmember concentration data for EC-AFC models are given in Appendix 13. Parental magma compositions are for a ~ 4 Ma Pircas Negras andesite from the upper Rio Salado (CO 309; Goss et al., Chapter 2) that largely reflects uncontaminated melt of mafic lower crust. Crustal assimilants used in the models include average central Andean Paleozoic granitoids (PzG; models A, B, and E; Becchio et al., 1999; Lucassen et al., 2001; 2002) and average bulk upper crust (UC; models C, D, and F; Rudnick and Fountain, 1995). Average bulk upper crust trace elements are paired with isotopic values from average central Andean Paleozoic granitoids. More enriched Paleozoic Sr and Nd isotopic values are from a ~ 500 Ma orthogneiss from El Peñon in the southern Puna (PzG-EP; Becchio et al., 1999). All crustal assimilant Pb isotopic values are from Lucassen et al. (2002). Thermodynamic conditions for EC-AFC models are: Temperature of the melt liquidus (Tlm = 1050 °C); initial melt (Tm° = 1050 °C), assimilant liquidus (Tla= 900 °C), initial assimilant (Ta° = 600 °C), and assimilant solidus (Ts= 750 °C). Model [C] uses Ta° = 300 °C to replicate cold upper crust. F = fraction of liquid remaining after fractional crystallization and addition of anatectic upper crustal melt. r(Ma*/Mc) = ratio of mass of anatectic melt to mass of fractionated cumulates (DePaolo, 1981). Bulk partition coefficients for fractionating mineral assemblage (f) are given in Appendix 14 and are from (1) the modal abundances in the biotite-bearing amphibolite xenoliths (xeno; models A-D; shown in Figure 4.6) and (2) from a similar shallow-level hypothetical assemblage with greater abundance of plagioclase $(\sim 40 \%; \text{ models E-F}).$

Trace element results for EC-AFC chemical models of Incapillo magmas									
	EC-AFC								
				[A]	[B]	[C]	[D]	[E]	[F]
			f	xeno	xeno	xeno	xeno	pl-xeno	pl-xeno
	Incapillo	magmas	A	PzG	PzG-EP	UC	UC	PzG-EP	UC
	Ignimbrite	Domes	F	0.62	0.67	0.60	0.69	0.69	0.71
	<i>n</i> =6	n=10	r	0.81	0.67	0.40	0.63	0.63	0.58
Sr	527 ± 70	620 ± 121		741	793	864	826	638	673
Rb	162 ± 16	144 ± 12		93	88	84	81	86	79
Pb	17.5 ± 4.1	20 ± 2.6		16.2	15.5	16.8	16.6	15.1	16.1
Ba	812 ± 72	1027 ± 235		1017	1055	1149	1065	1068	1078
La	38.4 ± 6.1	43.9 ± 9.3		46.7	47.1	50.8	47.7	47.5	47.7
Nd	34.5 ± 4.0	35.3 ± 8.4		36.9	38.8	39.3	40.1	41.9	42.8
Sm	$6.00 \hspace{0.1in} \pm \hspace{0.1in} 0.73$	6.58 ± 1.6		5.9	6.3	5.7	6.3	7.2	7.1
Eu	$0.98 \hspace{0.2cm} \pm \hspace{0.2cm} 0.16$	1.14 ± 0.24		1.19	1.24	1.14	1.22	1.36	1.34
Yb	0.84 ± 0.12	0.94 ± 0.21		1.28	1.18	1.03	1.10	1.25	1.17
Hf	5.2 ± 0.5	5.6 ± 1.1		5.8	6.0	6.6	6.1	6.2	6.3
Та	0.94 ± 0.12	1.04 ± 0.19		1.04	1.04	1.54	1.61	1.07	1.58
Th	17.4 ± 2.5	19.8 ± 4.3		11.4	11.1	10.2	10.2	10.9	9.9
Ba/Ta	869 ± 115	994 ± 143		980	1012	746	661	1003	682
La/Ta	$40.8 \hspace{0.2cm} \pm \hspace{0.2cm} 6.0$	$42.5 \hspace{0.2cm} \pm \hspace{0.2cm} 4.6$		45.0	45.2	33.0	29.6	44.6	30.2
La/Yb	46.1 ± 6.2	47.2 ± 4.6		36.5	39.9	49.3	43.4	38.0	40.8
Sm/Yb	7.2 ± 0.41	7.0 ± 0.6		4.6	5.4	5.5	5.7	5.8	6.0
Sr/Yb	637 ± 87	$670 \hspace{0.1in} \pm \hspace{0.1in} 88$		579	672	839	751	510	575
⁸⁷ Sr/ ⁸⁶ Sr	0.7066 to	o 0.7067	(0.70668	0.70664	0.70669	0.70673	0.70667	0.70674
ε _{Nd}	-4.19 t	o -4.73		-4.34	-4.76	-4.01	-4.13	-4.54	-3.95
²⁰⁶ Pb/ ²⁰⁴ Pb	18.73 to	o 18.75		18.77	18.75	18.75	18.75	18.74	18.75

Ta	ble	e 4	.8
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Models A-F correspond to EC-AFC models in presented in Table 4.7. The average trace element abundances and range of isotopic values in Incapillo dome and ignimbrite rhyodacites are given in the first two columns for comparison with modeled results. Error values are 1σ standard deviations.

Thermodynamic parameters used in our models are similar to those used by Bohrson and Spera (2001) with the exception of a lower magma liquidus temperature ($T^{o}_{L} = 1050 \text{ °C}$) to account for the andesitic, rather than basaltic ($T^{o}_{L} (B+S) = 1280 \text{ °C}$), initial magma composition. This liquidus temperature is consistent with (1) calculated pre-eruptive temperatures for a compositionally-similar Pircas Negras andesite based on two pyroxene phase equilibria (1050-1090 °C; Goss et al., Chapter 2), (2) MELTSmodeled (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) two pyroxene saturation temperatures for various Pircas Negras andesite compositions with 7 wt % H₂O at 5 kb (1060-1070 °C; Goss et al., Chapter 2), and (3) the upper thermal stability limit of pargasitic amphibole in equilibrium with andesite during hydrous fractional crystallization experiments of Mt. Shasta basaltic andesite (1065 °C; Grove et al., 2003). Both cold ($T_a^{\circ} = 300$ °C, *standard upper crustal case*) and hot (T_a° 600 °C; *case with crustal heating due to magma underplating*) ambient upper crustal temperatures were modeled. Hotter temperatures are justified by the presence of sustained arc volcanism in the Incapillo region since 6 Ma. Bulk trace element partition coefficients (Kd) for the fractionating mineral assemblage in the model are presented in Appendix 14 and were calculated from the mineral proportions in the biotite-bearing amphibolite xenoliths. Also given are bulk Kd's for assimilated wall rock that reflect modal proportions estimated from a least squares mineral fit of sialic endmember compositions and are broadly similar to the normative mineralogy of the upper continental crust in Taylor and McLennan (1985).

The results for the EC-AFC modeling calculations are shown graphically in Figure 4.13a and numerically in Table 4.8. Assimilation of average Paleozoic granitoids (Lucassen et al., 2001; Lucassen et al., 2002) and bulk upper continental crust (Rudnick and Fountain, 1995) into a fractionated Pircas Negras andesite can reproduce the isotopic and trace element trends in the Incapillo lavas. The best fit to the Sr, Nd, and ²⁰⁶Pb isotopic data is attained using the hotter ambient upper crustal temperatures at r-values ($r = M_{anatectic melt}/M_{cumulates}$) of 0.81 and 0.63 for Paleozoic and average upper crust respectively. These models (A and D) generate melts with trace element concentrations within the ranges measured in Incapillo ignimbrites (Pb = ~ 16; Ba = ~ 1017-1065; La = 47-48; Nd = 37-40; Sm = ~ 6; Yb = 1.1-1.3; Hf~ 6, all in ppm). Using the more enriched isotopic values for southern Puna Paleozoic crust (model B; Becchio et al., 1999), similar results are obtained with less addition of anatectic melt (r = 0.67). Modeled Sr concentrations (741-826 ppm) are

high for Incapillo lavas (450-740 ppm), but are improved by increasing the abundance of plagioclase in the fractionating assemblage to 40 % (638-673 ppm; models E-F), consistent with mineral fractionation at shallower depths or lower water contents. Trace element ratios in modeled magmas (i.e., Ba/Ta, La/Ta, La/Yb, and Sr/Yb) are less extreme than in the Pircas Negras precursor melt and generally agree with ratios from the Incapillo dacites (Table 4.8). Modeled assimilation of a colder upper crust (Ta^o = 300 °C; model C) yields hybrid magmas with similar trace element and isotopic concentrations with a significantly smaller component of assimilated melt (r = 0.40).

Though EC-AFC models replicate the trace element and isotopic characteristics of Incapillo magmas, they uniformly under-predict concentrations of Rb and Th regardless of the fractionating assemblage, crustal endmember, or initial thermal conditions. A potential explanation is that Incapillo melts rising through the uppermost crust assimilated Permo-Triassic Choiyoi granite-rhyolite (shown on map in Figure 4.2) with high concentrations of these elements (Rb = 160-185 ppm, Th =14-18; Mpodozis and Kay, 1992). Late-stage assimilation of Choiyoi crust into the evolving Incapillo magma chamber could also explain the deviation of Incapillo Pb isotopes from the Pb-Pb mixing line towards lower ²⁰⁷Pb/²⁰⁴Pb and higher ²⁰⁸Pb/²⁰⁴Pb (Figure 4.13b and c). Goss et al. (Chapter 2) explained similar Pb isotopic trends in Quaternary CVZ mantle-derived basalts and 7-3 Ma Pircas Negras andesites by buffering of mantle Pb with non-radiogenic Pb from in situ Choiyoi crustal basement $(^{206}\text{Pb}/^{204}\text{Pb} < 18.6; ^{207}\text{Pb}/^{204}\text{Pb} < 15.61; \text{ and } ^{208}\text{Pb}/^{204}\text{Pb} < 39.0; \text{ Moscoso et al., } 1993).$ Alternatively, these trends can be attributed to the large isotopic heterogeneity in central Andean Paleozoic Pb (206 Pb/ 204 Pb = 18-24; 207 Pb/ 204 Pb = 15.6-16.0; 208 Pb/ 204 Pb = 38-43; Lucassen et al., 1999; 2001). Based on these models, a hypothetical mixing line from the Pircas Negras andesite towards the more evolved 6-2 Ma dacitic centers and 3-0.5 Ma Incapillo rhyodacites predicts a radiogenic crustal endmember that (1)

falls within the isotopically heterogeneous Paleozoic field and (2) is consistent with other late Miocene to recent lavas from the flatslab and southern CVZ regions (Kay and Abbruzzi, 1996; Kay et al., 1999).

In sum, our multi-stage model for the genesis of Incapillo ignimbritic and dome lavas begins with an adakitic Pircas Negras andesite derived by melting of mafic *in situ* lower crust or eroded forearc crust in equilibrium with garnet-amphibolitic or eclogitic residues (Goss et al., Chapter 2). As predicted by the EC-AFC modeling, these melts evolved within the upper crust (10-30 km depth) towards more silicic compositions due to the combined effects of low-P fractional crystallization and assimilation of sialic Paleozoic crust. This model is distinct from the large-scale crustal melting models proposed for the APVC and Galán ignimbrites (de Silva, 1989a; Francis et al., 1989; Lindsay et al., 2001) and is similar to that proposed for the small to medium volume ignimbrites of the southernmost Puna (25-26.5° S) that have been modeled as fractionated melts of contaminated mantle-derived arc magmas (Siebel et al., 2001; Schnurr et al., 2007).

Relationship to Tectonic Instability - Witness to the death of an active Andean arc

The Incapillo Caldera and Dome Complex, with its young volcanism and potentially present hydrothermal system, exists as the last remaining evidence to a once active Andean volcanic arc in this region. Compared to other ignimbritic calderas from the central Andes, its distinctive geochemical composition and small size are the direct result of its spatial and temporal position at the end of a 7-3 Ma period of arc instability.

Geochemical indicators support an ephemeral hydration of the back-arc mantle wedge during the peak of late Miocene tectonic instability. This claim is based on the unusually high Ba/Ta and La/Ta ratios in syn-migration (7-3 Ma) and esitic and dacitic lavas from the flatslab and southernmost Puna compared to lower ratios in early to middle Miocene lavas (Kay et al., 1987; 1991; Kay and Mpodozis, 2002; Goss et al., Chapter 2). Barium, along with other fluid-mobile large ionic lithophile elements, is thought to be efficiently transported to the mantle wedge via slab-derived fluids whereas tantalum, a non-fluid mobile high-field strength element, is retained by the slab and/or is compatible in oxide phases such as rutile or titanite stable in hydrous oxidized crust. High Ba/Ta and La/Ta ratios are therefore indicative of a strong arc signature and have been interpreted as evidence for increased slab fluid concentrations in Andean arc magmas at times of shallow subduction and arc migration (e.g., Kay et al., 1991; Kay and Mpodozis, 2002; Kay et al., 2006).

The geochemical characteristics of the Incapillo dome rhyodacites show that by 3 Ma, the unusually strong slab signature characteristic of late Miocene dacites had been greatly subdued either by a reduction in slab derived fluids delivered to the sub-arc mantle or through dilution as precursor magmas assimilated upper crust. The EC-AFC models that reproduce the lower Ba/Ta and La/Ta ratios in Incapillo magmas show that crustal assimilation into an andesitic Pircas Negras precursor melt with strong HFSE depletion is a viable petrogenetic mechanism to generate these geochemical trends. Moreover, a reduced slab fluid flux since 3 Ma cannot explain a temporal shift to more radiogenic isotopic values, lower Sr/Yb ratios, and the presence of a negative Eu/Eu^{*} ratio compared to late Miocene dacitic centers that generally lack these characteristics.

The following summarizes the 3-0.5 Ma tectonomagmatic model shown in Figure 4.15 for the rhyodacitic Incapillo domes and ignimbrites. The development of a cooler mantle wedge below the northern flatslab region during the end of backarc slab shallowing (~ 5 Ma) would have led to reduced production of mantle-derived arc basalts. Before magmatism entirely shut off along the margin, anatexis of mafic lower

crust by these ponded mantle-derived basalts generated both the older oxidized domes and dacitic centers of the latest Miocene-Pliocene arc with strong arc signatures and adakitic characteristics. As cooler conditions prevailed and the flux of adakitic melts waned, rising dacitic magma slowed and ultimately stalled within the Andean upper crust.



Figure 4.15 Schematic cross-sectional cartoon across the northern flatslab transition zone at 27.9° S showing major tectonomagmatic features associated with the Incapillo Caldera and Dome Field. Lower crust is delineated at ~ 45 km, marking the 1.5 GPa stability field of eclogite (garnet + cpx). Shape of the subducted Nazca plate is based on geophysical imaging of the modern Wadati-Benioff zone at 27.5° S (Comte et al., 2002; Pardo et al., 2002). Dashed plate margins and dark arrows show relative back-arc slab shallowing. Topography is exaggerated by $\sim 10x$. Crustal thicknesses are based on MOHO depths reported by Fromm et al. (2004), McGlashan et al. (2007), and Yuan et al. (2002). Lower crustal melts similar to the 3-2 Ma Pircas Negras adakites (Goss et al., Chapter 2) are shown as the precursor magma to Incapillo rhyodacites and rhyolites. Stored at shallow depths (~ 20-30 km), the Incapillo magma chamber partially crystallizes and assimilates sialic upper crust. Eruption of the Incapillo Caldera at 0.51 ± 0.04 Ma marked the last eruption for ~ 700 km along the arc within the currently amagmatic flatslab segment.

Unlike the latest Miocene-Pliocene magma chambers (i.e., Bonete Chico, Pissis, and Veladero) that were continuously recharged by dacitic lower crustal melts, the perched Incapillo magma chamber lost thermal and chemical contact with the mantle and lower crust. At shallow depths, fractional crystallization and assimilation of sialic upper crust pushed Incapillo magmas towards more evolved compositions, diluted the high-P trace element signature, and bestowed the melt with a more-enriched isotopic signature. Occasionally, small crystal-rich batches of this volatile-poor melt leaked out along pre-existing fractures forming the eastern and western dome fields. At ~ 0.51 Ma, a final pulse of dacitic magma intersected the crystal-rich rhyolitic magma chamber, catalyzed the "boiling over cauldron" eruption, and generated the highly-crystalline Incapillo ignimbrite.

The model for the eruption of the Incapillo Caldera and Dome Complex is characteristic of waning siliceous volcanism over a shallowing subduction zone. In the Andes, this type of volcanism is characterized by effusive dome-eruptions of Na₂O-rich magmas with TTD-like geochemical signatures and is preceded by the sustained eruption of less evolved adakitic magmas similar to the 8-2 Ma Pircas Negras andesites. A temporally and chemically parallel magmatic sequence is seen within the Chilean flatslab region at 30° S, as the last magmatic event at this latitude, the 6-5 Ma Vallecito ignimbrite, was similarly preceded by mid-late Miocene adakitic andesites of the Cerro de las Tórtolas and Tambo formations (Kay et al., 1991; Kay and Mpodozis, 2002). This waning-magmatism model contrasts with the model for siliceous volcanism over a steepening subduction zone (Kay et al., 1999) that is dominated by voluminous explosive eruptions (500-3000 km³) of peraluminous magmas with flatter REE patterns, diminished arc signatures, and dominantly crustal isotopic ratios.

X CONCLUSIONS

The Incapillo Caldera and Dome Complex, situated within northernmost margin of the Chilean flatslab region at 28° S and 68.8° W, is the southernmost Quaternary explosive caldera of the Central Andes. This study marks the first detailed investigation of the morphology, petrology, and geochemistry of this center. The main conclusions are summarized below:

(1) The dominant eruptive mechanism of the Incapillo magmatic system was the effusive non-explosive eruption of more than 40 crystal-rich steep-sided rhyodacitic domes. The alignments of the domes suggest that magmas ascended along pre-existing structural weaknesses in the crust that parallel regional faults. K-Ar and 40 Ar/ 39 Ar dating of the dome lavas indicate effusive eruptions began at ~ 5 Ma during the migration of the frontal arc at this latitude and continued until ~ 0.8 Ma.

(2) The ~ 250 m high walls of the elliptical Incapillo caldera (5 x 6 km) are principally composed of a homogeneous pumice-rich and lithic-poor ignimbrite that radiates up to 15 km in all directions from the caldera. Biotites from both proximal and distal outflow pumices of the Incapillo ignimbrite yield 40 Ar/ 39 Ar ages of 0.51 ± 0.04 Ma, which date the caldera-forming explosive eruption. The lack of ash fall deposits covering any preexisting domes suggests a "boiling over cauldron" style of eruption, where erupted pyroclastic flows followed topographic lows.

(3) Observable evidence for magma mixing in the Incapillo ignimbrite comes from pumice rafts at the distal end of the ignimbrite. Large (< 40 cm) compositionally mixed pumices record the mixing of a dacitic magma (SiO₂ = 67 wt %) into a

partially-crystalline rhyolitic host (SiO₂ = 71 wt %). Vigorous thermal convection and super-saturation of volatiles caused by mixing catalyzed the explosive eruption.

(4) The final stage of the Incapillo complex was marked by the deposition of a lithic-rich debris flow that unconformably overlays the Incapillo ignimbrite. The debris flow likely formed from a lahar following the caldera-forming eruption. Lastly, resurgent domes erupted within the center of the Incapillo caldera. A potentially active hydrothermal system below the Incapillo caldera is evidenced by highly-altered resurgent domes and a crater lake with elevated temperatures compared to ambient non-volcanic lakes nearby (Markham and Barker, 1986).

(5) Volume estimates indicate over 16 km³ of Incapillo dome material effusively erupted before the formation of the Incapillo caldera, which itself has a volume of $\sim 4.3 \text{ km}^3$. The total volume of Incapillo ignimbrite inflow and outflow units converted to DRE is estimated at $\sim 20 \text{ km}^3$. The debris flow has a DRE volume of $\sim 0.5 \text{ km}^3$. The total volume for the Incapillo Caldera and Dome Complex is $\sim 37 \text{ km}^3$, which is similar to the small- to medium-sized ignimbrites (< 50 km³) from the southern Puna (Siebel et al., 2001), but far smaller than the huge Altiplano-Puna megacalderas with erupted volumes ranging from 650 -2500 km³.

(6) Compositionally, the Incapillo dome lavas and ignimbritic pumices form a generally homogenous suite of high-Na rhyodacites and rhyolites with trace elements characterized by steep REE patterns (La/Yb 30-45) marked by HREE depletion (Sm/Yb = 6-8), high Sr/Yb ratios (500-850), and strong slab-fluid signatures (Ba/Ta = 600-1200; La/Ta = 30-50). Incapillo geochemical signatures are less extreme than those from nearby ~ 6 Ma Jotabeche rhyodacites and 5-2 Ma Pircas

Negras adakitic andesites. Like the silicic ignimbrites from the Chilean flatslab (Kay et al., 1991), Jotabeche (Kay et al., 1994b; Mpodozis et al., 1995), and the Cordillera Blanca (Petford and Atherton, 1996), Incapillo precursor melts initially equilibrated at lower crustal depths in the presence of residual garnet. In comparison, the high-pressure geochemical signature is less evident in ignimbrites from the Puna-Altiplano plateau that have been previously modeled as low-pressure melts of sialic crust by intruding mantle-derived basalt (e.g., Francis et al., 1989; de Silva, 1991).

(7) Incapillo domes and ignimbritic pumices have Sr, Nd, and Pb isotopic ratios $({}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.7065 \cdot 0.7066; \epsilon\text{Nd} = -4.2 \text{ to } -4.7; {}^{206}\text{Pb}/{}^{204}\text{Pb} = 18.73 \cdot 18.75; {}^{207}\text{Pb}/{}^{204}\text{Pb} = 15.62 \cdot 15.63; {}^{208}\text{Pb}/{}^{204}\text{Pb} = 38.77 \cdot 38.80)$ that are distinct from other siliceous centers from the northernmost flatslab transition zone. Based on their chemical homogeneity, Incapillo domes and ignimbrites most likely originated from the same magma chamber and share a common source. In light of trace element and isotopic trends, Incapillo magmas are best explained by the combined effects of low-pressure fractional crystallization and upper crustal assimilation that altered the composition of lower crustal precursor melts.

(8) The small size, non-explosive eruptive style, and muted high-pressure geochemical signature are characteristic features of the Incapillo Caldera and Dome Complex that resulted from its eruption over a partially shallowed slab. In sum, the Incapillo Caldera and Dome Complex represents the model of a caldera erupting during the *waning* stages of a dying central Andean arc and contrasts with the "ignimbrite flare-up" model for the 11-4 Ma Altiplano-Puna calderas that erupted in a *waxing* arc over a steepening slab.

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APPENDIX 1

ANALYTICAL METHODS

Major elements

Major elements for whole rock powders and in situ mineral grains were obtained by electron microprobe at the Cornell University Center for Materials Research (CCMR). Rock samples were cut into ~ 1 cm thick slabs and then polished (300 and 450 grit) to remove any metallic residue from the saw blades. Slabs were crushed into small chips and later ground using a corundum-lined (Al₂O₃) vessel in a shatterbox. Major elements were obtained following methods in Kay et al. (1987) using a three-spectrometer JEOL-733 Superprobe[©] in WDS mode with a beam diameter of 30 µm, a 15 kV accelerating voltage, and a 20 nA incident current. Microprobe data was reduced using a Tracor-Northern system and Bence-Albee matrix corrections (Albee and Ray, 1970). For each sample, an average of five spot analyses were obtained and normalized using correction factors calculated by secondary standard analyses. Smithsonian standards A-99 and JDF (Juan de Fuca glass) and internal standard RHA-Z were each analyzed at the beginning, middle, and end of each session. Only fluxed whole rock glasses were normalized to 100.0 wt %. Minerals were analyzed *in situ* using a focused spot beam diameter ($\sim 1 \mu m$). Natural mineral standards (Kakanui hornblende, P140 olivine, PX-1 clinopyroxene, Johnstown hypersthene, Lake County plagioclase; Jarosewich et al., 1980) were additionally run as secondary standards during *in situ* mineral analyses and average mineral standard analyses are given in Appendices 5-10. Error is 2-5 % for major elements with concentrations > 1 wt % and \pm 10-20 % for elements with < 1 wt %.

Trace elements

Trace element data were obtained using Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the Department of Geological Sciences at Cornell University. Atomic absorption (AAS) data were determined by the Chilean Geological Survey (SERNAGEOMIN). ICP-MS and AAS data were used as an independent check of INAA data and to obtain high precision data on elements not analyzed by INAA due to either low signal to noise ratios or a substantial peak interference by neutron activation (i.e., Rb, Nb, Zr, Pb).

Methodology and standard concentration data for selected trace element analyses using INAA are published in Kay et al. (1987). Sample powder (~ 0.5 g) was packed into ultrapure Suprasil[®] quartz tubing that was pre-cleaned in 6N nitric acid (HNO₃). Eleven samples and 3 internal standards (PAL, SIT, and WBD-2) were irradiated at Ward Laboratory TRIGA reactor at Cornell University. All irradiated samples were counted at Cornell University on an Ortec intrinsic Ge detector both 6 and ~ 40 days post-irradiation. Acceptable in-run statistics were achieved by counting for ~ 3-4 hours per sample with standards counted for ~ 12 hours. Replicate analyses of internal standards (Appendix 2) yield analytical precision (2σ) of \pm 2-7 % for most elements and between \pm 8-16 % for U, Sr, Nd, and Ni, especially at lower concentrations.

ICP-MS data were obtained by digesting ~ 20 mg of sample powder in a 10 ml aqua regia and HF acid mixture (6 mL of 7N nitric acid + 2 mL of 7N hydrochloric acid + 2 mL of 7N hydrofluoric acid) in Milestone[©] ETHOS microwave system Teflon vessels. Pressurized digestions were brought to 210 °C over 10 minutes and held at this temperature for an additional 15 minutes. Free fluorine ions were complexed to tetrafluoroboric acid (HBF₄) by adding 10 mL of saturated boric acid (H_3BO_3) in QD H₂O and subsequently refluxing in the microwave for 25 minutes under the same P-T conditions (Coedo et al., 1998). This step inhibits the precipitation of complex fluorine compounds of Ca, Mg, Sr, Ba, U, and REE without an additional matrix effect and allows the solution to be run through the ICP-MS quartz spray-chamber without corrosion. Digestions were sonicated in a heat bath for 10 minutes before 10 mL of solution were diluted with 90 mL of QD H₂O forming a ~ 10,000 fold dilution of the original sample powder in a ~ 2 % QD HNO₃⁻ solution. Calibration curves were obtained following methodology of Grove et al. (2002) by diluting USGS AGV-1 and French (CNRS) BEN solutions with 2% QD HNO₃ to form 2-, 4-, 10-, and 25-fold dilutions. Diluted solutions were sonicated for an additional ~ 30 minutes immediately preceding analysis. Thirty-one (31) trace elements were analyzed using a high-resolution ThermoFinnegan ELEMENT2 magnetic sector ICP-MS at Cornell University. One or two isotopes were chosen of each element based on abundance and absence of interferences. All elements were run using both analog and counting mode to ensure no detector saturation. Except for the REE, Cs and Ba, all elements were analyzed in medium resolution. BEN standard solution was run repeatedly every 8 samples to correct for instrumental drift. During each run, 1 ppb standard solutions of Ba, La, Ce, Pr, Nd, and Sm were analyzed to correct for polyatomic ion oxide interferences on the MREE (Cao et al., 2001). Both an acid and procedural blank were analyzed as unknowns to monitor contamination in lab acids and vessels respectively. The procedural blank was subtracted from the concentration totals of unknown samples. Precision estimates for ICP-MS data (Appendix 4) are < 5 % (relative standard deviation = standard deviation/mean) for all trace elements measured. ICP-MS data for replicate digestions of the USGS BCR-2 rock standard are accurate to within acceptable error for all trace elements except Ta, which is ~ 6 % high.

Isotopic ratios

Sr and Nd isotopes were analyzed with a VG Sector 54 Thermal Ionization Mass Spectrometer (TIMS) in the Keck Isotope Lab at Cornell University. Sample preparation and analytical methodology is described by White and Duncan (1996). A \sim 50 mg aliquot of sample powder was leached with 1 mL of hot 6N 2QD HCl for one hour in 15 mL Savillex teflon vessels and subsequently dissolved overnight using 2 ml of HF and ~ 0.1 ml of concentrated perchloric acid (HClO₄). Digestions were dried down to liberate SiF₆ and twice re-dissolved in 6N HCl to breakdown polyatomic fluorides before being dissolved in 1.15 mL of 2.5N HCl and centrifuged for 10 minutes. Sr and the REE were separated by elution with 2.5N and 6N HCl through AG50W-x12 resin cation exchange columns. Nd elution was accomplished using HDHEP-coated resin and with a 0.16N HCl eluent. Sr and Nd isotopic ratios were normalized to 88 Sr/ 86 Sr = 0.1194 and 146 Nd/ 144 Nd = 0.7219 respectively. Average isotopic values for Sr standard NBS 987 and Nd standards Ames and La Jolla are given in Tables 2.6 and 4.6. Pb separations were obtained using the technique outlined by White and Dupré (1986) at Cornell University and analyzed at the University of Florida Nu-Plasma multi collector (MC) ICP-MS using the Tl mass-bias normalization technique by Kamenov et al. (2004). A procedural blank spiked with $2.3 \text{ mg of}^{208}\text{Pb}^{/206}\text{Pb}$ solution yielded 0.654 ng of excess Pb.

Oxygen isotopes were analyzed by ArF laser fluorination on select olivine and quartz mineral grains at the Universität Göttingen following the procedures of Fiebig et al. (1999). Measured values for unknowns were corrected to the average measured value for the Gore Mountain garnet standard (UWG-2, $\delta^{18}O = 5.7$). In run error (2 σ) is estimated at \pm 0.2 ‰. External precision from repeat analyses averaged \pm 0.2-0.5 per mil.

⁴⁰Ar/³⁹Ar sample preparation methods

Dated samples were pre-selected based on hand specimen and thin section inspection for no signs of hydrothermal or low-T chloritization between [001] biotite cleavage planes. Biotite (> 0.5 mm) and hornblende phenocrysts (< 0.75 mm) were hand picked from coarsely crushed pumice and dome lavas and washed with QD H₂O to remove micron-scale ash from mineral surfaces. Using a binocular stereoscope, final selection for ⁴⁰Ar/³⁹Ar dating included only clean independent euhedral phenocrysts. Irradiated aliquots contained between 15-30 biotites and hornblende crystals each with a mass of ≤ 2 mg.

Before irradiation, a second clean up step involving gentle low power heating to remove adsorbed air and water was applied to 4 of the 5 biotite separates. Mineral separates were irradiated at the University of Oregon TRIGA reactor for 20-30 minutes following the methods of Singer et al. (2004). Nucleogenic interferences on ⁴⁰K and ⁴⁰Ca were corrected using the constant ratios of $({}^{40}\text{Ar}/{}^{39}\text{Ar})_{\text{K}} = 0.00086$, $({}^{36}\text{Ar}/{}^{37}\text{Ar})_{\text{Ca}} = 0.000264$, and $({}^{39}\text{Ar}/{}^{37}\text{Ar})_{\text{Ca}} = 0.000673$ (Singer et al., 2004). J-values were calculated relative to 28.34 Ma for the Taylor Creek rhyolite sanidine (Renne et al., 1998).

Laser Fusion Gas Extraction and Mass Spectrometry

Irradiated mineral separates were individually fused using a 0.88-6.25 W CO₂ laser with the released gas collected and isotopically analyzed in a MAP 215-50 mass spectrometer following procedures outlined in Hora et al. (2007). During the analytical run, mass discrimination consistently ranged 1.0075 \pm 0.05 % (1 σ) per atomic mass unit as monitored by an automated air pipette. Data was reduced using ArArCALC software (Koppers, 2002) and all ⁴⁰Ar/³⁹Ar ages were calculated using the accepted decay constants of Steiger and Jäger (λ^{40} K = 5.543 x 10⁻¹⁰ yr⁻¹; 1977).
Long te	erm values for	internal IN	AA standards	(1997-2002)					
	PA	L-889 n=	73	SI	Г-RK5 n=	73	W	/BD2 n=7	3
		Obse	erved		Obse	erved		Obse	erved
	Accepted	Mean	2σ	Accepted	Mean	2σ	Accepted	Mean	2σ
La	10.52	10.39	0.40	14.61	14.5	0.48	82.9	-	-
Ce	23.6	23.8	2.35	32.3	33.5	2.19	158	-	-
Nd	13	12.2	3.59	18.3	19.7	4.06	58	-	-
Sm	3.42	3.44	0.22	4.68	4.82	0.42	8.23	-	-
Eu	1.07	1.02	0.09	1.09	1.00	0.15	2.14	2.21	0.20
Tb	0.67	-	-	0.76	0.706	0.07	0.62	0.630	0.20
Yb	2.18	-	-	3.42	3.51	0.32	0.61	0.634	0.10
Lu	0.304	-	-	0.5	0.513	0.05	0.85	-	-
Sr	183	213	38	-	-	-	620	0.088	0.03
Ва	197	-	-	1045	1045	194	1280	646	152
Cs	2.19	2.05	0.17	1.18	1.18	0.12	1.81	1040	180
U	0.497	0.540	0.323	2.77	2.76	0.27	2.35	-	-
Th	2.07	1.97	0.203	5.20	5.21	0.61	11	-	-
Hf	2.56	2.58	0.165	4.50	4.50	0.30	3.92	-	-
Та	0.65	0.64	0.051	0.53	0.53	0.05	8.3	-	-
Sc	37.5	38.1	1.7	9.18	9.18	1.13	20.2	-	-
Cr	314	305	14	2	2	3	1910	-	-
Ni	88.6	88	6.2	2	2	2	991	-	-
Co	53	53	2.4	34	34	2	88	-	-
Na ₂ O	2.07	2.07	0.07	5.3	-	-	0.11	-	-

APPENDIX 2

PAL = Palisades Sill (New York); SIT = Sitkin Island dacite (Aleutian Islands, Alaska); WBD2 = Williams Brook Dike (Ithaca, NY); Accepted standard values were determined by analyzing standard powders as unknowns against USGS BCR-1 (Govindaraju, 1989). Dashes indicate standard value used to calculate unknown samples and reported values for the other two standards. INAA analytical methods are described in detail in Kay et al., (1987) and in Appendix 1.

ICP-MS trace e	element analys	ses for basalts	s and andesit	tes from the no	orthern flat	slab transitio	on zone (~27°-2	28°)		
	PPN	Jotabech	e/Gallina	•	Valle Anch	0		Rio S	alado	
element (ppm)	CO 412	CO 416	CO 427	CC 262	CC 101	CO 24	CO 163	CO 170	CO 179	CO 309
Sc	15.9	8.4	11.2	18.5	23.0	22.2		17.8	6.4	7.7
V	142	102	117	203	211	169		162	82	101
Cr	141	46	73	188	196	575		210	29	59
Co	20	12	15	25	26	37		22	9	13
Ni	82	23	27	49	46	175		62	8	19
Rb	47	55	47	35	35	31		48	76	60
Sr	912	850	934	672	612	767		848	783	899
Y	17	12	14	17	18	20		17	11	11
Zr	229	231	246	192	190	165		250	304	254
Nb	11.2	12.0	11.4	10.3	9.9	10.4		11.9	11.0	12.1
Cs	1.08	1.93	1.40	0.91	1.28	0.91		1.36	1.33	2.05
Ba	791	810	840	588	555	624		744	1070	920
La	36.7	30.4	36.0	24.2	23.9	28.5	45.0	32.9	44.2	39.2
Ce	70.1	61.2	70.9	54.8	52.5	63.0	89.1	72.8	87.9	78.4
Pr	9.2	8.3	8.7	6.8	6.5	7.9	11.0	8.8	10.2	9.9
Nd	35.7	32.9	33.7	27.7	26.3	31.2	41.4	34.7	38.3	38.2
Sm	6.5	6.1	6.0	5.7	5.4	5.7	7.2	6.6	6.3	6.4
Eu	1.87	1.81	1.75	1.81	1.73	1.61	2.01	1.93	1.69	1.84
Gd	4.9	4.4	4.2	4.7	4.7	4.5	5.0	5.0	3.7	4.0
Tb	0.60	0.50	0.51	0.61	0.62	0.67	0.58	0.64	0.50	0.51
Dy	3.1	2.3	2.5	3.2	3.3	3.7	2.7	3.2	2.3	2.4
Но	0.55	0.36	0.42	0.55	0.59	0.74	0.43	0.56	0.40	0.41
Er	1.54	0.98	1.17	1.51	1.64	1.91	1.14	1.54	0.92	0.97
Tm	0.202	0.124	0.153	0.197	0.216	0.298	0.146	0.204	0.135	0.142
Yb	1.33	0.81	0.99	1.27	1.41	1.73	0.94	1.34	0.79	0.82
Lu	0.196	0.114	0.144	0.185	0.205	0.250	0.135	0.195	0.109	0.116
Hf	5.3	5.5	5.6	4.8	4.7	4.0		6.0	6.8	5.8
Та	0.64	0.73	0.58	0.60	0.60	0.56		0.73	0.65	0.73
Pb	8.0	8.9	8.3	6.6	7.1	8.3		8.8	12.1	10.5
Th	5.1	3.8	4.5	2.9	3.0	4.1		4.7	7.3	4.8
U	1.05	1.11	0.90	0.77	0.77	0.85		1.02	1.48	1.40

APPENDIX 3

ICP-MS analytical methodologies are described in Appendix 1. Analyzed standard values are given in Appendix 4.

ICP-MS t	trace elemer	nt analyses	for basalts	and andes	sites from t	the norther	m flatslab t	transition z	zone (~27°-28	8 °)		
				Rio Sa	alado (cont	inued)					Estanzuela	ı
element	CO 310	CO 312	CO 313	CO 327	CO 329	CO 331	CO 332	CO 504	CO 507	CO 144	CO 145	CO 146
Sc	7.6	7.0	6.5	7.4	13.5	8.5	13.1	11.5	9.4	12.1	7.9	17.3
V	99	94	82	95	128	94	136	115	101	126	86	146
Cr	71	29	28	42	132	36	131	100	30	82	56	201
Co	13	11	10	11	18	11	18	15	11	16	8	21
Ni	21	23	12	17	41	18	65	36	14	29	16	60
Rb	61	68	76	44	61	78	71	51	81	43	70	50
Sr	820	863	921	990	882	789	991	932	901	935	849	828
Y	11	12	12	12	16	13	18	15	15	15	12	22
Zr	253	313	291	301	270	269	284	270	253	263	243	244
Nb	11.2	11.1	11.2	11.6	11.9	12.0	12.7	12.6	12.1	14.9	12.4	12.9
Cs	2.82	1.16	1.34	3.93	2.18	1.77	1.83	1.06	1.97	0.99	0.77	1.28
Ba	918	984	1121	1016	882	949	968	884	952	885	952	717
La	36.4	40.5	42.1	36.4	37.7	43.2	42.7	42.0	46.8	38.6	42.6	35.7
Ce	73.1	91.2	94.9	85.0	82.0	87.0	96.5	85.2	89.7	74.7	81.4	70.9
Pr	9.4	11.1	11.2	10.4	10.2	10.5	11.9	10.7	10.9	9.8	10.3	9.3
Nd	36.2	41.8	41.9	40.1	39.8	39.8	45.8	40.9	41.1	37.9	39.0	36.7
Sm	6.2	6.9	6.9	6.9	7.0	6.8	8.0	7.3	7.1	6.9	6.8	7.0
Eu	1.76	1.78	1.78	1.94	1.89	1.76	2.07	2.11	1.85	2.06	1.90	1.91
Gd	4.0	4.1	4.0	4.3	4.6	4.2	5.1	5.1	4.7	5.2	4.6	5.6
Tb	0.49	0.54	0.52	0.56	0.63	0.56	0.70	0.61	0.58	0.60	0.52	0.72
Dy	2.4	2.5	2.5	2.6	3.2	2.7	3.5	2.9	2.8	2.9	2.4	3.8
Ho	0.40	0.43	0.43	0.45	0.57	0.47	0.62	0.47	0.47	0.47	0.36	0.70
Er	0.92	1.00	1.01	1.07	1.40	1.13	1.52	1.28	1.32	1.25	0.96	1.95
Tm	0.135	0.145	0.146	0.154	0.210	0.169	0.224	0.169	0.173	0.160	0.121	0.262
Yb	0.79	0.84	0.87	0.91	1.23	0.98	1.29	1.09	1.13	1.04	0.77	1.72
Lu	0.112	0.116	0.121	0.127	0.173	0.138	0.182	0.157	0.163	0.149	0.109	0.255
Hf	5.9	7.3	6.7	6.7	6.2	6.2	6.4	6.2	5.9	6.0	6.0	5.9
Та	0.71	0.60	0.60	0.66	0.67	0.65	0.70	0.69	0.67	0.84	0.73	0.76
Pb	10.2	11.5	12.2	9.3	9.8	12.1	10.6	9.0	11.3	9.3	11.3	9.4
Th	4.5	7.8	8.4	6.2	5.8	8.5	8.0	5.8	9.2	5.1	6.6	5.6
U	1.31	1.13	1.28	1.04	1.03	1.23	1.37	1.05	1.44	1.03	1.35	1.22

As trace element engineers for boselts and endesites from the northern flatsleb transition zone ($.27^{\circ}$ 28 $^{\circ}$)

ICP-MS analytical methodologies are described in Appendix 1. Analyzed standard values are given in Appendix 4.

ICP-MS tra	ce element analyses for	[.] basalts and a	andesites fror	n the northern fla	tslab transition zone		
	Laguna Brava	Dos He	rmanos	Redonda	Veladero PN	Cadillal	Rodrigo
element	CO 333	CO 428	CC81	CC 94	CO 324	CO 447	CO 296a
Sc	7.8	9.3	9.5	7.2	10.3	10.6	8.4
V	88	121	115	92	103	80	98
Cr	39	55	57	17	105	32	70
Со	11	17	16	9	14	11	12
Ni	16	26	20	9	28	17	20
Rb	87	64	66	79	138	61	93
Sr	831	1402	1278	793	588	616	821
Y	13	14	14	10	16	16	11
Zr	273	229	246	223	239	101	256
Nb	11.7	12.9	12.9	9.9	15.7	10.5	9.4
Cs	3.30	1.03	1.99	1.63	7.83	3.20	1.27
Ва	998	1231	1156	1034	720	602	958
La	36.2	62.8	57.6	41.6	43.8	21.5	36.8
Ce	83.7	104.8	116.7	79.9	85.9	46.2	80.8
Pr	9.9	14.9	13.6	9.5	10.3	5.8	9.6
Nd	37.1	56.1	51.1	34.0	38.1	22.5	35.7
Sm	6.3	8.6	7.9	5.5	6.6	4.3	5.9
Eu	1.61	2.31	2.24	1.47	1.55	1.15	1.50
Gd	3.8	5.1	4.5	3.4	4.4	3.4	3.5
Tb	0.52	0.62	0.61	0.38	0.62	0.51	0.47
Dy	2.5	2.9	2.9	1.7	3.2	2.8	2.3
Ho	0.44	0.50	0.51	0.26	0.57	0.55	0.39
Er	1.07	1.18	1.19	0.77	1.42	1.45	0.94
Tm	0.159	0.170	0.174	0.100	0.217	0.228	0.136
Yb	0.94	0.97	1.00	0.66	1.25	1.35	0.79
Lu	0.134	0.134	0.140	0.095	0.181	0.199	0.110
Hf	6.2	5.3	5.8	5.6	6.0	2.9	5.8
Та	0.68	0.66	0.72	0.58	1.24	0.73	0.53
Pb	15.5	13.0	14.6	13.8	17.0	10.2	11.2
Th	8.0	10.1	8.7	8.2	16.8	3.8	11.0
U	1.64	1.26	1.41	1.29	5.63	1.08	1.37

ICP-MS analytical methodologies are described in Appendix 1. Analyzed standard values are given in Appendix 4.

ICP-MS standar	rd analyse	S					
	8_9_04	8_10_05	repor	ted	8_10_05	kay	white
element (ppm)	BCR-2	BCR-2	BCR-2	error	PAL	PAL	PAL
Sc	32.1	36.5	33	2	41.2	38	
V	421	470	416	14	314		
Cr	20	25	18	2	299	314	
Со	38	37	37	3	49	53	
Ni	16	16	12		84	89	
Rb	51	47	48	2	30		33.8
Sr	341	341	346	14	173	183	177
Y	37	37	37	2	23	22	
Zr	180	185	184	8.5	93.9	88.8	
Nb	12.3	12.6	12.50	0.4	7.3	6.6	
Cs	1.28	1.18	<u>1.1</u>	0.1	2.05	2.19	2.25
Ba	692	676	683	28	183	188	197
La	26.3	24.3	25.0	1	10.2	10.52	11.41
Ce	53.9	52.9	53.0	2	22.0	23.6	25.5
Pr	7.0	6.6	6.80	0.3	2.9		3.41
Nd	29.5	27.6	28.0	2	12.9	13.0	14.5
Sm	6.8	6.6	6.70	0.3	3.4	3.4	3.67
Eu	1.95	2.01	2.00	0.1	1.15	1.07	1.190
Gd	7.0	7.1	6.8	0.3	4.1		4.22
Tb	1.10	1.06	1.07	0.04	0.64	0.67	0.770
Dy	6.4	6.2	6.35		3.9		4.37
Ho	1.33	1.28	1.33	0.06	0.79		0.909
Er	3.61	3.63	3.63		2.28		2.44
Tm	0.570	0.499	0.54		0.315		
Yb	3.29	3.30	3.5	0.2	2.05	2.2	2.32
Lu	0.484	0.493	0.51	0.02	0.303	0.33	0.362
Hf	4.7	4.8	4.7	0.1	2.6	2.56	
Та	0.78	0.79	0.740	0.019	0.61	0.65	
Pb	10.5	10.5	11	2	3.9	4.6	
Th	6.5	6.1	6.2	0.7	2.26	2.07	
U	1.62	1.7	1.69	0.19	0.53	0.5	

APPENDIX 4

Black = USGS certificate values (Govindaraju, 1989; 1994); italics = Eggins et al. (1997) measured values; underlined = USGS information values; HFSE values on BCR-2 are from isotope dilution (Willbold and Jochum, 2005); PAL values are from Kay INAA working values and isotope dilution REE values from White.

Major element am	phibole analy	ses from s	elected Pir	cas Negra	s andesites								
analysis #	••			0		82	83	84	85	86	87	88	89
type						с	с	r	r	с	с	c	r
sample	KNUI-act ¹	KNUIav ²	Meas/Act	KNUIav ²	Meas/Act	309-1	309-1	309-1	309-1	309-1	309-2	309-2	309-2
SiO ₂	40.38	40.20	1.00	40.35	1.00	40.20	40.98	42.54	42.29	43.22	41.83	41.94	42.24
TiO ₂	4.72	4.77	1.01	4.77	1.01	2.82	2.92	2.74	2.74	2.69	2.81	2.69	3.00
Al_2O_3	14.90	14.77	0.99	14.73	0.99	16.12	13.36	11.79	12.04	11.43	13.01	12.45	12.06
FeO	10.92	10.81	0.99	10.81	0.99	13.16	13.08	11.34	10.96	10.78	11.64	10.98	10.98
MnO	0.09	0.08	0.91	0.09	1.01	0.14	0.13	0.10	0.10	0.12	0.13	0.10	0.14
MgO	12.81	12.66	0.99	12.61	0.98	11.87	12.60	14.77	14.85	15.11	13.40	14.36	14.06
CaO	10.31	10.31	1.00	10.32	1.00	11.15	11.15	11.00	11.41	11.45	11.33	11.57	11.73
Na ₂ O	2.61	2.61	1.00	2.61	1.00	2.70	2.70	2.60	2.60	2.54	2.68	2.57	2.36
K ₂ O	2.05	2.05	1.00	2.05	1.00	0.84	0.78	0.77	0.78	0.76	0.86	0.86	0.69
Cr ₂ O ₃		0.02		0.01		0.00	0.01	0.00	0.03	0.01	0.06	0.05	0.17
Total	98.79	98.28		98.36		99.01	97.72	97.64	97.80	98.11	97.76	97.57	97.42
Si	5.846	5.859		5.880		5.798	6.001	6.139	6.112	6.218	6.100	6.101	6.164
Ti	0.514	0.523		0.523		0.306	0.322	0.297	0.297	0.291	0.308	0.294	0.329
Al (iv)	2.154	2.141		2.120		2.202	1.999	1.861	1.888	1.782	1.900	1.899	1.836
Al (vi)	0.388	0.396		0.408		0.539	0.307	0.144	0.162	0.156	0.336	0.237	0.237
Fe ²⁺	0.896	0.961		0.995		0.896	0.966	0.518	0.606	0.632	0.939	0.763	0.883
Fe ³⁺	0.426	0.356		0.322		0.691	0.635	0.851	0.719	0.665	0.481	0.573	0.457
Mn	0.011	0.010		0.011		0.017	0.016	0.012	0.012	0.015	0.016	0.012	0.018
Mg	2.765	2.751		2.740		2.551	2.752	3.179	3.200	3.241	2.914	3.115	3.058
Ca	1.601	1.611		1.613		1.725	1.750	1.702	1.768	1.766	1.772	1.805	1.836
Na _(B)	0.399	0.389		0.387		0.275	0.250	0.298	0.232	0.234	0.228	0.195	0.164
Na _(A)	0.333	0.348		0.350		0.481	0.515	0.430	0.497	0.474	0.529	0.530	0.502
K	0.379	0.381		0.381		0.155	0.146	0.141	0.144	0.140	0.160	0.160	0.129
Cr	0.000	0.002		0.001		0.000	0.002	0.000	0.004	0.001	0.007	0.006	0.019
Total						15.636	15.661	15.571	15.641	15.613	15.689	15.690	15.631
$(Na + K)_A$	0.712	0.729		0.731		0.636	0.661	0.571	0.641	0.613	0.689	0.690	0.631
(Ca + Na) _B	2.000	2.000		2.000		2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
$Mg^{2+}/(Mg^{2+}+Fe_T)$	0.755	0.741		0.734		0.616	0.632	0.699	0.707	0.714	0.672	0.700	0.695

APPENDIX 5

¹Kakanui hornblende values reported by Jarosewich et al. (1980). ²Values obtained for the Kakanui hornblende are composites of 5 spot analyses run before and after unknown samples. All unknowns and KNUI were corrected by deviation from standards JDF and A99. Cations were calculated on the basis of 23 oxygens with all Fe as Fe²⁺. Cation totals were normalized to (Na+Ca+K)=13 and Na_(B) is calculated following Leake et al. (1997); Fe²⁺/Fe³⁺ ratio is estimated following Droop (1987); c = core, r = rim.

Major element amp	ohibole ana	lyses from	selected P	ircas Negra	as andesite	S						
analysis #	90	91	92	93	94	95	108	109	110	111	115	117
type	r	с	с	с	r	r	с	с	r	r	r	r
sample	309-2	309-3	309-3	309-3	309-3	309-3	309-6	309-6	309-6	309-6	309-7	309-7
SiO ₂	42.25	42.44	42.93	42.42	41.51	42.37	41.49	41.56	42.48	42.37	42.47	43.13
TiO ₂	2.89	2.78	2.83	2.90	2.96	2.99	2.86	2.87	2.82	2.91	2.69	2.70
Al_2O_3	12.20	12.16	12.13	11.93	12.78	11.98	13.04	13.26	11.99	12.03	12.06	11.54
FeO	11.42	10.30	10.46	10.61	12.27	11.19	11.81	12.34	10.98	10.86	11.19	10.90
MnO	0.11	0.06	0.08	0.09	0.13	0.12	0.12	0.13	0.11	0.10	0.13	0.10
MgO	13.83	15.03	14.87	14.65	13.34	14.36	13.95	13.26	14.53	14.39	15.09	15.60
CaO	11.65	11.40	11.37	11.41	11.47	11.74	11.38	11.49	11.33	11.64	10.93	11.00
Na ₂ O	2.37	2.52	2.60	2.51	2.42	2.42	2.70	2.83	2.61	2.49	2.78	2.67
K ₂ O	0.76	0.76	0.75	0.76	0.81	0.69	0.83	0.83	0.72	0.78	0.77	0.71
Cr ₂ O ₃	0.13	0.06	0.05	0.04	0.03	0.17	0.13	0.08	0.02	0.10	0.00	0.15
Total	97.62	97.52	98.07	97.32	97.71	98.03	98.32	98.65	97.59	97.67	98.12	98.50
Si	6.160	6.131	6.175	6.163	6.058	6.139	6.001	6.030	6.157	6.159	6.089	6.138
Ti	0.317	0.302	0.307	0.317	0.325	0.326	0.311	0.313	0.308	0.318	0.290	0.289
Al (iv)	1.840	1.869	1.825	1.837	1.942	1.861	1.999	1.970	1.843	1.841	1.911	1.862
Al (vi)	0.256	0.202	0.230	0.206	0.256	0.184	0.224	0.298	0.206	0.220	0.127	0.075
Fe ²⁺	0.911	0.567	0.652	0.700	0.893	0.806	0.730	0.986	0.703	0.821	0.413	0.330
Fe ³⁺	0.481	0.678	0.607	0.589	0.604	0.549	0.698	0.511	0.628	0.499	0.929	0.967
Mn	0.014	0.007	0.010	0.011	0.016	0.014	0.014	0.016	0.014	0.012	0.016	0.012
Mg	3.006	3.238	3.189	3.173	2.903	3.101	3.009	2.867	3.139	3.118	3.225	3.310
Ca	1.821	1.766	1.753	1.778	1.796	1.824	1.764	1.788	1.761	1.814	1.681	1.679
Na _(B)	0.179	0.234	0.247	0.222	0.204	0.176	0.236	0.212	0.239	0.186	0.319	0.321
Na _(A)	0.491	0.473	0.478	0.485	0.482	0.505	0.523	0.584	0.496	0.516	0.453	0.417
K	0.141	0.140	0.138	0.141	0.151	0.128	0.154	0.154	0.134	0.145	0.141	0.128
Cr	0.015	0.007	0.005	0.005	0.003	0.019	0.015	0.009	0.002	0.012	0.000	0.017
Total	15.633	15.613	15.616	15.626	15.633	15.633	15.677	15.738	15.629	15.661	15.594	15.545
$(Na + K)_A$	0.633	0.613	0.616	0.626	0.633	0.633	0.677	0.738	0.629	0.661	0.594	0.545
$(Ca + Na)_B$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
$Mg^{2+}/(Mg^{2+}+Fe_T)$	0.683	0.722	0.717	0.711	0.660	0.696	0.678	0.657	0.702	0.703	0.706	0.718

¹Kakanui hornblende values reported by Jarosewich et al. (1980). ²Values obtained for the Kakanui hornblende are composites of 5 spot analyses run before and after unknown samples. All unknowns and KNUI were corrected by deviation from standards JDF and A99. Cations were calculated on the basis of 23 oxygens with all Fe as Fe²⁺. Cation totals were normalized to (Na+Ca+K) =13 and Na_(B) is calculated following Leake et al. (1997); Fe^{2+}/Fe^{3+} ratio is estimated following Droop (1987); c = core, r = rim.

Major element am	phibole an	alyses fro	om selecte	ed Pircas	Negras a	ndesites								
analysis #	124	125	126	127	128	129	130	131	138	139	140	141	146	147
type	с	с	r	r	с	с	r	r	c	с	r	r	c	c
sample	427-1	427-1	427-1	427-1	427-2	427-2	427-2	427-2	427-3	427-3	427-3	427-3	427-4	427-4
SiO ₂	43.29	42.86	43.33	42.10	43.76	43.21	43.27	43.21	42.38	41.48	43.37	43.08	43.91	44.27
TiO ₂	2.36	2.41	2.25	2.62	2.38	2.69	2.66	2.39	2.30	2.50	2.38	2.45	2.26	2.21
Al_2O_3	11.73	11.90	10.86	11.96	11.20	11.41	11.06	11.36	11.96	12.52	11.26	11.63	11.17	10.72
FeO	8.80	8.77	9.86	11.14	9.56	9.05	9.21	8.57	11.15	12.71	8.58	9.60	9.74	9.24
MnO	0.09	0.10	0.10	0.11	0.07	0.08	0.11	0.10	0.10	0.13	0.08	0.11	0.10	0.10
MgO	16.15	16.09	15.97	15.15	16.04	16.27	16.45	16.65	14.98	13.64	16.70	15.87	16.42	16.70
CaO	10.96	11.09	10.97	11.02	10.95	11.03	11.01	11.30	11.01	10.99	10.98	11.36	10.92	10.81
Na ₂ O	2.59	2.54	2.58	2.73	2.48	2.51	2.49	2.47	2.61	2.64	2.59	2.42	2.66	2.61
K ₂ O	0.65	0.64	0.56	0.53	0.59	0.59	0.57	0.66	0.59	0.57	0.64	0.63	0.57	0.57
Cr ₂ O ₃	0.04	0.04	0.00	0.04	0.15	0.07	0.00	0.06	0.00	0.00	0.10	0.06	0.00	0.00
Total	96.65	96.44	96.47	97.41	97.18	96.92	96.83	96.77	97.09	97.19	96.69	97.21	97.75	97.24
Si	6.223	6.181	6.262	6.068	6.263	6.198	6.208	6.205	6.125	6.046	6.219	6.192	6.241	6.305
Ti	0.255	0.261	0.244	0.284	0.256	0.290	0.287	0.258	0.250	0.274	0.257	0.265	0.241	0.237
Al (iv)	1.777	1.819	1.738	1.932	1.737	1.802	1.792	1.795	1.875	1.954	1.781	1.808	1.759	1.695
Al (vi)	0.211	0.205	0.111	0.100	0.152	0.127	0.078	0.128	0.162	0.197	0.123	0.163	0.111	0.104
Fe ²⁺	0.227	0.228	0.277	0.352	0.247	0.196	0.150	0.174	0.390	0.626	0.109	0.336	0.155	0.109
Fe ³⁺	0.831	0.830	0.915	0.991	0.897	0.889	0.954	0.855	0.958	0.923	0.920	0.817	1.003	0.992
Mn	0.010	0.012	0.012	0.014	0.008	0.010	0.013	0.013	0.012	0.016	0.010	0.013	0.012	0.012
Mg	3.461	3.459	3.441	3.255	3.422	3.480	3.518	3.565	3.228	2.964	3.570	3.399	3.478	3.545
Ca	1.690	1.715	1.700	1.703	1.681	1.697	1.694	1.740	1.707	1.717	1.688	1.751	1.663	1.651
Na _(B)	0.310	0.285	0.300	0.297	0.319	0.303	0.306	0.260	0.293	0.283	0.312	0.249	0.337	0.349
Na _(A)	0.412	0.424	0.422	0.467	0.370	0.394	0.387	0.428	0.439	0.463	0.408	0.424	0.396	0.371
K	0.119	0.117	0.102	0.098	0.107	0.108	0.105	0.121	0.109	0.105	0.117	0.116	0.104	0.103
Cr	0.005	0.005	0.000	0.004	0.017	0.007	0.000	0.006	0.000	0.000	0.012	0.007	0.000	0.001
Total	15.531	15.541	15.525	15.565	15.478	15.502	15.492	15.549	15.548	15.569	15.525	15.541	15.500	15.474
$(Na + K)_A$	0.531	0.541	0.525	0.565	0.478	0.502	0.492	0.549	0.548	0.569	0.525	0.541	0.500	0.474
$(Ca + Na)_B$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
$Mg^{2+}/(Mg^{2+}+Fe_T)$	0.766	0.766	0.743	0.708	0.749	0.762	0.761	0.776	0.705	0.657	0.776	0.747	0.750	0.763

¹Kakanui hornblende values reported by Jarosewich et al. (1980). ²Values obtained for the Kakanui hornblende are composites of 5 spot analyses run before and after unknown samples. All unknowns and KNUI were corrected by deviation from standards JDF and A99. Cations were calculated on the basis of 23 oxygens with all Fe as Fe²⁺. Cation totals were normalized to (Na+Ca+K) = 13 and Na_(B) is calculated following Leake et al. (1997); Fe^{2+}/Fe^{3+} ratio is estimated following Droop (1987); c = core, r = rim.

Major element an	nphibole an	alyses fro	m selected	l Pircas N	legras and	lesites							
analysis #	148	149	150	151	152	153	201	202	203	204	221	222	223
type	r	r	с	с	r	r	с	с	r	r	с	с	r
sample	427-4	427-4	427-7	427-7	427-7	427-7	324-1	324-1	324-1	324-1	324-3	324-3	324-3
SiO ₂	44.25	43.54	43.24	43.40	43.59	43.67	43.16	43.19	43.40	43.38	43.47	43.64	42.61
TiO ₂	2.37	2.35	2.09	1.97	2.26	2.23	2.49	2.40	2.57	2.47	2.28	2.24	3.04
Al_2O_3	10.77	10.96	11.59	11.75	11.15	11.08	12.39	12.32	11.85	11.85	12.41	12.68	12.17
FeO	10.29	10.66	7.75	7.58	8.32	7.84	8.95	8.48	8.79	8.97	9.36	9.18	10.17
MnO	0.11	0.12	0.09	0.06	0.09	0.08	0.15	0.11	0.12	0.12	0.11	0.12	0.06
MgO	16.40	16.41	16.52	16.68	16.80	16.76	16.20	16.20	16.20	16.22	15.85	15.97	15.73
CaO	11.06	10.88	11.04	10.87	11.21	11.25	11.28	11.45	11.50	11.34	11.12	11.18	12.12
Na ₂ O	2.69	2.66	2.58	2.61	2.49	2.41	2.65	2.65	2.43	2.50	2.35	2.40	2.56
K ₂ O	0.56	0.56	0.71	0.76	0.65	0.65	0.72	0.70	0.62	0.67	0.70	0.71	0.59
Cr ₂ O ₃	0.00	0.01	0.72	1.23	0.18	0.23	0.38	0.50	0.25	0.33	0.14	0.17	0.09
Total	98.50	98.15	96.34	96.92	96.76	96.20	98.36	98.00	97.71	97.87	97.79	98.29	99.13
Si	6.262	6.173	6.229	6.203	6.251	6.295	6.120	6.153	6.193	6.180	6.178	6.169	6.066
Ti	0.253	0.250	0.227	0.211	0.244	0.241	0.266	0.257	0.276	0.265	0.244	0.238	0.325
Al (iv)	1.738	1.827	1.771	1.797	1.749	1.705	1.880	1.847	1.807	1.820	1.822	1.831	1.934
Al (vi)	0.058	0.004	0.197	0.183	0.135	0.176	0.189	0.221	0.186	0.170	0.257	0.280	0.108
Fe ²⁺	0.237	0.081	0.158	0.051	0.153	0.198	0.232	0.313	0.309	0.266	0.213	0.204	0.562
Fe ³⁺	0.981	1.182	0.776	0.855	0.845	0.747	0.830	0.697	0.740	0.803	0.899	0.880	0.649
Mn	0.013	0.014	0.011	0.007	0.011	0.010	0.018	0.013	0.015	0.014	0.013	0.014	0.007
Mg	3.460	3.468	3.548	3.554	3.591	3.601	3.424	3.442	3.447	3.445	3.358	3.364	3.338
Ca	1.678	1.654	1.706	1.667	1.724	1.739	1.715	1.749	1.759	1.733	1.695	1.694	1.851
Na _(B)	0.322	0.346	0.294	0.333	0.276	0.261	0.285	0.251	0.241	0.267	0.305	0.306	0.149
Na _(A)	0.415	0.385	0.426	0.391	0.417	0.414	0.444	0.481	0.430	0.425	0.343	0.353	0.558
K	0.102	0.101	0.130	0.139	0.119	0.119	0.129	0.128	0.112	0.123	0.126	0.129	0.107
Cr	0.000	0.001	0.083	0.139	0.021	0.027	0.042	0.056	0.028	0.037	0.016	0.019	0.010
Total	15.517	15.486	15.557	15.530	15.536	15.533	15.573	15.608	15.543	15.547	15.469	15.481	15.665
$(Na + K)_A$	0.517	0.486	0.557	0.530	0.536	0.533	0.573	0.608	0.543	0.547	0.469	0.481	0.665
$(Ca + Na)_B$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
$Mg^{2+}/(Mg^{2+}+Fe_T)$	0.740	0.733	0.792	0.797	0.783	0.792	0.763	0.773	0.767	0.763	0.751	0.756	0.734

¹Kakanui hornblende values reported by Jarosewich et al. (1980). ²Values obtained for the Kakanui hornblende are composites of 5 spot analyses run before and after unknown samples. All unknowns and KNUI were corrected by deviation from standards JDF and A99. Cations were calculated on the basis of 23 oxygens with all Fe as Fe²⁺. Cation totals were normalized to (Na+Ca+K) = 13 and Na_(B) is calculated following Leake et al. (1997); Fe²⁺/Fe³⁺ ratio is estimated following Droop (1987); c = core, r = rim.

Major element an	nphibole an	alyses fro	m selected	l Pircas N	legras and	lesites							
analysis #	224	234	235	236	237	250	251	252	253	1	2	3	4
type	r	с	с	r	r	с	с	r	r	с	с	с	с
sample	324-3	324-6	324-6	324-6	324-6	324-7	324-7	324-7	324-7	412-3	412-3	412-3	412-3
SiO ₂	42.49	43.00	43.21	43.17	43.19	42.67	44.29	43.73	42.23	43.30	43.04	42.86	42.89
TiO ₂	2.63	2.37	2.39	2.46	2.44	2.42	2.17	2.58	2.98	1.82	1.80	1.90	2.08
Al_2O_3	12.59	12.40	12.22	11.94	12.11	12.98	11.62	11.61	11.98	12.21	12.35	12.65	12.48
FeO	12.09	9.54	9.96	8.54	8.66	10.22	9.02	8.75	10.89	8.40	7.85	7.85	8.77
MnO	0.17	0.16	0.11	0.08	0.09	0.10	0.10	0.11	0.11	0.12	0.12	0.13	0.14
MgO	14.03	15.43	15.64	16.33	16.29	15.22	16.55	16.47	15.38	16.54	16.37	16.71	16.58
CaO	11.78	11.35	11.18	11.53	11.36	10.84	11.07	11.68	11.54	11.71	11.87	11.72	11.48
Na ₂ O	2.34	2.54	2.56	2.63	2.46	2.49	2.56	2.50	2.40	2.61	2.55	2.48	2.46
K ₂ O	0.87	0.75	0.74	0.67	0.66	0.75	0.69	0.64	0.61	0.69	0.73	0.68	0.77
Cr ₂ O ₃	0.00	0.09	0.05	0.40	0.46	0.03	0.10	0.29	0.02	0.75	0.98	0.95	0.22
Total	98.98	97.63	98.04	97.75	97.71	97.72	98.17	98.35	98.14	98.16	97.67	97.94	97.87
Si	6.105	6.172	6.160	6.170	6.153	6.087	6.259	6.211	6.051	6.156	6.162	6.087	6.094
Ti	0.284	0.256	0.256	0.265	0.262	0.259	0.231	0.275	0.321	0.195	0.194	0.203	0.222
Al (iv)	1.895	1.828	1.840	1.830	1.847	1.913	1.741	1.789	1.949	1.844	1.838	1.913	1.906
Al (vi)	0.236	0.268	0.213	0.181	0.186	0.269	0.193	0.154	0.074	0.202	0.246	0.205	0.183
Fe ²⁺	0.802	0.446	0.335	0.331	0.216	0.240	0.172	0.349	0.399	0.246	0.334	0.113	0.104
Fe ³⁺	0.650	0.700	0.852	0.689	0.816	0.979	0.894	0.691	0.906	0.753	0.605	0.819	0.938
Mn	0.021	0.019	0.013	0.009	0.011	0.011	0.012	0.013	0.014	0.015	0.014	0.016	0.017
Mg	3.006	3.301	3.325	3.480	3.459	3.237	3.488	3.487	3.284	3.505	3.495	3.538	3.512
Ca	1.814	1.747	1.709	1.767	1.736	1.659	1.678	1.779	1.773	1.786	1.823	1.785	1.749
Na _(B)	0.186	0.253	0.291	0.233	0.264	0.341	0.322	0.221	0.227	0.214	0.177	0.215	0.251
Na _(A)	0.466	0.454	0.415	0.496	0.414	0.347	0.379	0.468	0.440	0.504	0.532	0.469	0.428
Κ	0.160	0.138	0.134	0.123	0.120	0.136	0.124	0.115	0.111	0.125	0.133	0.122	0.140
Cr	0.000	0.010	0.006	0.045	0.052	0.004	0.011	0.032	0.003	0.085	0.111	0.107	0.024
Total	15.626	15.592	15.548	15.619	15.534	15.484	15.504	15.584	15.552	15.630	15.665	15.591	15.567
$(Na + K)_A$	0.626	0.592	0.548	0.619	0.534	0.484	0.504	0.584	0.552	0.630	0.665	0.591	0.567
$(Ca + Na)_B$	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
$Mg^{2+}/(Mg^{2+}+Fe_T)$	0.674	0.742	0.737	0.773	0.770	0.726	0.766	0.770	0.716	0.778	0.788	0.791	0.771

Cations were calculated on the basis of 23 oxygens with all Fe as Fe^{2+} . Cation totals were normalized to (Na+Ca+K) = 13 and $Na_{(B)}$ is calculated following Leake et al. (1997); Fe^{2+}/Fe^{3+} ratio is estimated following Droop (1987); c = core, r = rim.

Maje	or element cli	nopyroxene a	nalyses	from sele	cted Pirc	as Negras,	Dos Herm	anos, and	Valle An	cho lavas				
	analysis #						27	28	29	30	31	32	33	34
	type						с	с	r	r	с	c	r	r
	sample	PX1-actual	PX1av ²	Meas/Act	PX1av ²	Meas/Act	428-1	428-1	428-1	428-1	428-2	428-2	428-2	428-2
SiO ₂		53.94	53.99	1.00	54.12	1.00	50.60	51.03	49.06	49.61	50.11	50.81	49.01	50.34
TiO ₂		0.26	0.24	0.93	0.25	0.97	0.74	0.76	1.21	1.03	0.76	0.66	1.32	0.74
Al_2O_3		0.66	0.73	1.10	0.63	0.96	4.39	3.19	4.59	4.02	4.51	4.10	4.59	3.24
FeO		2.93	2.98	1.02	3.13	1.07	6.82	6.20	7.84	7.18	6.75	6.92	7.75	6.82
MnO		0.07	0.07	0.95	0.09	1.24	0.16	0.18	0.16	0.14	0.13	0.14	0.14	0.17
MgO		16.93	16.71	0.99	16.61	0.98	14.71	15.63	14.46	14.69	14.54	14.93	14.57	15.50
CaO		24.55	25.32	1.03	25.35	1.03	21.64	22.53	22.06	21.93	22.30	21.59	22.14	22.69
Na ₂ O		0.24	0.29	1.21	0.30	1.26	0.66	0.41	0.42	0.43	0.67	0.67	0.41	0.43
K_2O		0.01	0.00	0.14	0.00	0.09	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.01
Cr_2O_3		0.21	0.20	0.95	0.18	0.86	0.50	0.30	0.07	0.12	0.58	0.36	0.08	0.07
Total		99.80	100.53		100.67		100.22	100.22	99.89	99.18	100.35	100.18	100.01	100.02
Si							1.857	1.869	1.814	1.844	1.837	1.864	1.810	1.849
Ti							0.021	0.021	0.034	0.029	0.021	0.018	0.037	0.021
Al (iv)							0.143	0.131	0.186	0.156	0.163	0.136	0.190	0.140
Al (vi)							0.047	0.007	0.014	0.020	0.032	0.041	0.010	0.000
Fe^{2^+}							0.122	0.088	0.109	0.117	0.088	0.117	0.105	0.059
Fe ³⁺							0.087	0.102	0.133	0.106	0.119	0.096	0.134	0.150
Mn							0.005	0.005	0.005	0.004	0.004	0.004	0.004	0.005
Mg							0.805	0.854	0.797	0.814	0.795	0.817	0.802	0.849
Ca							0.852	0.885	0.875	0.874	0.877	0.849	0.876	0.894
Na							0.047	0.029	0.030	0.031	0.047	0.048	0.029	0.031
Κ							0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.001
Cr							0.015	0.009	0.002	0.004	0.017	0.010	0.002	0.002
Total							4.029	4.034	4.045	4.036	4.040	4.032	4.045	4.051
En							52.2	53.2	53.4	52.2	53.9	52.6	53.6	55.9
Fs							7.9	5.5	7.3	7.5	5.9	7.5	7.0	3.9
Wo							39.9	41.3	39.3	40.3	40.2	39.9	39.4	40.1

APPENDIX 6

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe^{2+} . The Fe^{2+}/Fe^{3+} ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major element cli	nopyroxen	e analyse	s from sel	ected Pir	cas Negra	as, Dos H	ermanos	, and Val	le Ancho	lavas				
analysis #	35	36	37	38	39	40	41	42	43	44	45	46	47	48
type	с	c	r	r	с	с	r	r	c	с	r	r	c	c
sample	428-3	428-3	428-3	428-3	428-4	428-4	428-4	428-4	428-5	428-5	428-5	428-5	428-6	428-6
SiO ₂	50.21	49.54	48.92	50.19	49.76	49.69	46.83	46.61	51.33	50.55	49.57	49.54	50.34	50.40
TiO ₂	0.66	0.77	1.14	1.03	0.69	0.87	1.64	1.73	0.42	0.64	0.81	0.81	0.68	0.67
Al_2O_3	4.28	4.80	4.16	3.72	4.45	4.64	5.98	5.59	2.70	3.99	3.11	3.13	4.30	4.24
FeO	6.81	7.01	7.78	7.05	7.18	7.46	9.37	9.00	6.93	6.64	7.72	7.82	6.72	7.29
MnO	0.18	0.16	0.19	0.17	0.15	0.17	0.16	0.15	0.12	0.17	0.20	0.18	0.12	0.18
MgO	14.94	14.53	14.68	14.93	14.54	14.50	13.30	13.66	15.93	14.89	15.43	15.07	14.93	14.59
CaO	21.72	21.30	22.04	22.37	21.70	21.53	22.04	21.93	21.62	22.16	21.78	22.00	21.50	21.57
Na ₂ O	0.63	0.71	0.41	0.40	0.68	0.67	0.45	0.42	0.54	0.66	0.37	0.33	0.69	0.70
K ₂ O	0.00	0.00	0.03	0.01	0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.02	0.00	0.00
Cr ₂ O ₃	0.41	0.61	0.00	0.06	0.57	0.21	0.02	0.00	0.24	0.32	0.01	0.03	0.36	0.17
Total	99.83	99.42	99.35	99.91	99.72	99.74	99.80	99.10	99.83	100.00	98.99	98.93	99.63	99.81
Si	1.848	1.833	1.817	1.851	1.837	1.834	1.743	1.745	1.886	1.857	1.844	1.847	1.855	1.858
Ti	0.018	0.021	0.032	0.029	0.019	0.024	0.046	0.049	0.012	0.018	0.023	0.023	0.019	0.019
Al (iv)	0.152	0.167	0.182	0.149	0.163	0.166	0.257	0.246	0.114	0.143	0.136	0.138	0.145	0.142
Al (vi)	0.033	0.042	0.000	0.013	0.030	0.036	0.006	0.000	0.002	0.029	0.000	0.000	0.041	0.042
Fe ²⁺	0.093	0.101	0.090	0.111	0.096	0.106	0.101	0.083	0.093	0.088	0.081	0.097	0.102	0.117
Fe ³⁺	0.116	0.116	0.151	0.106	0.126	0.124	0.191	0.199	0.120	0.116	0.158	0.146	0.105	0.108
Mn	0.006	0.005	0.006	0.005	0.005	0.005	0.005	0.005	0.004	0.005	0.006	0.006	0.004	0.006
Mg	0.819	0.801	0.813	0.821	0.800	0.798	0.738	0.762	0.872	0.815	0.855	0.838	0.820	0.802
Ca	0.857	0.845	0.878	0.885	0.859	0.852	0.880	0.880	0.852	0.873	0.869	0.880	0.850	0.852
Na	0.045	0.051	0.030	0.028	0.048	0.048	0.032	0.031	0.038	0.047	0.027	0.024	0.049	0.050
K	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000
Cr	0.012	0.018	0.000	0.002	0.017	0.006	0.000	0.000	0.007	0.009	0.000	0.001	0.010	0.005
Total	4.039	4.039	4.051	4.036	4.042	4.042	4.065	4.067	4.040	4.039	4.054	4.049	4.035	4.036
En	54.5	54.6	54.6	51.9	54.4	53.7	55.1	56.7	54.3	53.6	56.4	54.6	53.8	52.5
Fs	6.2	6.9	6.1	7.0	6.5	7.2	7.5	6.2	5.8	5.8	5.4	6.4	6.7	7.6
Wo	39.3	38.6	39.3	41.0	39.1	39.1	37.4	37.2	40.0	40.6	38.2	39.0	39.5	39.9

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe^{2+} . The Fe^{2+}/Fe^{3+} ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major element c	linopyroxe	ene analy	ses from s	selected I	Pircas Neg	ras, Dos He	ermanos,	and Valle	e Ancho l	avas				
analysis #	49	50	51	52	53	13	14	15	16	17	18	19	20	21
type	r	r	с	c	с	с	с	r	r	c	с	r	r	c
sample	428-6	428-6	428-7	428-7	428-7	81-1	81-1	81-1	81-1	81-2	81-2	81-2	81-2	81-3
SiO ₂	51.07	51.15	52.67	53.10	53.21	50.83	50.76	51.92	50.98	52.48	52.44	50.47	49.79	52.60
TiO ₂	0.51	0.50	0.19	0.24	0.22	0.73	0.90	0.64	0.73	0.50	0.48	0.83	0.97	0.34
Al_2O_3	3.12	2.87	0.75	0.56	0.71	3.88	4.27	3.21	3.08	1.78	2.15	3.77	3.99	3.15
FeO	6.48	6.23	7.84	8.34	7.58	6.75	6.80	6.34	6.09	6.88	7.01	7.16	7.13	6.90
MnO	0.14	0.12	0.14	0.22	0.20	0.13	0.10	0.14	0.12	0.16	0.16	0.16	0.15	0.15
MgO	15.23	15.32	16.07	15.72	15.99	15.26	14.97	15.67	15.41	17.03	16.19	14.97	14.75	15.52
CaO	21.92	21.94	20.75	21.25	21.19	22.16	21.64	22.01	22.49	20.52	21.23	22.27	21.95	20.37
Na ₂ O	0.59	0.59	0.54	0.52	0.52	0.61	0.60	0.48	0.43	0.28	0.38	0.37	0.44	0.77
K ₂ O	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.02	0.00
Cr ₂ O ₃	0.16	0.24	0.00	0.03	0.00	0.35	0.31	0.31	0.40	0.13	0.14	0.32	0.12	0.52
Total	99.22	98.97	98.96	99.98	99.62	100.70	100.37	100.74	99.74	99.76	100.18	100.32	99.31	100.32
Si	1.889	1.896	1.958	1.960	1.966	1.854	1.860	1.892	1.878	1.928	1.923	1.855	1.847	1.924
Ti	0.014	0.014	0.005	0.007	0.006	0.020	0.025	0.018	0.020	0.014	0.013	0.023	0.027	0.009
Al _(iv)	0.111	0.104	0.033	0.024	0.031	0.146	0.140	0.108	0.122	0.072	0.077	0.145	0.153	0.076
Al (vi)	0.025	0.021	0.000	0.000	0.000	0.020	0.044	0.030	0.011	0.005	0.016	0.018	0.022	0.060
Fe ²⁺	0.105	0.102	0.164	0.178	0.172	0.087	0.128	0.126	0.097	0.155	0.157	0.121	0.115	0.174
Fe ³⁺	0.096	0.091	0.080	0.079	0.062	0.119	0.080	0.067	0.090	0.056	0.058	0.099	0.106	0.037
Mn	0.004	0.004	0.004	0.007	0.006	0.004	0.003	0.004	0.004	0.005	0.005	0.005	0.005	0.005
Mg	0.840	0.846	0.890	0.865	0.880	0.830	0.818	0.851	0.846	0.933	0.885	0.820	0.816	0.846
Ca	0.870	0.872	0.827	0.841	0.839	0.866	0.850	0.860	0.888	0.808	0.835	0.878	0.873	0.799
Na	0.042	0.042	0.039	0.037	0.037	0.043	0.043	0.034	0.031	0.020	0.027	0.027	0.032	0.055
K	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Cr	0.005	0.007	0.000	0.001	0.000	0.010	0.009	0.009	0.012	0.004	0.004	0.009	0.004	0.015
Total	4.032	4.030	4.027	4.027	4.021	4.040	4.027	4.023	4.030	4.019	4.019	4.033	4.036	4.012
En	52.1	51.9	49.7	48.3	48.0	54.1	51.8	51.3	52.1	52.1	50.5	52.1	52.3	49.1
Fs	6.5	6.3	9.1	9.9	9.4	5.7	8.1	7.6	6.0	8.7	8.9	7.7	7.4	10.1
Wo	41.4	41.9	41.2	41.8	42.6	40.2	40.1	41.1	41.8	39.2	40.6	40.2	40.3	40.8

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe²⁺. The Fe²⁺/Fe³⁺ ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major eleme	ent clinop	yroxene	analyses f	rom seleo	cted Pirca	is Negras	, Dos Her	manos, a	nd Valle	Ancho la	ivas				
analysis #	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
type	с	r	r	с	с	r	r	с	с	r	r	с	с	r	r
sample	81-3	81-3	81-3	81-4	81-4	81-4	81-4	81-5	81-5	81-5	81-5	81-6	81-6	81-6	81-6
SiO ₂	52.29	50.28	51.28	51.29	52.08	52.09	47.54	52.57	51.84	52.33	50.91	52.29	51.58	50.80	51.92
TiO ₂	0.37	0.75	0.60	0.64	0.46	0.50	1.57	0.53	0.61	0.58	0.66	0.62	0.59	0.72	0.55
Al_2O_3	3.35	4.78	4.11	4.17	2.94	2.32	6.30	1.91	2.22	1.86	3.34	3.81	3.39	4.19	3.70
FeO	6.34	7.47	6.68	6.93	6.73	6.18	9.42	7.03	7.51	6.82	7.68	6.38	6.31	6.78	6.98
MnO	0.12	0.17	0.14	0.14	0.16	0.13	0.21	0.15	0.19	0.17	0.15	0.13	0.14	0.12	0.19
MgO	15.61	14.59	15.12	15.14	15.97	15.76	13.29	16.90	16.50	16.78	15.02	15.19	15.49	15.05	15.55
CaO	21.01	21.36	21.37	21.52	21.18	21.85	21.67	21.39	20.93	20.88	22.36	21.68	21.84	21.38	21.21
Na ₂ O	0.85	0.64	0.65	0.67	0.65	0.36	0.50	0.25	0.27	0.27	0.39	0.63	0.59	0.64	0.64
K ₂ O	0.00	0.01	0.01	0.00	0.00	0.02	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00
Cr_2O_3	0.45	0.15	0.31	0.42	0.33	0.17	0.04	0.21	0.06	0.13	0.00	0.39	0.39	0.43	0.37
Total	100.40	100.21	100.28	100.92	100.48	99.38	100.56	100.95	100.12	99.83	100.54	101.12	100.33	100.12	101.10
Si	1.906	1.847	1.877	1.867	1.899	1.925	1.756	1.911	1.903	1.923	1.867	1.899	1.886	1.864	1.886
Ti	0.010	0.021	0.017	0.018	0.013	0.014	0.044	0.015	0.017	0.016	0.018	0.017	0.016	0.020	0.015
Al (iv)	0.094	0.153	0.123	0.133	0.101	0.075	0.244	0.082	0.096	0.077	0.133	0.101	0.114	0.136	0.114
Al (vi)	0.050	0.054	0.055	0.046	0.026	0.026	0.031	0.000	0.000	0.004	0.012	0.062	0.032	0.046	0.044
Fe ²⁺	0.122	0.130	0.133	0.125	0.119	0.147	0.130	0.136	0.149	0.152	0.123	0.156	0.112	0.125	0.136
Fe ³⁺	0.071	0.100	0.072	0.086	0.086	0.044	0.160	0.078	0.082	0.058	0.112	0.038	0.081	0.083	0.076
Mn	0.004	0.005	0.004	0.004	0.005	0.004	0.007	0.005	0.006	0.005	0.005	0.004	0.004	0.004	0.006
Mg	0.848	0.799	0.825	0.822	0.868	0.868	0.732	0.916	0.903	0.920	0.822	0.822	0.844	0.823	0.842
Ca	0.821	0.841	0.839	0.840	0.828	0.866	0.858	0.834	0.824	0.823	0.879	0.844	0.856	0.841	0.826
Na	0.060	0.046	0.046	0.047	0.046	0.026	0.036	0.018	0.019	0.020	0.028	0.045	0.042	0.045	0.045
K	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Cr	0.013	0.004	0.009	0.012	0.010	0.005	0.001	0.006	0.002	0.004	0.000	0.011	0.011	0.012	0.011
Total	4.024	4.034	4.024	4.029	4.029	4.015	4.054	4.026	4.027	4.019	4.038	4.013	4.027	4.028	4.025
En	52.1	52.7	51.9	52.5	52.8	49.5	53.6	52.9	52.4	51.6	51.7	48.2	52.2	52.5	52.2
Fs	7.5	8.5	8.4	8.0	7.2	8.4	9.5	7.8	8.7	8.5	7.8	9.1	6.9	8.0	8.5
Wo	40.4	38.8	39.7	39.5	39.9	42.1	36.9	39.2	38.9	39.8	40.5	42.7	40.8	39.5	39.3

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe²⁺. The Fe²⁺/Fe³⁺ ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major element c	linopyroxe	ene analys	ses from s	selected P	ircas Ne	gras, Dos	Herman	os, and Va	alle Ancho lav	vas				
analysis #	66	67	68	69	78	79	80	81	96	97	98	99	100	101
type	c	c	r	r	c	c	с	r	cum	cum	cum	cum	cum	cum
sample	101-1	101-1	101-1	101-1	101-2	101-2	101-2	101-2	309-1	309-1	309-2	309-2	309-3	309-3
SiO ₂	51.11	51.70	49.41	47.52	48.27	46.60	49.13	49.75	52.24	52.47	52.12	52.09	50.22	51.70
TiO ₂	0.58	0.53	1.20	1.71	1.28	1.82	1.33	0.97	0.41	0.40	0.42	0.45	0.67	0.39
Al_2O_3	2.18	2.14	3.62	5.65	5.60	6.90	3.86	3.40	2.77	2.47	2.78	2.89	5.03	3.06
FeO	6.61	6.57	10.20	9.98	7.54	8.64	9.93	8.25	6.92	7.16	7.77	7.43	9.21	8.43
MnO	0.17	0.15	0.31	0.23	0.14	0.14	0.28	0.22	0.15	0.13	0.16	0.16	0.20	0.20
MgO	16.32	16.56	14.37	13.52	14.09	13.38	14.37	15.27	15.77	16.13	15.46	15.66	14.76	16.02
CaO	21.35	20.98	19.07	20.00	22.19	21.59	19.48	20.83	20.57	20.32	21.27	20.85	19.06	19.33
Na ₂ O	0.21	0.22	0.36	0.40	0.33	0.34	0.35	0.18	0.64	0.59	0.68	0.70	0.91	0.66
K ₂ O	0.01	0.00	0.02	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Cr ₂ O ₃	0.28	0.24	0.03	0.10	0.26	0.18	0.01	0.04	0.25	0.28	0.17	0.19	0.04	0.19
Total	98.83	99.08	98.58	99.13	99.70	99.58	98.75	98.92	99.72	99.95	100.83	100.42	100.10	99.98
Si	1.899	1.914	1.865	1.785	1.789	1.736	1.850	1.859	1.922	1.926	1.901	1.905	1.847	1.900
Ti	0.016	0.015	0.034	0.048	0.036	0.051	0.038	0.027	0.011	0.011	0.012	0.012	0.018	0.011
Al _(iv)	0.096	0.086	0.135	0.215	0.211	0.264	0.150	0.141	0.078	0.074	0.099	0.095	0.153	0.100
Al _(vi)	0.000	0.008	0.026	0.035	0.034	0.040	0.021	0.008	0.042	0.033	0.021	0.029	0.065	0.032
Fe ²⁺	0.124	0.147	0.255	0.205	0.112	0.128	0.233	0.167	0.161	0.167	0.139	0.141	0.168	0.171
Fe ⁵⁺	0.081	0.057	0.067	0.109	0.121	0.141	0.079	0.091	0.052	0.053	0.097	0.086	0.115	0.089
Mn	0.005	0.005	0.010	0.007	0.004	0.004	0.009	0.007	0.005	0.004	0.005	0.005	0.006	0.006
Mg	0.904	0.914	0.809	0.757	0.779	0.743	0.806	0.851	0.865	0.883	0.841	0.854	0.809	0.878
Ca	0.851	0.833	0.772	0.806	0.882	0.863	0.787	0.834	0.811	0.800	0.832	0.817	0.752	0.762
Na	0.015	0.015	0.026	0.029	0.024	0.024	0.026	0.013	0.046	0.042	0.048	0.050	0.065	0.047
K	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.008	0.007	0.001	0.003	0.008	0.005	0.000	0.001	0.007	0.008	0.005	0.006	0.001	0.005
Total	4.027	4.019	4.023	4.037	4.041	4.048	4.027	4.031	4.018	4.018	4.033	4.029	4.039	4.030
En	53.1	52.1	48.3	50.5	53.9	54.3	49.0	51.8	50.5	50.9	51.3	51.6	53.8	53.2
Fs	7.3	8.3	15.2	13.7	7.8	9.4	14.2	10.2	9.4	9.6	8.5	8.5	11.2	10.3
Wo	39.6	39.6	36.5	35.8	38.3	36.3	36.9	38.0	40.1	39.5	40.2	39.8	35.0	36.5

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe²⁺. The Fe²⁺/Fe³⁺ ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major element o	clinopyrox	ene analy	ses from	selected I	Pircas Neg	gras, Dos	Herman	os, and V	alle Anch	no lavas				
analysis #	102	103	104	105	106	107	112	113	114	116	121	122	123	134
type	cum	cum	cum	cum	cum	cum	с	с	с	r-hbde	r-qz	r-qz	r-qz	r-qz
sample	309-4	309-4	309-5	309-5	309-6	309-6	309-7	309-7	309-7	309-8	309-9	309-9	309-9	427-1
SiO ₂	50.02	50.35	53.11	52.80	51.95	52.13	51.37	50.53	50.95	51.46	53.30	53.11	53.37	54.55
TiO ₂	0.75	0.81	0.16	0.18	0.37	0.28	0.60	0.71	0.67	0.73	0.19	0.37	0.34	0.15
Al_2O_3	4.74	4.82	0.31	0.34	1.85	1.07	4.27	4.80	4.59	3.83	0.24	1.65	1.63	0.23
FeO	7.25	7.72	8.92	9.01	7.78	8.41	7.56	8.70	7.58	7.50	8.51	7.59	8.31	8.40
MnO	0.12	0.13	0.21	0.22	0.16	0.17	0.18	0.19	0.11	0.17	0.26	0.27	0.21	0.16
MgO	14.42	14.30	14.97	14.75	14.91	14.97	14.89	14.14	14.78	14.85	14.80	14.73	14.69	14.50
CaO	21.01	21.47	21.94	21.94	22.60	22.31	20.85	20.74	20.76	19.62	22.04	21.03	20.54	21.13
Na ₂ O	0.83	0.82	0.39	0.47	0.42	0.40	0.74	0.87	0.78	0.72	0.35	0.39	0.37	0.34
K ₂ O	0.00	0.00	0.00	0.01	0.01	0.04	0.00	0.01	0.00	0.04	0.02	0.09	0.10	0.02
Cr ₂ O ₃	0.42	0.27	0.00	0.00	0.04	0.01	0.12	0.05	0.26	0.38	0.01	0.00	0.01	0.00
Total	99.56	100.70	100.01	99.71	100.10	99.79	100.57	100.73	100.47	99.31	99.71	99.23	99.59	99.48
Si	1.848	1.842	1.970	1.965	1.917	1.934	1.878	1.851	1.864	1.908	1.984	1.980	1.986	2.038
Ti	0.021	0.022	0.004	0.005	0.010	0.008	0.016	0.020	0.018	0.020	0.005	0.010	0.010	0.004
Al _(iv)	0.152	0.158	0.013	0.015	0.081	0.047	0.122	0.149	0.136	0.092	0.011	0.020	0.014	0.000
Al _(vi)	0.054	0.049	0.000	0.000	0.000	0.000	0.062	0.058	0.062	0.076	0.000	0.053	0.058	0.010
Fe ²⁺	0.120	0.122	0.211	0.201	0.147	0.160	0.156	0.154	0.148	0.216	0.229	0.237	0.259	0.262
Fe ³⁺	0.105	0.114	0.066	0.079	0.093	0.101	0.076	0.112	0.084	0.017	0.036	0.000	0.000	0.000
Mn	0.004	0.004	0.007	0.007	0.005	0.005	0.006	0.006	0.004	0.005	0.008	0.008	0.007	0.005
Mg	0.794	0.780	0.828	0.818	0.821	0.828	0.812	0.772	0.807	0.821	0.821	0.819	0.815	0.808
Ca	0.832	0.842	0.873	0.876	0.894	0.887	0.817	0.814	0.815	0.780	0.880	0.841	0.820	0.846
Na	0.059	0.058	0.028	0.034	0.030	0.029	0.052	0.061	0.055	0.051	0.025	0.028	0.027	0.025
K	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.002	0.001	0.005	0.005	0.001
Cr	0.012	0.008	0.000	0.000	0.001	0.000	0.003	0.001	0.007	0.011	0.000	0.000	0.000	0.000
Total	4.035	4.039	4.022	4.027	4.031	4.034	4.025	4.038	4.028	4.006	4.012	3.993	3.989	3.977
En	53.0	52.5	45.3	45.6	48.4	48.5	51.2	51.4	51.9	49.0	43.3	45.9	46.0	43.0
Fs	8.0	8.2	11.5	11.2	8.7	9.4	9.8	10.3	9.5	12.9	12.1	13.3	14.6	14.0
Wo	39.0	39.3	43.1	43.2	43.0	42.2	39.0	38.3	38.6	38.1	44.7	40.8	39.4	43.0

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe^{2+} . The Fe^{2+}/Fe^{3+} ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major element	clinopyro	oxene ana	alyses fro	m selecte	ed Pircas	Negras, I	Dos Herma	nos, and	Valle A	ncho lava	S				
analysis #	135	136	137	143	144	145	262	263	264	265	266	267	268	269	270
type	r-qz	r-qz	r-qz	r-qz	r-qz	r-qz	с	с	c	c	c	c	r	r	c
sample	427-1	427-1	427-1	427-2	427-2	427-2	412-1	412-1	412-1	412-1	412-2	412-2	412-2	412-2	412-3
SiO ₂	53.78	53.63	52.89	52.79	53.05	52.85	51.98	52.36	51.93	53.49	46.62	45.84	51.94	51.73	50.00
TiO ₂	0.19	0.43	0.25	0.20	0.23	0.15	0.43	0.43	0.40	0.14	2.26	2.85	0.74	0.81	1.50
Al_2O_3	0.26	1.24	0.88	0.54	0.26	0.33	3.47	3.29	2.81	2.69	6.56	7.05	1.13	1.28	4.38
FeO	8.54	7.46	8.02	8.35	8.96	7.93	6.22	5.82	5.58	6.38	6.64	6.74	8.65	8.10	6.80
MnO	0.21	0.23	0.25	0.26	0.24	0.28	0.15	0.17	0.14	0.28	0.12	0.13	0.35	0.37	0.19
MgO	14.75	14.27	15.34	15.61	15.19	15.44	16.55	16.66	16.59	16.22	13.63	13.18	15.90	15.85	15.27
CaO	21.06	20.94	21.10	21.17	21.00	21.74	21.21	21.15	21.47	21.48	23.00	22.91	20.47	20.12	21.22
Na ₂ O	0.36	0.36	0.38	0.37	0.44	0.32	0.51	0.50	0.48	0.47	0.67	0.62	0.46	0.48	0.56
K ₂ O	0.01	0.03	0.03	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02
Cr ₂ O ₃	0.04	0.01	0.00	0.00	0.00	0.00	0.22	0.23	0.33	0.19	0.16	0.22	0.00	0.01	0.16
Total	99.20	98.60	99.14	99.32	99.40	99.06	100.74	100.60	99.74	101.34	99.65	99.55	99.64	98.77	100.11
Si	2.013	2.018	1.972	1.964	1.978	1.972	1.885	1.900	1.901	1.934	1.725	1.704	1.926	1.932	1.837
Ti	0.005	0.012	0.007	0.006	0.006	0.004	0.012	0.012	0.011	0.004	0.063	0.080	0.021	0.023	0.042
Al (iv)	0.000	0.000	0.028	0.024	0.011	0.015	0.115	0.100	0.099	0.066	0.275	0.296	0.049	0.057	0.163
Al _(vi)	0.011	0.055	0.010	0.000	0.000	0.000	0.033	0.041	0.022	0.049	0.011	0.012	0.000	0.000	0.026
Fe^{2^+}	0.267	0.235	0.217	0.196	0.227	0.190	0.101	0.112	0.091	0.157	0.024	0.045	0.176	0.185	0.118
Fe ³⁺	0.000	0.000	0.033	0.064	0.053	0.057	0.088	0.064	0.080	0.036	0.182	0.164	0.092	0.068	0.090
Mn	0.007	0.007	0.008	0.008	0.008	0.009	0.004	0.005	0.004	0.009	0.004	0.004	0.011	0.012	0.006
Mg	0.823	0.800	0.852	0.866	0.844	0.859	0.895	0.901	0.905	0.874	0.752	0.730	0.879	0.883	0.836
Ca	0.845	0.845	0.843	0.844	0.840	0.870	0.825	0.823	0.843	0.833	0.912	0.913	0.814	0.806	0.836
Na	0.026	0.026	0.028	0.027	0.032	0.023	0.036	0.035	0.034	0.033	0.048	0.045	0.033	0.035	0.040
K	0.001	0.002	0.002	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001
Cr	0.001	0.000	0.000	0.000	0.000	0.000	0.006	0.007	0.010	0.005	0.005	0.006	0.000	0.000	0.005
Total	3.992	3.971	4.011	4.022	4.018	4.019	4.029	4.022	4.027	4.012	4.061	4.055	4.031	4.023	4.030
En	43.1	45.8	45.6	47.6	45.3	46.7	55.3	54.2	54.5	50.6	57.6	55.6	50.5	49.3	52.8
Fs	14.0	13.4	11.6	10.7	12.2	10.3	6.2	6.8	5.5	9.1	1.8	3.5	10.1	10.4	7.5
Wo	42.9	40.8	42.8	41.7	42.5	43.0	38.5	39.0	40.0	40.4	40.6	41.0	39.4	40.3	39.7

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe^{2+} . The Fe^{2+}/Fe^{3+} ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major element	clinopyroz	xene anal	lyses fror	n selecte	d Pircas I	Negras, Dos	Herman	ios, and V	Valle And	ho lavas				
analysis #	271	9	10	11	12	225	226	227	228	229	230	231	232	233
type	с	cum	cum	cum	cum	с	с	c	r	r	c	с	r	r
sample	412-3	412-4	412-5	412-6	412-7	324-1	324-1	324-1	324-1	324-1	324-2	324-2	324-2	324-2
SiO ₂	47.66	52.99	53.05	53.80	52.91	51.46	51.39	51.32	51.71	51.76	51.57	51.50	52.51	51.71
TiO ₂	2.27	0.18	0.17	0.10	0.16	0.41	0.41	0.42	0.57	0.58	0.42	0.43	0.31	0.30
Al_2O_3	6.37	0.92	1.06	0.47	0.93	3.18	3.15	3.08	2.74	2.70	2.60	2.69	2.39	2.84
FeO	6.99	8.67	9.00	8.59	9.66	10.55	10.40	10.61	7.01	6.78	10.36	10.70	6.61	8.23
MnO	0.16	0.19	0.28	0.24	0.25	0.28	0.26	0.29	0.17	0.15	0.28	0.27	0.24	0.26
MgO	14.14	15.55	15.99	16.60	15.32	13.62	13.66	13.73	16.35	16.31	14.10	14.13	16.26	14.87
CaO	21.71	21.15	20.10	20.07	20.37	20.07	20.14	20.49	21.71	21.75	19.98	20.25	21.21	21.54
Na ₂ O	0.69	0.54	0.54	0.36	0.55	0.87	0.85	0.83	0.35	0.33	0.71	0.71	0.51	0.60
K ₂ O	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00
Cr ₂ O ₃	0.12	0.02	0.02	0.02	0.03	0.13	0.14	0.02	0.15	0.14	0.06	0.09	0.12	0.10
Total	100.14	100.20	100.21	100.27	100.19	100.57	100.41	100.78	100.77	100.52	100.08	100.76	100.16	100.45
Si	1.754	1.953	1.953	1.978	1.956	1.903	1.903	1.893	1.883	1.889	1.915	1.901	1.921	1.900
Ti	0.063	0.005	0.005	0.003	0.004	0.011	0.012	0.012	0.016	0.016	0.012	0.012	0.008	0.008
Al (iv)	0.246	0.040	0.046	0.021	0.041	0.097	0.097	0.107	0.117	0.111	0.085	0.099	0.079	0.100
Al (vi)	0.030	0.000	0.000	0.000	0.000	0.041	0.040	0.027	0.001	0.006	0.029	0.018	0.024	0.022
Fe ²⁺	0.077	0.184	0.200	0.220	0.221	0.235	0.231	0.212	0.108	0.114	0.239	0.225	0.131	0.152
Fe ³⁺	0.138	0.083	0.077	0.044	0.077	0.092	0.091	0.115	0.106	0.093	0.082	0.106	0.072	0.101
Mn	0.005	0.006	0.009	0.007	0.008	0.009	0.008	0.009	0.005	0.005	0.009	0.009	0.007	0.008
Mg	0.776	0.855	0.877	0.910	0.844	0.751	0.754	0.755	0.888	0.888	0.780	0.777	0.887	0.815
Ca	0.857	0.836	0.794	0.791	0.808	0.796	0.800	0.810	0.848	0.851	0.796	0.801	0.832	0.848
Na	0.049	0.038	0.039	0.026	0.040	0.062	0.061	0.059	0.025	0.023	0.051	0.050	0.036	0.043
Κ	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Cr	0.004	0.001	0.000	0.001	0.001	0.004	0.004	0.001	0.004	0.004	0.002	0.003	0.003	0.003
Total	4.047	4.028	4.026	4.015	4.026	4.031	4.031	4.039	4.036	4.031	4.028	4.036	4.024	4.034
En	55.3	48.1	49.1	48.3	47.2	46.3	46.5	47.4	54.1	53.4	46.5	47.5	52.1	50.3
Fs	5.5	10.4	11.2	11.7	12.4	14.5	14.2	13.3	6.6	6.9	14.3	13.7	7.7	9.4
Wo	39.2	41.5	39.7	39.9	40.4	39.2	39.3	39.3	39.3	39.8	39.3	38.8	40.3	40.4

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe^{2+} . The Fe^{2+}/Fe^{3+} ratio is calculated from the cation total following Droop (1987). The En = Enstatite component (Mg/Mg+Fe+Ca); Fs = Ferrosilite component (Fe/Mg+Fe+Ca); Wo = Wollastonite component (Ca/Mg+Fe+Ca) are all calculated after subtracting out non-quadrilateral components from the cation totals following Lindsley (1983), c = core, r = rim.

Major element of	clinopyroxe	ene analy	ses from a	selected la	avas			
analysis #	242	243	244	245	258	259	260	261
type	с	с	r	r	с	с	r	r
sample	324-3	324-3	324-3	324-3	324-4	324-4	324-4	324-4
SiO ₂	50.97	51.00	52.99	52.81	51.42	51.52	52.50	52.79
TiO ₂	0.50	0.46	0.38	0.37	0.38	0.34	0.26	0.27
Al_2O_3	3.28	3.34	2.02	2.24	1.96	1.85	0.86	0.87
FeO	10.85	10.67	6.31	6.34	10.32	10.10	8.95	9.48
MnO	0.32	0.31	0.12	0.15	0.30	0.30	0.33	0.33
MgO	13.17	13.41	17.10	16.87	14.08	13.90	14.74	14.73
CaO	20.03	20.08	20.85	20.66	21.08	20.97	21.52	21.62
Na ₂ O	0.85	0.89	0.42	0.42	0.58	0.62	0.39	0.36
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02
Cr_2O_3	0.05	0.03	0.37	0.38	0.03	0.00	0.00	0.03
Total	100.00	100.18	100.56	100.25	100.15	99.60	99.55	100.50
Si	1.900	1.894	1.927	1.928	1.911	1.925	1.958	1.953
Ti	0.014	0.013	0.010	0.010	0.011	0.010	0.007	0.008
Al (iv)	0.100	0.106	0.073	0.072	0.086	0.075	0.038	0.038
Al (vi)	0.044	0.040	0.014	0.024	0.000	0.006	0.000	0.000
Fe^{2+}	0.249	0.228	0.134	0.146	0.208	0.221	0.219	0.227
Fe ³⁺	0.089	0.103	0.058	0.048	0.113	0.095	0.060	0.066
Mn	0.010	0.010	0.004	0.005	0.010	0.009	0.010	0.010
Mg	0.731	0.742	0.927	0.918	0.780	0.774	0.819	0.812
Ca	0.800	0.799	0.813	0.809	0.840	0.840	0.860	0.858
Na	0.061	0.064	0.030	0.030	0.042	0.045	0.028	0.026
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Cr	0.001	0.001	0.011	0.011	0.001	0.000	0.000	0.001
Total	4.030	4.035	4.019	4.016	4.038	4.032	4.020	4.022
En	45.1	46.6	52.8	52.4	46.9	45.6	45.2	45.2
Fs	15.4	14.3	7.6	8.3	12.5	13.0	12.1	12.6
Wo	39.5	39.1	39.5	39.3	40.5	41.4	42.8	42.1

¹PX-1 values reported by Jarosewich et al. (1980). ²Values obtained for PX-1 standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and PX-1 are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe²⁺.

Major element or	thopyroxene ar	nalyses fr	om selected	Pircas Neg	gras andesites							
analysis #					, ,	205	206	207	208	211	212	213
type						с	c	r	r	r-oliv	r-oliv	с
sample	JHS-actual	JHSav ²	Meas/Act	JHSav ²	Meas/Act	324-1	324-1	324-1	324-1	324-2	324-2	324-3
SiO ₂	54.09	54.84	1.01	55.16	1.02	53.00	52.92	53.35	53.55	53.85	51.84	53.02
TiO ₂	0.17	0.10	0.58	0.10	0.56	0.17	0.17	0.20	0.20	0.41	0.41	0.18
Al ₂ O ₃	1.24	1.02	0.82	1.06	0.85	0.87	0.83	0.94	1.02	1.10	1.50	0.80
FeO	15.22	15.13	0.99	14.93	0.98	22.04	21.57	21.55	20.04	17.00	16.69	21.78
MnO	0.50	0.50	1.00	0.50	1.00	0.87	0.85	0.85	0.80	0.49	0.39	0.92
MgO	26.79	27.57	1.03	27.48	1.03	22.72	22.84	23.15	23.59	26.19	31.68	22.85
CaO	1.52	1.17	0.77	1.15	0.76	1.28	1.34	1.16	1.21	1.58	1.10	1.20
Na ₂ O		0.01		0.01		0.03	0.01	0.04	0.02	0.03	0.02	0.02
K ₂ O		0.00		0.00		0.00	0.00	0.01	0.00	0.01	0.01	0.00
Cr_2O_3	0.75	0.68	0.91	0.65	0.87	0.02	0.00	0.01	0.00	0.04	0.00	0.01
Total	100.28	101.01	1.01	101.04	1.01	100.99	100.53	101.27	100.45	100.72	103.65	100.78
Si						1.951	1.955	1.954	1.968	1.941	1.777	1.955
Ti						0.005	0.005	0.006	0.006	0.011	0.011	0.005
Al (iv)						0.038	0.036	0.040	0.032	0.047	0.061	0.035
Al (vi)						0.000	0.000	0.000	0.012	0.000	0.000	0.000
Fe ²⁺						0.627	0.620	0.617	0.605	0.463	0.112	0.626
Fe ³⁺						0.052	0.046	0.043	0.011	0.050	0.366	0.046
Mn						0.027	0.026	0.026	0.025	0.015	0.011	0.029
Mg						1.247	1.258	1.264	1.292	1.408	1.619	1.256
Ca						0.050	0.053	0.046	0.048	0.061	0.041	0.047
Na						0.002	0.001	0.003	0.002	0.002	0.002	0.001
K						0.000	0.000	0.001	0.000	0.001	0.001	0.000
Cr						0.001	0.000	0.000	0.000	0.001	0.000	0.000
Total						4.017	4.015	4.014	4.004	4.017	4.126	4.015
En						2.6	2.7	2.4	2.4	3.2	2.3	2.5
Fs						64.8	65.1	65.6	66.4	72.9	91.4	65.1
Wo						32.6	32.1	32.0	31.1	24.0	6.3	32.4

APPENDIX 7

¹Johnstown hypersthene (JSH) values reported by Jarosewich et al. (1980). ²Values obtained for JSH standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and JSH are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe^{2+} . Endmember components are the same as in Appendix 6 and are calculated following Lindsley (1983).

Major element or	thopyroxen	e analyse	s from se	lected Pi	rcas Negr	as andesi	ites				
analysis #	214	215	216	254	255	256	257	6	7	8	9
type	с	r	r	с	c	r	r	с	с	r	r
sample	324-3	324-3	324-3	324-4	324-4	324-4	324-4	412-1	412-1	412-1	412-1
SiO ₂	52.97	53.57	52.79	52.96	52.88	52.87	52.85	54.11	54.10	53.71	54.19
TiO ₂	0.18	0.19	0.19	0.19	0.17	0.18	0.19	0.19	0.21	0.22	0.19
Al_2O_3	0.79	0.97	0.85	1.21	1.18	1.19	1.26	3.06	2.98	2.89	2.75
FeO	21.79	22.38	21.05	21.25	21.16	21.24	21.49	10.63	10.76	10.65	10.97
MnO	0.85	0.89	0.88	0.58	0.55	0.53	0.58	0.23	0.19	0.20	0.22
MgO	22.98	22.88	22.73	23.22	23.00	22.90	22.85	30.22	29.81	29.27	29.72
CaO	1.21	1.20	1.24	1.26	1.35	1.29	1.30	1.12	1.46	1.64	1.27
Na ₂ O	0.02	0.04	0.02	0.03	0.05	0.02	0.04	0.04	0.04	0.04	0.06
K ₂ O	0.00	0.03	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.05	0.01	0.03	0.02	0.01	0.03	0.01	0.70	0.57	0.53	0.47
Fotal	100.85	102.15	99.77	100.71	100.38	100.27	100.57	100.29	100.13	99.14	99.84
Si	1.951	1.951	1.963	1.947	1.951	1.954	1.949	1.902	1.907	1.914	1.917
Гі	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.006	0.006	0.005
Al (iv)	0.034	0.041	0.037	0.052	0.049	0.046	0.051	0.098	0.093	0.086	0.083
Al (vi)	0.000	0.000	0.000	0.000	0.002	0.006	0.003	0.028	0.031	0.035	0.031
Fe^{2+}	0.618	0.632	0.627	0.608	0.612	0.626	0.622	0.270	0.280	0.291	0.292
Fe^{3+}	0.053	0.050	0.027	0.045	0.041	0.031	0.040	0.043	0.037	0.026	0.033
Мn	0.027	0.027	0.028	0.018	0.017	0.017	0.018	0.007	0.006	0.006	0.007
Мg	1.261	1.242	1.260	1.273	1.265	1.262	1.256	1.583	1.567	1.555	1.567
Ca	0.048	0.047	0.049	0.050	0.054	0.051	0.051	0.042	0.055	0.063	0.048
Na	0.001	0.003	0.002	0.002	0.004	0.002	0.003	0.002	0.003	0.003	0.004
K	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.002	0.000	0.001	0.000	0.000	0.001	0.000	0.019	0.016	0.015	0.013
Fotal	4.018	4.017	4.009	4.015	4.014	4.010	4.013	4.014	4.012	4.009	4.011
En	2.5	2.4	2.6	2.6	2.8	2.6	2.7	2.2	2.9	3.3	2.5
Fs	65.5	64.7	65.1	65.9	65.5	65.1	65.1	83.5	82.4	81.5	82.2
Wo	32.1	32.9	32.4	31.5	31.7	32.3	32.3	14.2	14.7	15.2	15.3

^{w0} <u>32.1</u> <u>32.9</u> <u>32.4</u> <u>31.5</u> <u>31.7</u> <u>32.5</u> <u>32.5</u> <u>14.7</u> <u>15.2</u> <u>14.7</u> <u>15.2</u> <u>15.5</u> ¹Johnstown hypersthene (JSH) values reported by Jarosewich et al. (1980). ²Values obtained for JSH standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and JSH are corrected by deviation from standards JDF and A99. Cations are calculated on the basis of 6 oxygens with all Fe measured as Fe²⁺. Endmember components are the same as in Appendix 6 and are calculated following Lindsley (1983).

Majo	or element oli	vine analyses f	from select	ted Pircas	Negras ar	ndesites and	Valle Anch	o basaltic	c andesite	s				
	analysis #						54	55	56	57	58	59	60	61
	type						с	c	r	r	c	с	r	r
	sample	P140-act ¹	P140av ²	Meas/Act	P140av ²	Meas/Act	101-1	101-1	101-1	101-1	101-2	101-2	101-2	101-2
SiO ₂		40.85	41.44	1.01	41.23	1.01	39.23	39.21	37.55	37.56	37.79	37.91	36.92	36.93
TiO ₂			0.00		0.01		0.00	0.02	0.03	0.04	0.00	0.00	0.03	0.02
Al_2O_3		0.13	0.01	0.07	0.01	0.05	0.04	0.05	0.02	0.03	0.04	0.39	0.05	0.06
FeO		7.17	7.45	1.04	7.28	1.01	16.71	16.19	26.86	25.41	24.32	23.16	27.68	27.48
MnO		0.07	0.10	1.38	0.10	1.40	0.21	0.23	0.45	0.36	0.33	0.32	0.44	0.43
MgO		51.63	50.73	0.98	51.08	0.99	43.99	44.05	35.19	37.11	38.20	38.86	34.39	33.90
CaO			0.01		0.00		0.08	0.11	0.18	0.17	0.09	0.13	0.20	0.18
Na ₂ O		0.02	0.00	0.19	0.00	0.24	0.00	0.01	0.00	0.00	0.00	0.02	0.02	0.00
K ₂ O		0.00	0.00	0.60	0.00	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Cr_2O_3			0.01		0.00		0.04	0.04	0.00	0.03	0.00	0.05	0.02	0.02
Total		99.88	98.28	1.00	99.73	1.00	100.30	99.92	100.27	100.72	100.78	100.83	99.75	99.03
Si							0.991	0.992	0.997	0.986	0.986	0.983	0.991	0.997
Ti							0.000	0.000	0.001	0.001	0.000	0.000	0.001	0.000
Al							0.001	0.001	0.001	0.001	0.001	0.012	0.002	0.002
Fe^{2^+}							0.353	0.342	0.596	0.558	0.531	0.502	0.621	0.621
Mn							0.005	0.005	0.010	0.008	0.007	0.007	0.010	0.010
Mg							1.656	1.661	1.393	1.453	1.486	1.502	1.376	1.365
Ca							0.002	0.003	0.005	0.005	0.002	0.004	0.006	0.005
Na							0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000
Κ							0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr							0.001	0.001	0.000	0.001	0.000	0.001	0.000	0.000
Total							3.008	3.007	3.002	3.012	3.013	3.011	3.008	3.001
Fo							82.3	82.7	69.7	72.0	73.4	74.7	68.6	68.4
Fa							17.5	17.0	29.8	27.6	26.2	25.0	30.9	31.1
Тр							0.2	0.2	0.5	0.4	0.4	0.3	0.5	0.5

APPENDIX 8

¹P140 values reported by Jarosewich et al. (1980). ²Values obtained for P140 olivine standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and P140 are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2^+} . Cations are calculated on the basis of 4 oxygens. Fo = Forsterite content; Fa = Fayalite content; Tp = Tephroite content; c = core, r = rim.

Major element oli	vine analys	es from s	elected P	'ircas Neg	ras andes	sites and	Valle And	cho basal	tic andesi	ites			
analysis #	62	63	64	65	70	71	72	73	74	75	76	77	272
type	с	с	r	r	с	с	r	r	с	с	r	r	с
sample	101-3	101-3	101-3	101-3	101-4	101-4	101-4	101-4	101-5	101-5	101-5	101-5	412-1
SiO ₂	39.10	38.91	37.08	37.23	39.23	39.01	37.45	36.98	39.45	39.85	38.34	37.21	39.16
TiO ₂	0.02	0.02	0.03	0.03	0.01	0.02	0.04	0.04	0.02	0.00	0.01	0.01	0.05
Al_2O_3	0.03	0.03	0.04	0.07	0.01	0.05	0.04	0.04	0.01	0.04	0.03	0.02	0.05
FeO	16.37	16.66	26.49	26.45	16.61	15.51	27.73	29.89	16.28	15.85	23.65	27.63	17.34
MnO	0.22	0.23	0.39	0.40	0.22	0.22	0.43	0.45	0.22	0.19	0.32	0.44	0.36
MgO	43.73	43.41	35.55	35.70	43.50	43.30	33.95	32.34	44.33	44.43	37.52	34.04	42.78
CaO	0.10	0.11	0.16	0.19	0.06	0.11	0.20	0.23	0.11	0.11	0.11	0.18	0.18
Na ₂ O	0.00	0.00	0.04	0.00	0.01	0.00	0.03	0.02	0.00	0.01	0.00	0.03	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.01
Cr_2O_3	0.01	0.01	0.02	0.04	0.04	0.05	0.00	0.00	0.05	0.02	0.00	0.02	0.01
Total	99.58	99.38	99.80	100.10	99.68	98.28	99.87	100.01	100.47	100.50	99.98	99.59	99.93
Si	0.993	0.992	0.989	0.989	0.996	1.000	1.002	1.000	0.992	0.999	1.003	0.999	0.996
Ti	0.000	0.000	0.001	0.001	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.001
Al	0.001	0.001	0.001	0.002	0.000	0.002	0.001	0.001	0.000	0.001	0.001	0.001	0.001
Fe^{2^+}	0.348	0.355	0.591	0.588	0.353	0.333	0.621	0.676	0.342	0.332	0.517	0.620	0.369
Mn	0.005	0.005	0.009	0.009	0.005	0.005	0.010	0.010	0.005	0.004	0.007	0.010	0.008
Mg	1.656	1.650	1.413	1.414	1.647	1.655	1.355	1.304	1.662	1.660	1.464	1.363	1.622
Ca	0.003	0.003	0.004	0.005	0.002	0.003	0.006	0.007	0.003	0.003	0.003	0.005	0.005
Na	0.000	0.000	0.002	0.000	0.001	0.000	0.001	0.001	0.000	0.001	0.000	0.002	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Total	3.006	3.007	3.011	3.009	3.003	2.998	2.997	3.000	3.007	3.001	2.996	3.001	3.002
Fo	82.4	82.1	70.2	70.3	82.2	83.1	68.2	65.5	82.7	83.2	73.6	68.4	81.2
Fa	17.3	17.7	29.3	29.2	17.6	16.7	31.3	34.0	17.0	16.6	26.0	31.1	18.4
Тр	0.2	0.2	0.4	0.4	0.2	0.2	0.5	0.5	0.2	0.2	0.4	0.5	0.4

¹P140 values reported by Jarosewich et al. (1980). ²Values obtained for P140 olivine standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and P140 are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2+} . Cations are calculated on the basis of 4 oxygens. Fo = Forsterite content; Fa = Fayalite content; Tp = Tephroite content; c = core, r = rim.

Major element oliv	vine analys	es from s	elected P	ircas Neg	ras andes	sites and	Valle And	cho basal	tic andesi	ites				
analysis #	209	210	217	218	219	220	238	239	240	241	246	247	248	249
type	с	с	с	c	r	r	c	c	r	r	c	c	r	r
sample	324-1	324-1	324-2	324-2	324-2	324-2	324-3	324-3	324-3	324-3	324-4	324-4	324-4	324-4
SiO ₂	39.14	39.26	39.15	39.11	38.92	38.64	39.31	39.48	38.65	38.18	39.54	39.48	38.95	38.73
TiO ₂	0.01	0.01	0.02	0.03	0.00	0.02	0.01	0.00	0.03	0.02	0.02	0.01	0.00	0.04
Al_2O_3	0.01	0.00	0.00	0.03	0.02	0.01	0.00	0.02	0.05	0.05	0.04	0.01	0.01	0.02
FeO	17.14	17.02	19.26	19.60	20.25	19.91	16.20	16.45	21.94	23.66	16.69	16.62	19.34	20.54
MnO	0.24	0.26	0.29	0.27	0.31	0.29	0.24	0.24	0.43	0.44	0.22	0.25	0.31	0.33
MgO	43.90	43.63	42.63	42.84	41.35	41.64	44.64	44.77	40.20	38.05	44.54	44.41	41.94	41.31
CaO	0.10	0.11	0.10	0.11	0.09	0.08	0.11	0.11	0.08	0.11	0.08	0.09	0.05	0.10
Na ₂ O	0.01	0.02	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.01
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.01	0.02	0.01	0.04	0.03	0.01	0.02	0.02	0.03	0.03	0.00	0.01	0.00	0.01
Total	100.56	100.35	101.46	102.03	100.99	100.61	100.53	101.11	101.41	100.53	101.14	100.89	100.61	101.09
Si	0.988	0.993	0.989	0.984	0.992	0.988	0.988	0.988	0.990	0.995	0.990	0.991	0.993	0.988
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.001
Al	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.001	0.001	0.001	0.001	0.000	0.000	0.001
Fe ²⁺	0.362	0.360	0.407	0.412	0.432	0.426	0.341	0.344	0.470	0.515	0.349	0.349	0.412	0.438
Mn	0.005	0.006	0.006	0.006	0.007	0.006	0.005	0.005	0.009	0.010	0.005	0.005	0.007	0.007
Mg	1.653	1.645	1.605	1.607	1.572	1.588	1.673	1.670	1.535	1.478	1.662	1.661	1.594	1.572
Ca	0.003	0.003	0.003	0.003	0.003	0.002	0.003	0.003	0.002	0.003	0.002	0.002	0.001	0.003
Na	0.000	0.001	0.001	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000
Total	3.012	3.008	3.011	3.015	3.007	3.011	3.011	3.012	3.009	3.004	3.010	3.009	3.007	3.010
Fo	81.8	81.8	79.5	79.3	78.2	78.6	82.9	82.7	76.2	73.8	82.4	82.4	79.2	77.9
Fa	17.9	17.9	20.2	20.4	21.5	21.1	16.9	17.0	23.3	25.7	17.3	17.3	20.5	21.7
Тр	0.2	0.3	0.3	0.3	0.3	0.3	0.2	0.3	0.5	0.5	0.2	0.3	0.3	0.3

¹P140 values reported by Jarosewich et al. (1980). ²Values obtained for P140 olivine standard are each composites of 5 spot analyses run before and after unknown samples. All unknown samples and P140 are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2+} . Cations are calculated on the basis of 4 oxygens. Fo = Forsterite content; Fa = Fayalite content; Tp = Tephroite content; c = core, r = rim.

Major	element pla	agioclase analy	ses from s	selected Pin	cas Negr	as andesites	and Valle A	ncho bas	saltic and	esites				
ĩ	analysis #						153	156	134	135	137	142	143	144
	type						с	r	xeno-c	xeno-c	xeno-r	xeno-c	xeno-c	xeno-r
	sample	LCP-act ¹	LCPav ²	Meas/Act	LCPav ²	Meas/Act	324-4	324-4	324-1	324-1	324-1	324-2	324-2	324-2
SiO_2		51.08	51.08	1.00	51.39	1.01	57.47	54.16	60.43	60.67	59.70	59.91	62.08	60.48
TiO ₂		0.06	0.04		0.04		0.04	0.06	0.05	0.04	0.10	0.03	0.05	0.03
Al_2O_3		31.06	31.14	1.00	30.54	0.98	25.97	29.45	26.73	25.82	25.51	24.79	24.74	25.04
FeO		0.51	0.49	0.97	0.45	0.89	0.39	0.62	0.42	0.41	0.60	0.41	0.41	0.40
MnO		0.00	0.01		0.01		0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
MgO		0.22	0.14	0.62	0.15	0.69	0.07	0.04	0.02	0.01	0.05	0.04	0.01	0.02
CaO		13.85	14.05	1.01	13.98	1.01	9.10	12.01	7.91	7.16	7.31	6.54	5.97	6.33
Na ₂ O		3.38	3.46	1.02	3.60	1.06	5.89	4.26	5.76	6.58	4.69	6.47	6.43	6.68
K_2O		0.13	0.11		0.12		0.89	0.38	0.83	1.15	3.24	1.17	1.42	1.31
Cr_2O_3		-	-		-		-	-	-	-	-	-	-	-
Total		100.29	100.51		100.28		99.82	100.99	102.16	101.84	101.19	99.36	101.10	100.30
Si							10.368	9.719	10.557	10.657	10.633	10.763	10.923	10.768
Ti							0.005	0.008	0.007	0.005	0.013	0.004	0.007	0.004
Al							5.522	6.229	5.503	5.344	5.356	5.249	5.130	5.253
Fe ²⁺							0.058	0.093	0.061	0.060	0.089	0.061	0.060	0.060
Mn							0.001	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Mg							0.018	0.011	0.005	0.004	0.014	0.010	0.002	0.005
Ca							1.761	2.312	1.483	1.349	1.396	1.260	1.127	1.209
Na							2.059	1.483	1.950	2.239	1.619	2.254	2.192	2.307
Κ							0.205	0.088	0.184	0.259	0.735	0.269	0.318	0.298
Cr							-	-	-	-	-	-	-	-
Total							19.998	19.944	19.751	19.915	19.854	19.870	19.759	19.904
An							43.8	59.5	41.0	35.1	37.2	33.3	31.0	31.7
Ab							51.2	38.2	53.9	58.2	43.2	59.6	60.3	60.5
Or							5.1	2.3	5.1	6.7	19.6	7.1	8.7	7.8

APPENDIX 9

¹LCP values reported by Jarosewich et al. (1980). ²Values obtained for LCP plagioclase standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples and LCP are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2+} . Cations are calculated on the basis of 32 oxygens. An =Anorthite content; Ab = Albite content; Or = Orthoclase content; c = core, r = rim.

Major element plagioclase analyses from selected Pircas Negras andesites and Valle Ancho basaltic andesitesanalysis #145149157158159160161162163164167168169													
analysis #	145	149	157	158	159	160	161	162	163	164	167	168	169
type	xeno-r	xeno-c	xeno-c	xeno-c	xeno-r	xeno-r	xeno-c	xeno-c	xeno-r	xeno-r	с	c	r
sample	324-2	324-3	324-5	324-5	324-5	324-5	324-6	324-6	324-6	324-6	412-1	412-1	412-1
SiO ₂	59.78	60.24	61.25	59.71	58.73	61.37	61.09	61.44	60.22	63.08	52.50	53.01	53.12
TiO ₂	0.03	0.19	0.03	0.04	0.04	0.04	0.02	0.01	0.02	0.01	0.03	0.03	0.03
Al_2O_3	25.92	23.80	24.73	25.67	25.98	24.66	24.97	25.05	25.75	24.43	30.30	29.91	29.45
FeO	0.49	0.93	0.41	0.40	0.37	0.43	0.38	0.38	0.40	0.39	0.68	0.58	0.74
MnO	0.00	0.00	0.02	0.03	0.00	0.01	0.00	0.00	0.00	0.01	0.02	0.00	0.00
MgO	0.02	0.09	0.01	0.02	0.01	0.01	0.00	0.00	0.02	0.00	0.04	0.06	0.06
CaO	7.41	7.36	6.21	7.49	7.89	6.14	6.37	6.37	7.31	5.52	13.05	12.89	12.48
Na ₂ O	6.52	4.89	6.93	6.45	6.20	6.76	6.78	6.78	6.52	6.88	4.00	4.04	4.16
K ₂ O	1.01	1.81	1.21	1.03	0.90	1.45	1.28	1.21	1.02	1.53	0.29	0.27	0.34
Cr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	101.16	99.32	100.81	100.83	100.12	100.86	100.89	101.23	101.25	101.85	100.92	100.78	100.38
Si	10.583	10.858	10.841	10.604	10.510	10.860	10.807	10.822	10.638	11.015	9.474	9.561	9.621
Ti	0.004	0.026	0.005	0.005	0.005	0.006	0.003	0.002	0.002	0.001	0.005	0.004	0.004
Al	5.408	5.055	5.159	5.374	5.480	5.143	5.206	5.200	5.360	5.028	6.443	6.357	6.286
Fe ²⁺	0.072	0.140	0.061	0.059	0.056	0.063	0.056	0.055	0.059	0.057	0.103	0.088	0.112
Mn	0.000	0.000	0.003	0.004	0.000	0.001	0.000	0.000	0.000	0.001	0.004	0.000	0.001
Mg	0.005	0.024	0.002	0.005	0.004	0.002	0.000	0.000	0.005	0.000	0.012	0.017	0.015
Ca	1.406	1.423	1.179	1.426	1.513	1.164	1.208	1.202	1.385	1.033	2.526	2.493	2.424
Na	2.238	1.708	2.379	2.221	2.150	2.320	2.326	2.316	2.235	2.328	1.401	1.411	1.462
Κ	0.227	0.417	0.274	0.233	0.205	0.327	0.288	0.272	0.229	0.342	0.066	0.061	0.077
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	19.942	19.651	19.901	19.931	19.922	19.886	19.895	19.870	19.912	19.805	20.033	19.993	20.002
An	36.3	40.1	30.8	36.7	39.1	30.6	31.6	31.7	36.0	27.9	63.3	62.87	61.2
Ab	57.8	48.1	62.1	57.3	55.6	60.9	60.9	61.1	58.1	62.9	35.1	35.59	36.9
Or	5.9	11.7	7.1	6.0	5.3	8.6	7.5	7.2	5.9	9.2	1.7	1.54	2.0

¹LCP values reported by Jarosewich et al. (1980). ²Values obtained for LCP plagioclase standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples and LCP are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2+} . Cations are calculated on the basis of 32 oxygens. An =Anorthite content; Ab = Albite content; Or = Orthoclase content; c = core, r = rim.

Major element pla	Major element plagioclase analyses from selected Pircas Negras andesites and Valle Ancho basaltic andesitesanalysis #170171172173174175176177178179180185186187													
analysis #	170	171	172	173	174	175	176	177	178	179	180	185	186	187
type	r	c	r	c	r	с	r	с	r	c	r	c	r	с
sample	412-1	412-2	412-2	412-3	412-3	412-4	412-4	412-5	412-5	412-6	412-6	412-7	412-7	412-8
SiO ₂	53.51	52.13	52.84	54.29	53.30	53.49	54.10	53.31	52.56	53.59	52.74	52.60	53.79	53.72
TiO ₂	0.05	0.04	0.04	0.04	0.05	0.04	0.04	0.03	0.02	0.04	0.03	0.01	0.04	0.03
Al_2O_3	29.87	30.44	29.70	29.35	29.70	29.39	28.79	29.37	30.02	29.00	29.04	29.80	29.63	29.81
FeO	0.67	0.74	0.69	0.63	0.78	0.66	0.60	0.68	0.63	0.77	0.82	0.74	0.65	0.70
MnO	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.01	0.02	0.00
MgO	0.05	0.02	0.05	0.05	0.04	0.05	0.04	0.05	0.03	0.06	0.05	0.09	0.04	0.03
CaO	12.55	13.24	12.57	12.02	12.40	12.20	11.68	12.27	13.13	12.11	12.48	12.69	12.12	12.29
Na ₂ O	4.15	3.82	4.13	4.53	4.25	4.44	4.54	4.23	3.91	4.31	4.19	3.97	4.42	4.19
K ₂ O	0.29	0.29	0.34	0.39	0.35	0.33	0.39	0.39	0.29	0.37	0.33	0.29	0.39	0.35
Cr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	101.15	100.73	100.37	101.29	100.87	100.59	100.18	100.36	100.60	100.24	99.67	100.20	101.10	101.12
Si	9.609	9.432	9.574	9.725	9.607	9.660	9.787	9.651	9.510	9.708	9.629	9.548	9.661	9.643
Ti	0.006	0.005	0.005	0.005	0.006	0.005	0.005	0.004	0.003	0.005	0.003	0.002	0.006	0.003
Al	6.320	6.491	6.343	6.195	6.309	6.254	6.138	6.266	6.401	6.192	6.248	6.374	6.271	6.305
Fe ²⁺	0.101	0.111	0.104	0.094	0.117	0.100	0.091	0.103	0.095	0.116	0.126	0.112	0.097	0.106
Mn	0.002	0.002	0.000	0.000	0.000	0.000	0.002	0.004	0.000	0.000	0.001	0.001	0.003	0.000
Mg	0.013	0.006	0.013	0.012	0.012	0.013	0.010	0.014	0.008	0.017	0.013	0.025	0.012	0.009
Ca	2.417	2.568	2.443	2.309	2.397	2.362	2.265	2.383	2.548	2.352	2.443	2.470	2.334	2.366
Na	1.445	1.340	1.452	1.575	1.484	1.553	1.593	1.486	1.372	1.515	1.482	1.396	1.540	1.458
K	0.066	0.066	0.079	0.088	0.081	0.075	0.089	0.090	0.067	0.085	0.076	0.066	0.089	0.080
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	19.980	20.021	20.014	20.004	20.014	20.022	19.980	20.000	20.006	19.990	20.022	19.995	20.013	19.970
An	61.5	64.6	61.5	58.1	60.5	59.2	57.4	60.2	63.9	59.5	61.1	62.8	58.9	60.6
Ab	36.8	33.7	36.5	39.7	37.4	38.9	40.4	37.5	34.4	38.3	37.0	35.5	38.9	37.3
Or	1.7	1.7	2.0	2.2	2.0	1.9	2.3	2.3	1.7	2.1	1.9	1.7	2.2	2.1

¹ LCP values reported by Jarosewich et al. (1980). ²Values obtained for LCP plagioclase standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples and LCP are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2+} . Cations are calculated on the basis of 32 oxygens. An =Anorthite content; Ab = Albite content; Or = Orthoclase content; c = core, r = rim.

Major element plagioclase analyses from selected Pircas Negras andesites and Valle Ancho basaltic andesites analysis # 188 181 182 183 184 189 192 193 195 200 201 202 203													
analysis #	188	181	182	183	184	189	192	193	195	200	201	202	203
type	r	xeno-c	xeno-c	xeno-c	xeno-c	с	с	c	r	с	с	с	c
sample	412-8	412-9	412-9	412-9	412-9	427-1	427-1	427-2	427-2	427-3	427-4	427-5	427-6
SiO ₂	54.03	62.26	60.11	61.36	62.91	54.57	58.49	53.83	54.07	53.42	54.33	55.39	55.82
TiO ₂	0.03	0.01	0.02	0.00	0.01	0.05	0.10	0.05	0.05	0.03	0.05	0.08	0.07
Al_2O_3	29.44	23.90	24.63	25.41	24.01	28.61	25.51	29.26	29.02	29.91	29.60	28.04	27.90
FeO	0.80	0.03	0.00	0.05	0.00	0.78	0.98	0.74	0.73	0.60	0.73	0.77	0.88
MnO	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
MgO	0.04	0.00	0.30	0.00	0.00	0.04	0.17	0.07	0.08	0.06	0.05	0.05	0.07
CaO	12.28	5.30	6.84	6.50	5.34	11.33	7.77	12.16	11.83	12.76	12.27	10.62	10.32
Na ₂ O	4.39	7.40	6.88	7.28	7.76	4.72	6.29	4.48	4.58	4.22	4.40	5.17	4.97
K ₂ O	0.35	1.30	0.53	0.65	0.71	0.35	0.64	0.24	0.27	0.23	0.29	0.41	0.44
Cr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	101.36	100.21	99.31	101.27	100.72	100.44	99.94	100.82	100.66	101.22	101.73	100.53	100.47
Si	9.685	11.038	10.770	10.780	11.063	9.841	10.508	9.693	9.744	9.589	9.693	9.966	10.030
Ti	0.004	0.001	0.002	0.000	0.001	0.006	0.013	0.007	0.007	0.005	0.006	0.010	0.010
Al	6.220	4.994	5.202	5.262	4.976	6.081	5.400	6.210	6.163	6.327	6.224	5.947	5.909
Fe ²⁺	0.120	0.005	0.000	0.008	0.000	0.117	0.147	0.112	0.111	0.090	0.109	0.116	0.131
Mn	0.001	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.003	0.000	0.001	0.000	0.001
Mg	0.010	0.000	0.081	0.000	0.000	0.011	0.045	0.018	0.022	0.016	0.015	0.013	0.019
Ca	2.360	1.007	1.315	1.224	1.006	2.190	1.496	2.347	2.287	2.456	2.347	2.049	1.989
Na	1.524	2.543	2.391	2.481	2.646	1.649	2.191	1.564	1.599	1.468	1.521	1.803	1.730
K	0.080	0.295	0.122	0.145	0.158	0.081	0.147	0.054	0.061	0.052	0.066	0.095	0.101
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	20.003	19.883	19.883	19.902	19.850	19.977	19.948	20.004	19.997	20.002	19.982	19.999	19.921
An	59.5	26.19	34.35	31.80	26.41	55.87	39.01	59.19	57.94	61.78	59.67	51.92	52.07
Ab	38.5	66.15	62.46	64.44	69.44	42.07	57.15	39.44	40.51	36.92	38.66	45.69	45.28
Or	2.0	7.66	3.18	3.76	4.15	2.06	3.84	1.36	1.55	1.30	1.68	2.40	2.65

¹LCP values reported by Jarosewich et al. (1980). ²Values obtained for LCP plagioclase standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples and LCP are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2+} . Cations are calculated on the basis of 32 oxygens. An =Anorthite content; Ab = Albite content; Or = Orthoclase content; c = core, r = rim.

Major element plagioclase analyses from selected Pircas Negras andesites and Valle Ancho basaltic andesitesanalysis #207208204205206238240241242245246247248													
analysis #	207	208	204	205	206	238	240	241	242	245	246	247	248
type	с	с	xeno-c	xeno-c	xeno-r	с	с	с	с	с	с	с	с
sample	427-7	427-8	427-9	427-9	427-9	309-1	309-2	309-3	309-4	309-5	309-6	309-7	309-8
SiO ₂	52.90	52.38	53.51	61.10	56.64	54.81	56.72	56.03	59.66	52.66	54.20	53.07	53.95
TiO ₂	0.03	0.03	0.02	0.00	0.11	0.04	0.00	0.07	0.09	0.06	0.05	0.05	0.05
Al_2O_3	29.89	29.81	28.24	25.73	25.26	27.16	26.22	27.45	25.09	29.37	28.33	29.07	28.96
FeO	0.55	0.59	1.56	0.08	1.69	0.61	0.94	0.75	0.85	0.82	0.69	0.68	0.56
MnO	0.00	0.02	0.02	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.02	0.02
MgO	0.08	0.07	0.88	0.01	1.17	0.07	0.15	0.04	0.14	0.08	0.08	0.07	0.07
CaO	13.01	12.78	7.51	6.25	9.10	10.32	10.32	9.62	7.45	11.77	11.92	12.37	11.60
Na ₂ O	4.05	4.14	6.06	7.03	4.90	5.22	5.04	5.40	6.29	4.06	4.40	4.32	4.79
K ₂ O	0.16	0.17	0.74	1.06	0.57	0.30	0.01	0.51	0.65	0.28	0.24	0.19	0.23
Cr_2O_3	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	100.68	99.97	98.53	101.26	99.46	98.53	99.41	99.87	100.21	99.11	99.90	99.83	100.23
Si	9.551	9.527	9.841	10.745	10.290	10.045	10.268	10.116	10.652	9.636	9.830	9.656	9.754
Ti	0.004	0.004	0.003	0.000	0.015	0.006	0.000	0.009	0.013	0.009	0.006	0.007	0.006
Al	6.360	6.390	6.121	5.332	5.408	5.865	5.594	5.840	5.280	6.333	6.054	6.234	6.171
Fe ²⁺	0.084	0.090	0.239	0.012	0.256	0.094	0.143	0.114	0.127	0.126	0.105	0.104	0.085
Mn	0.001	0.002	0.002	0.002	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.003	0.003
Mg	0.021	0.018	0.240	0.002	0.318	0.019	0.041	0.011	0.037	0.023	0.023	0.020	0.019
Ca	2.518	2.493	1.482	1.178	1.772	2.028	2.004	1.862	1.425	2.309	2.318	2.413	2.250
Na	1.418	1.459	2.160	2.398	1.727	1.854	1.768	1.891	2.176	1.439	1.546	1.522	1.678
K	0.037	0.039	0.174	0.237	0.133	0.071	0.002	0.116	0.149	0.065	0.055	0.044	0.053
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	19.993	20.023	20.263	19.906	19.921	19.980	19.820	19.959	19.858	19.940	19.937	20.003	20.020
An	63.38	62.46	38.83	30.90	48.79	51.30	53.09	48.12	38.01	60.56	59.15	60.63	56.52
Ab	35.69	36.55	56.60	62.89	47.55	46.90	46.85	48.87	58.02	37.75	39.44	38.26	42.16
Or	0.93	0.98	4.56	6.21	3.66	1.80	0.06	3.01	3.97	1.70	1.41	1.11	1.33

¹LCP values reported by Jarosewich et al. (1980). ²Values obtained for LCP plagioclase standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples and LCP are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2^+} . Cations are calculated on the basis of 32 oxygens. An =Anorthite content; Ab = Albite content; Or = Orthoclase content; c = core, r = rim.

Major element pla	Tajor element plagioclase analyses from selected Pircas Negras andesites and Valle Ancho basaltic andesitesanalysis #249250251253255256258260209210211212214													
analysis #	249	250	251	253	255	256	258	260	209	210	211	212	214	
type	с	с	c	с	с	с	c	с	с	с	с	с	c	
sample	309-9	309-10	101-1	101-2	101-3	101-4	101-6	101-7	428-1	428-2	428-3	428-4	428-5	
SiO ₂	52.97	53.89	56.64	52.84	59.00	51.92	54.90	52.25	63.30	58.03	56.01	64.03	54.90	
TiO ₂	0.04	0.06	0.14	0.11	0.36	0.08	0.15	0.08	0.13	0.10	0.07	0.15	0.08	
Al_2O_3	28.60	28.92	26.33	28.61	25.02	29.23	27.24	29.41	22.30	26.17	27.82	21.39	28.45	
FeO	0.61	0.68	0.79	1.06	1.33	0.96	1.01	1.18	0.98	0.93	1.17	1.02	1.26	
MnO	0.00	0.01	0.00	0.00	0.02	0.02	0.01	0.00	0.00	0.01	0.02	0.00	0.01	
MgO	0.06	0.08	0.13	0.12	0.10	0.11	0.10	0.18	0.01	0.02	0.06	0.01	0.05	
CaO	12.30	11.97	9.36	12.56	8.88	13.11	10.80	13.39	3.83	8.81	10.18	3.51	10.98	
Na ₂ O	4.31	4.49	5.80	4.05	4.39	3.81	4.42	3.83	6.79	5.98	5.26	7.03	4.87	
K ₂ O	0.21	0.21	0.62	0.35	1.23	0.28	0.57	0.26	2.75	0.69	0.53	3.42	0.49	
Cr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-	
Total	99.09	100.30	99.81	99.69	100.33	99.53	99.18	100.58	100.08	100.73	101.10	100.56	101.10	
Si	9.705	9.742	10.243	9.656	10.570	9.518	10.016	9.494	11.285	10.376	10.028	11.400	9.860	
Ti	0.005	0.007	0.019	0.015	0.049	0.011	0.020	0.011	0.018	0.013	0.009	0.020	0.011	
Al	6.177	6.162	5.611	6.163	5.283	6.315	5.857	6.297	4.685	5.516	5.870	4.489	6.022	
Fe ²⁺	0.093	0.103	0.119	0.162	0.199	0.148	0.154	0.179	0.146	0.139	0.175	0.152	0.190	
Mn	0.000	0.001	0.001	0.000	0.003	0.003	0.001	0.000	0.000	0.002	0.002	0.000	0.002	
Mg	0.016	0.021	0.034	0.031	0.028	0.031	0.026	0.049	0.003	0.004	0.016	0.003	0.014	
Ca	2.417	2.321	1.815	2.462	1.706	2.577	2.113	2.610	0.733	1.690	1.955	0.670	2.114	
Na	1.530	1.575	2.035	1.434	1.524	1.355	1.564	1.350	2.346	2.072	1.825	2.426	1.696	
K	0.050	0.048	0.143	0.083	0.280	0.066	0.133	0.060	0.624	0.157	0.120	0.776	0.113	
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	
Total	19.992	19.981	20.021	20.006	19.642	20.023	19.884	20.051	19.840	19.968	20.001	19.936	20.022	
An	60.48	58.84	45.46	61.88	48.60	64.46	55.46	64.93	19.79	43.12	50.12	17.30	53.89	
Ab	38.27	39.93	50.96	36.04	43.41	33.89	41.05	33.57	63.35	52.87	46.79	62.66	43.24	
Or	1.25	1.23	3.57	2.07	7.99	1.66	3.49	1.50	16.86	4.01	3.09	20.04	2.87	

¹LCP values reported by Jarosewich et al. (1980). ²Values obtained for LCP plagioclase standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples and LCP are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2+} . Cations are calculated on the basis of 32 oxygens. An =Anorthite content; Ab = Albite content; Or = Orthoclase content; c = core, r = rim.

Major element	Tajor element plagioclase analyses from selected Pircas Negras andesites and Valle Ancho basaltic andesitesanalysis #219221225226228229230231232233234235236237two111111111111													
analysis #	219	221	225	226	228	229	230	231	232	233	234	235	236	237
type	с	c	с	c	r	r	c	с	c	c	с	с	r	r
sample	81-1	81-2	81-3	81-4	81-Line 1	81-Line 2	81-Line 3	81-Line 4	81-Line 5	81-Line 6	81-Line 7	81-Line 8	81-Line 9	81-Line 10
SiO ₂	53.48	56.01	60.06	62.00	56.69	52.81	56.16	53.77	51.00	55.89	52.53	54.70	49.61	55.08
TiO ₂	0.05	0.08	0.13	0.16	0.04	0.02	0.02	0.00	0.01	0.07	0.01	0.02	0.02	0.02
Al_2O_3	29.31	28.31	24.84	23.19	27.09	29.19	28.03	29.85	29.23	27.66	29.67	28.50	31.09	27.83
FeO	0.88	1.11	1.05	0.99	0.36	0.34	0.35	0.44	0.43	0.74	0.37	0.32	0.35	0.46
MnO	0.02	0.01	0.01	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
MgO	0.05	0.06	0.11	0.14	0.03	0.03	0.04	0.04	0.02	0.08	0.04	0.03	0.03	0.04
CaO	11.93	10.32	6.61	5.11	9.49	11.88	10.29	12.63	12.24	10.43	12.84	11.42	12.85	10.76
Na ₂ O	4.35	5.39	6.07	6.58	5.61	4.55	5.35	4.16	4.15	5.11	4.01	4.43	3.50	4.94
K ₂ O	0.40	0.56	1.40	1.84	0.68	0.40	0.53	0.31	0.37	0.54	0.29	0.38	0.28	0.51
Cr ₂ O ₃	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	100.46	101.84	100.28	100.04	99.98	99.23	100.76	101.21	97.44	100.52	99.75	99.81	97.74	99.64
Si	9.672	9.966	10.729	11.063	10.208	9.658	10.051	9.638	9.519	10.048	9.567	9.895	9.234	9.988
Ti	0.007	0.011	0.018	0.022	0.006	0.002	0.003	0.000	0.002	0.009	0.001	0.003	0.003	0.003
Al	6.248	5.935	5.229	4.878	5.747	6.290	5.912	6.307	6.430	5.861	6.367	6.076	6.820	5.946
Fe ²⁺	0.133	0.165	0.157	0.147	0.054	0.052	0.052	0.066	0.066	0.111	0.056	0.049	0.055	0.070
Mn	0.003	0.001	0.001	0.003	0.000	0.002	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000
Mg	0.013	0.016	0.030	0.038	0.008	0.008	0.010	0.011	0.005	0.021	0.010	0.008	0.009	0.010
Ca	2.313	1.969	1.266	0.978	1.833	2.330	1.974	2.428	2.450	2.011	2.507	2.214	2.565	2.092
Na	1.524	1.860	2.101	2.277	1.958	1.611	1.858	1.446	1.500	1.780	1.416	1.554	1.263	1.736
K	0.093	0.127	0.319	0.419	0.155	0.093	0.120	0.072	0.087	0.124	0.066	0.087	0.066	0.118
Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	20.005	20.049	19.850	19.824	19.969	20.047	19.979	19.967	20.058	19.965	19.990	19.885	20.017	19.963
An	58.86	49.77	34.33	26.62	46.45	57.75	49.95	61.53	60.69	51.36	62.85	57.43	65.87	53.02
Ab	38.78	47.02	57.00	61.96	49.61	39.94	47.01	36.66	37.16	45.47	35.49	40.30	32.44	43.98
Or	2.35	3.21	8.67	11.42	3.94	2.30	3.03	1.81	2.15	3.17	1.67	2.27	1.69	3.00

¹LCP values reported by Jarosewich et al. (1980). ²Values obtained for LCP plagioclase standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples and LCP are corrected by deviation from standards JDF and A99. All Fe is shown as Fe^{2^+} . Cations are calculated on the basis of 32 oxygens. An =Anorthite content; Ab = Albite content; Or = Orthoclase content; c = core, r = rim. Line is for a transect across the only plagioclase phenocryst in Dos Hermanos sample CC 81.

Major element or	cide analyses	from sele	cted Pircas	Negras a	ndesites and	Valle And	cho basal	tic andesi	ites				
analysis #	· ·			0		294	295	292	293	296	297	299	298
type							CO 32	4-pair 1			CO 32-	4-pair 2	
sample	ILM-act ¹	ILMav ²	Meas/Act	ILMav ²	Meas/Act	Mt-1	Mt-1	Ilm-1	Ilm-1	Mt-2	Mt-2	Mt-2	Ilm-2
TiO ₂	45.71	45.71	n.a.	45.71	n.a.	9.76	10.06	42.21	43.22	12.03	12.21	10.35	41.11
Al_2O_3		0.04		0.12		1.72	1.74	0.42	0.43	3.76	2.10	3.12	6.25
FeO	46.5	45.7	0.98	45.51	0.98	78.71	78.51	49.58	48.50	74.94	75.92	75.88	44.67
MnO	4.77	4.77		4.77		0.34	0.37	0.42	0.43	0.39	0.38	0.37	0.34
MgO	0.32	0.31	0.98	0.32	1.00	1.66	1.63	2.40	3.14	1.88	2.12	1.65	2.70
Total	97.30	96.57		96.43		95.02	95.71	92.18	95.71	93.00	92.73	91.37	95.06
Ti						0.276	0.284	0.806	0.815	0.335	0.343	0.294	0.762
Al						0.077	0.078	0.013	0.013	0.166	0.094	0.141	0.184
Fe ²⁺						1.171	1.180	0.705	0.687	1.217	1.211	1.188	0.655
Fe ³⁺						1.371	1.353	0.376	0.357	1.164	1.221	1.272	0.291
Mn						0.011	0.012	0.009	0.009	0.012	0.012	0.012	0.007
Mg						0.094	0.093	0.092	0.119	0.105	0.119	0.094	0.101
Total						3.000	3.000	2.000	2.000	3.000	3.000	3.000	2.000
ILM								0.788	0.792				0.794
HEM								0.212	0.208				0.206
USP						0.283	0.291			0.361	0.355	0.312	
MT						0.717	0.709			0.639	0.645	0.688	

APPENDIX 10

¹ILM values reported by Jarosewich et al. (1980). ²Values obtained for the ilmenite standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples are corrected by deviation from internal magnetite and ilmenite (Ti-only) oxide standards. Magnetite and ilmenite analyses were recalculated on the basis of 3 and 4 oxygens and normalized to 2 and 3 total cations respectively. Fe^{2+}/Fe^{3+} ratio is calculated from the un-normalized cation total with all Fe measured as Fe^{2+} . Endmembers were calculated following Ghiorso and Carmichael (1981) and include ILM = Ilmenite (FeTiO₃); HEM = Hematite (Fe₂O₃); USP = Ulvospinel (Fe₂TiO₂); MAG = Magnetite (Fe₃O₄).

Major element ox	Major element oxide analyses from selected Pircas Negras andesites and Valle Ancho basaltic andesitesanalysis #301303304305306307308309310311314312313													
analysis #	301	303	304	305	306	307	308	309	310	311	314	312	313	
type	CO 32	4-pair 3		CO 32	4-pair 4			CO 32	4-pair 5		C	CO 427-pair	1	
sample	Mt-3	Ilm-3	Mt-4	Mt-4	Ilm-4	Ilm-4	Mt-5	Mt-5	Mt-5	Ilm-5	Mt-1	Ilm-1	Ilm-1	
TiO ₂	9.28	45.63	11.93	10.97	40.96	41.87	10.59	11.65	18.52	42.25	7.16	33.43	33.66	
Al_2O_3	1.84	0.46	4.12	2.48	0.60	0.27	2.20	1.84	3.42	2.67	1.81	0.36	0.34	
FeO	78.78	44.23	74.54	76.61	47.61	49.77	77.49	76.37	67.88	45.79	76.06	53.30	54.72	
MnO	0.31	0.53	0.32	0.33	0.35	0.35	0.33	0.33	0.37	0.38	0.34	0.32	0.28	
MgO	1.56	3.85	1.64	1.94	3.58	2.94	1.79	1.91	1.68	2.98	2.00	3.08	2.76	
Total	91.77	94.69	92.55	92.34	93.10	95.21	92.39	92.10	91.87	94.06	87.36	90.49	91.77	
Ti	0.264	0.868	0.334	0.309	0.789	0.794	0.298	0.330	0.528	0.803	0.212	0.659	0.657	
Al	0.083	0.014	0.183	0.111	0.018	0.008	0.098	0.083	0.155	0.081	0.085	0.011	0.011	
Fe ²⁺	1.164	0.709	1.231	1.189	0.643	0.675	1.186	1.210	1.420	0.681	1.082	0.530	0.542	
Fe ³⁺	1.390	0.251	1.149	1.272	0.404	0.403	1.305	1.258	0.789	0.312	1.491	0.670	0.676	
Mn	0.010	0.011	0.010	0.011	0.008	0.008	0.011	0.011	0.012	0.008	0.011	0.007	0.006	
Mg	0.089	0.147	0.092	0.110	0.138	0.112	0.101	0.109	0.096	0.114	0.119	0.122	0.108	
Total	3.000	2.000	3.000	3.000	2.000	2.000	3.000	3.000	3.000	2.000	3.000	2.000	2.000	
ILM		0.849								0.804		0.610	0.614	
HEM		0.151								0.196		0.390	0.386	
USP	0.271		0.364	0.323	0.758	0.769	0.310	0.340	0.570		0.217			
MT	0.729		0.636	0.677	0.242	0.231	0.690	0.660	0.430		0.783			

¹ILM values reported by Jarosewich et al. (1980). ²Values obtained for the ilmenite standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples are corrected by deviation from internal magnetite and ilmenite (Ti-only) oxide standards. Magnetite and ilmenite analyses were recalculated on the basis of 3 and 4 oxygens and normalized to 2 and 3 total cations respectively. Fe^{2+}/Fe^{3+} ratio is calculated from the unnormalized cation total with all Fe measured as Fe^{2+} . Endmembers were calculated following Ghiorso and Carmichael (1981) and include ILM = Ilmenite (FeTiO₃); HEM = Hematite (Fe₂O₃); USP = Ulvospinel (Fe₂TiO₂); MAG = Magnetite (Fe₃O₄).

Major elem	ent oxide	analyses	s from sele	cted Pircas	s Negras	andesites	s and Val	lle Ancho	basaltic an	desites					
analysis #	320	322	323	324	325	327	328	333	337	338	341	342	343	344	346
type	(CC 101-pair	1		CO 428-0	xide microp	henocrysts				CC 81-02	kide micropł	nenocrysts		
sample	Mt-1	Ilm-1	Ilm-1	Mt-1	Mt-2	Ilm-1	Ilm-2	Ilm-3	Mt-1	Mt-2	Mt-3	Mt-3	Ilm-1	Ilm-1	Ilm-1
TiO ₂	0.69	17.48	18.37	1.79	1.79	17.32	18.43	16.66	5.86	6.05	6.85	7.22	43.64	49.48	43.91
Al_2O_3	1.02	2.05	2.80	2.07	1.58	0.42	0.38	0.32	3.64	2.00	1.96	2.52	6.83	1.22	5.11
FeO	80.88	64.97	63.40	81.36	82.10	71.06	69.33	71.59	77.45	78.55	78.23	77.11	33.28	37.13	32.68
MnO	0.05	0.32	0.45	0.74	0.75	0.15	0.19	0.14	0.49	0.46	0.52	0.52	0.10	0.10	0.11
MgO	0.38	1.07	2.13	4.21	4.19	1.33	1.25	1.08	3.70	3.71	3.89	2.99	3.81	4.54	3.34
Total	83.01	85.88	87.15	90.16	90.42	90.28	89.57	89.79	91.14	90.77	91.45	90.35	87.66	92.47	85.15
Ti	0.022	0.359	0.368	0.050	0.050	0.340	0.366	0.329	0.163	0.170	0.191	0.205	0.871	0.961	0.913
Al	0.051	0.067	0.089	0.092	0.070	0.013	0.012	0.010	0.161	0.090	0.087	0.114	0.217	0.038	0.169
Fe ²⁺	0.996	0.307	0.271	0.789	0.790	0.284	0.311	0.283	0.941	0.945	0.956	1.017	0.715	0.781	0.771
Fe ³⁺	1.906	1.215	1.176	1.808	1.829	1.307	1.257	1.331	1.513	1.571	1.531	1.477	0.042	0.041	0.004
Mn	0.002	0.007	0.010	0.024	0.024	0.003	0.004	0.003	0.015	0.015	0.017	0.017	0.002	0.002	0.003
Mg	0.024	0.044	0.086	0.237	0.236	0.052	0.050	0.043	0.207	0.210	0.218	0.171	0.153	0.178	0.140
Total	3.000	2.000	2.000	3.000	3.000	2.000	2.000	2.000	3.000	3.000	3.000	3.000	2.000	2.000	2.000
ILM		0.311	0.279			0.298	0.327	0.295	0.1702	0.1714	0.1927	0.2100			
HEM		0.689	0.721			0.702	0.673	0.705	0.8298	0.8286	0.8073	0.7900			
USP	0.021			0.041	0.040								0.967	0.974	0.997
MT	0.979			0.959	0.960								0.033	0.026	0.003

¹ILM values reported by Jarosewich et al. (1980). ²Values obtained for the ilmenite standard are each composites of 8 spot analyses run before and after unknown samples. All unknown samples are corrected by deviation from internal magnetite and ilmenite (Ti-only) oxide standards. Magnetite and ilmenite analyses were recalculated on the basis of 3 and 4 oxygens and normalized to 2 and 3 total cations respectively. Fe^{2+}/Fe^{3+} ratio is calculated from the unnormalized cation total with all Fe measured as Fe^{2+} . Endmembers were calculated following Ghiorso and Carmichael (1981) and include ILM = Ilmenite (FeTiO₃); HEM = Hematite (Fe₂O₃); USP = Ulvospinel (Fe₂TiO₂); MAG = Magnetite (Fe₃O₄).

List of samp	led Incapillo volcanic units							
Extrusive - o	domes and lava flows	type	lat (DD)	lon (DD)	elev (m)	Age (Ma)	min	location
sample	Pre-Caldera Unit (proto-cone)							
CO 516	Intra-caldera dacite	RD	27.902	68.788	5438	0.87 ± 0.03	bio ¹	Lower north caldera wall
	Incapillo Caldera Domes							
CO 136	Incapillo dome	R	27.904	68.850	5570	1.1 ± 0.4	bio ²	West rim of caldera
CO 137	Incapillo dome	RD	27.901	68.858	5498	2.9 ± 0.4	bio ²	NE-flank of Veladero
CO 317	Incapillo dome	RD	27.904	68.850	5533			West rim of caldera
CO 318	Incapillo dome	RD	27.906	68.861	5473			West rim of caldera
CO 319	Incapillo dome	D	27.897	68.861	5476			West rim of caldera
CO 139	Incapillo dome	RD	27.964	68.822	5234			South of caldera along stream
	Eastern Incapillo Domes							
CO 323	Eastern Incapillo dome	R	27.915	68.769	5605	1.34 ± 0.13	bio ¹	NW flank of Bonete Chico
CO 517	Eastern Incapillo dome	R	27.902	68.788	5420			East rim of caldera
	<u>Older Oxidized Domes</u>							
CO 322	Eastern Incapillo	RD	27.935	68.760	5760			NW flank of Bonete Chico
CO 140	S. Incapillo dome	D	27.964	68.822	5186	1.9 ± 0.7	wr ²	NE-flank of Veladero
CO 518	S. Incapillo dome	RD	27.971	68.801	5198			Q. Veladero - south of Incapillo
CO 135	S. Incapillo dome	D	27.922	68.815	5367			Q. Veladero - south of Incapillo
CO 525	S. Incapillo dome	RD	28.020	68.837	4976			Q. Veladero - below ignimbrite
CO 522	S. Incapillo dome	RD	28.021	68.825	4983			Q. Veladero - south of Incapillo
CO 142	S. Incapillo dome	D	28.038	68.848	4863	4.6 ± 0.2	wr ²	Q. Veladero - below ignimbrite
CO 151	Fandango dome	D	28.148	68.845	4589	4.7 ± 0.5	wr ²	Q. Veladero- Fandango
CO 157	Fandango dome	D	28.184	68.838	4694	3.6 ± 0.5	wr ²	Q. VeladeroFandango
	Western (Rio Salado) Domes							
CO 184	Rio Salado dome	D	27.831	68.975	4818			Headwaters of Rio Salado
CO 314	Rio Salado dome	D	27.916	69.088	4615			West side of Rio Salado
CO 316	Rio Salado dome	D	27.911	69.101	4596			West side of Rio Salado
CO 505	Rio Salado dome	RD	27.920	69.009	4739			East side of Rio Salado
CO 506	Rio Salado dome	R	27.938	69.034	4725			East side of Rio Salado
CO 508	Rio Salado dome	R	27.938	69.055	4990	2.55 ± 0.03	bio ¹	East side of Rio Salado
CO 509	Rio Salado dome	RD	27.940	69.054	4766			East side of Rio Salado
CO 510	Rio Salado dome	RD	27.890	69.008	4680			East side of Rio Salado
CO 511	Rio Salado dome	RD	27.934	69.002	4838			East side of Rio Salado
CO 513	Rio Salado dome	R	27.909	68.993	4817			East side of Rio Salado

APPENDIX 11

Ignimbrites	and Debris Flows	type	lat (DD)	lon (DD)	elev (m)	Age (Ma)	min	location
	Incapillo Ignimbrite							
CO 138	Incapillo pumice	RD	27.916	68.864	5484			Caldera-southwest rim
CO 320	Incapillo pumice	R	27.935	68.851	5410			Caldera - south rim
CO 514	Incapillo pumice	RD	27.950	68.821	5200	0.51 ± 0.02	bio ¹	Caldera - south rim
CO 141	Incapillo pumice	RD	27.939	68.860	5186	1.6 ± 0.5	bio ²	Q. Veladero - proximal
CO 325	Incapillo pumice	RD	28.015	68.829	5044			Q. Veladero - medial
CO 524	Incapillo pumice	R	28.024	68.836	4967	0.51 ± 0.04	bio ¹	Q. Veladero - medial
CO 143	Incapillo pumice	RD	28.038	68.848	4863			Q. Veladero - distal
CO 527	Incapillo pumice	R	28.038	68.848	4863			Q. Veladero distal
CO 183	W. Incapillo pumice	RD	27.802	69.005	4668			Headwaters of Rio Salado
	<u>Veladero Debris Flow</u>							
CO 515	Veladero welded ignimbrite	-	27.969	68.807	5156			Q. Veladero
CO 523	Veladero welded ignimbrite	-	28.009	68.824	4967			Q. Veladero
CO 526	Veladero welded ignimbrite	-	28.026	68.855	4859			Q. Veladero
Late Miocene	- Pliocene Arc							
	<u>Volcan Pissis</u>							
CO 37	Lava flow	D	27.730	68.760	5186	4.1 ± 0.4	bio ²	North face of Pissis
CO 38	Lava flow	А	27.710	68.770	5028	6.2 ± 0.5	bio ²	North face of Pissis
CO 39	Lava flow	А	27.690	68.780	4959	4.2 ± 0.2	wr ²	North face of Pissis
CO 180	Lava flow	D	27.756	69.029	4631	3.2 ± 0.3	wr ²	West face of Pissis
CO 182	Lava flow	D	27.800	68.998	4749	4.6 ± 0.7	wr ²	West face of Pissis
	<u>Sierras de Veladero</u>							
CO 152	Veladero dome	D	28.109	68.944	4853	4.2 ± 0.4	bio ²	Sierras de Veladero
CO 153	Lava flow	D	28.109	68.944	4853	5.6 ± 1.0	wr ²	Southeast Veladero
CO 154	Lava flow	А	28.090	68.934	5016		wr	Southeast Veladero
	Bonete Chico							
CO 147	Lava flow	D	28.140	68.672	4512	2.5 ± 0.4	wr ²	Southern Bonete Chico
CO 148	Lava flow	D	28.124	68.743	4954	4.0 ± 0.2	wr ²	South face of Bonete Chico
CO 149	Lava flow	D	28.080	68.754	5088	4.2 ± 0.3	wr ²	South face of Bonete Chico
CO 150	Lava flow	А	28.130	68.787	4890	-		South face of Bonete Chico
CO 321	Lava flow	D	27.935	68.760	5760	-		North face of Bonete Chico

¹Ar/Ar fusion ages reported in Table 4.2, ²K-Ar ages obtained at SERNAGEOMIN and are presented in Table 4.1, R=rhyolite (SiO₂ > 70 wt %); RD = rhyodacite (SiO₂ = 67-70 wt %); D = dacite (SiO₂ = 63-67 wt %), A = andesite (SiO₂ = 60-63 wt %).
Represenative major element mineral analyses from Incapillo dome xenoliths											
	amphibole analyses				biotite analyses				plagioclase analyses		
analysis #	29	73	90	85	31	61		44	48	77	97
type	CO512b	CO512b	CO512b	CO512b	CO512b	CO512b		CO512b	CO512b	CO512b	CO512b
sample	r	c	r	r	c	c		c	c	c	c
SiO ₂	45.24	44.17	47.98	45.64	38.29	38.48		55.38	58.91	56.30	60.91
TiO ₂	1.48	1.74	1.31	1.53	3.15	2.92		0.01	0.00	0.01	0.02
Al_2O_3	9.47	11.56	7.35	9.14	14.65	14.83		28.31	26.32	28.35	24.96
FeO	14.05	12.39	14.11	14.75	14.24	11.81		0.21	0.16	0.17	0.23
MnO	0.38	0.31	0.39	0.37	0.20	0.16		0.00	0.00	0.00	0.01
MgO	13.56	13.93	14.28	13.37	17.50	17.91		0.00	0.02	0.01	0.00
CaO	12.09	12.25	12.05	11.96	0.06	0.04		10.25	7.53	10.08	6.03
Na ₂ O	1.68	2.01	1.36	1.69	0.72	0.64		5.35	6.60	5.37	7.18
K ₂ O	0.82	0.78	0.68	0.75	9.26	9.36		0.34	0.55	0.33	0.82
Cr ₂ O ₃	-	-	-	-	-	-		-	-	-	-
Total	98.77	99.14	99.50	99.20	98.07	96.15		99.85	100.10	100.61	100.16
Si	6.549	6.345	6.851	6.582	2.790	2.840		2.497	2.628	2.515	2.705
Ti	0.161	0.188	0.141	0.166	0.173	0.162		0.000	0.000	0.000	0.001
Al (iv)	1.451	1.655	1.149	1.418	0.210	0.160		1.504	1.384	1.492	1.306
Al (vi)	0.165	0.302	0.089	0.136	1.048	1.129		-	-	-	-
Fe ²⁺	1.112	0.988	1.095	1.139	0.867	0.728		0.008	0.006	0.006	0.009
Fe ³⁺	0.589	0.501	0.589	0.640	-	-		-	-	-	-
Mn	0.046	0.037	0.047	0.045	0.012	0.010		0.000	0.000	0.000	0.000
Mg	2.926	2.983	3.039	2.874	1.900	1.970		0.000	0.001	0.001	0.000
Ca	1.876	1.88/	1.845	1.849	0.004	0.003		0.496	0.360	0.483	0.28/
Na _(B)	0.124	0.115	0.155	0.323	0.102	0.091		0.408	0.571	0.405	0.018
K	0.152	0.142	0.124	0.138	0.861	0.881		0.019	0.032	0.019	0.046
Cr	-	-	-	-	-	-		-	-	-	-
Total	15.699	15.76	15.54	15.68	7.967	7.975		4.993	4.982	4.981	4.973
$(Na + K)_A$	0.498	0.588	0.344	0.461	_	-	An	50.5	37.4	49.9	30.2
$(Ca + Na)_B$	2.000	2.000	2.000	2.000	-	-	Ab	47.6	59.3	48.1	64.9
$Mg^{2+}/(Mg^{2+}+Fe_T)$	0.632	0.667	0.643	0.618	0.69	0.73	Or	2.0	3.3	1.9	4.9

APPENDIX 12

All unknown mineral analyses were corrected by deviation from Smithsonian standards JDF and A99 and in-house standard RHA. Methods and replicated analyses of USGS secondary standards are reported in Appendices 1, 5, and 9 relative to published values by Jarosewich et al. (1980). Amphiboles, biotites, and plagioclase phenocrysts were calculated on the basis of 23, 11, and 32 oxygens respectively. An = Anorthite Ab = Albite Or = Orthoclase

Endmember compositions used in Incapillo mixing models								
	source magma	crustal assimilants						
	Pircas Negras	Average Paleozoic	Average UC					
	CO 309	Pz G	UC					
SiO_2	61.7	68.8	66.0					
TiO ₂	0.95	0.41	0.50					
Al_2O_3	16.2	14.6	15.2					
FeO _t	4.83	3.82	4.50					
MnO	0.08	0.08	0.08					
MgO	2.61	1.29	2.20					
CaO	6.46	3.02	4.20					
Na ₂ O	4.52	3.60	3.90					
K ₂ O	2.51	2.83	3.40					
P_2O_5	0.36	0.12	0.40					
Total	100.3	98.6	100.4					
S.r	800	190	250					
Dh	899 60	189	550					
RU Dh	10.5	113	20.0					
I U Ra	10.5	525	20.0					
La	39.1	23.1	30.0					
Nd	38.2	20.1	26.0					
Sm	6.7	4.4	4.5					
Eu	1.6	1.1	0.9					
Yb	0.83	2.31	2.20					
Hf	5.8	5.0	5.8					
Та	0.69	0.80	2.20					
Th	4.9	11.0	10.7					

APPENDIX 13

Pircas Negras composition is from Goss et al. (Chapter 2). Major and trace element data for Paleozoic is from Lucassen (2001) and bulk upper crust from Rudnick and Fountain (1995). Ta concentrations for average Paleozoic are calculated from the Nb concentration (15 ppm) using a Nb/Ta ratio of 17.5.

Partiti	Partition coefficients used in Incapillo EC-AFC mixing models											
	plag	amph	biotite	mag	K-spar	qz	zircon	xenolith¹ crystal/melt	plag-rich² crystal/melt	Paleozoic ³ assimilant/melt	Av. Upper Crust ⁴ assimilant/melt	
Sr	3.40	0.01	0.52	0.01	5.40	-	-	0.73	1.43	2.20	2.17	
Rb	0.30	0.40	4.20	0.01	1.75	0.011	-	0.52	0.50	0.77	0.96	
Pb	0.27	0.30	5.36	0.10	11.45	-	-	0.52	0.52	0.55	0.54	
Ва	0.53	0.53	0.10	0.71	2.44	0.011	-	0.50	0.49	2.04	2.22	
La	0.18	0.31	3.18	0.66	0.08	0.013	16.9	0.41	0.39	0.45	0.60	
Nd	0.09	1.20	2.23	0.93	0.04	0.011	13.3	1.01	0.78	0.32	0.43	
Sm	0.06	2.00	1.55	1.20	0.025	0.01	14.1	1.56	1.16	0.25	0.32	
Eu	0.75	1.90	0.87	0.91	4.45	0.038	16	1.59	1.35	0.99	1.00	
Yb	0.10	2.10	0.54	0.44	0.03	0.011	527	1.57	1.15	0.66	0.68	
Hf	0.03	0.54	0.60	0.24	0.03	0.017	3193	0.43	0.32	3.33	3.36	
Та	0.3	0.59	1.34	1.2	0.01	0.006	47	0.52	0.41	0.29	0.343	
Th	0.01	0.16	1.22	0.01	0.02	0.006	76.8	0.17	0.14	0.28	0.33	

APPENDIX 14

REFERENCES

- Abratis, M., 1998, Geochemical variations in magmatic rocks from southern Costa Rica as a consequence of Cocos Ridge subduction and uplift of the Cordillera de Talamanca: Göttingen, Germany, Ph.D. thesis, Universität Göttingen.
- Abratis, M., and Wörner, G., 2001, Ridge collision, slab-window formation, and the flux of Pacific asthenosphere into the Caribbean realm: Geology, v. 29, p. 127-130.
- Aitcheson, S.J., and Forrest, A.H., 1994, Quantification of crustal contamination in open magmatic systems: Journal of Petrology, v. 35, p. 461-488.
- Aitcheson, S.J., Harmon, R.S., Moorbath, S., Schneider, A., Soler, P., Soria-Escalante, E., Steele, G., Swainbank, I., and Wörner, G., 1995, Pb isotopes define basement domains of the Altiplano, central Andes: Geology, v. 23, p. 555-558.
- Albee, A.L., and Ray, L., 1970, Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates, and sulfates: Analytical Chemistry, v. 42, p. 1408-1414.
- Allégre, C.J., 1982, Chemical geodynamics: Tectonophysics, v. 81, p. 109-132.
- Alonso-Perez, R., Ulmer, P., Muentener, O., and Thompson, A.B., 2004, Role of garnet fractionation in H₂O-undersaturated andesite liquids at high pressure (abstract): Lithos, v. 73, p. S1-S2.
- Alonso, R.N., Jordan, T.E., Tabutt, K.T., and Vandervoort, D.S., 1991, Giant evaporite belts of the Neogene central Andes: Geology, v. 19, p. 401-404.
- Alvarado, G.E., Kussmaul, S., Chiesa, S., Gillot, P.Y., Appel, H., Woerner, G., and Rundle, C., 1993, Resumen cronoestratigráfico de las rocas ígneas de Costa Rica basado en dataciones radiométricas: Journal of South American Earth Sciences, v. 6, p. 151-168.
- Anderson, D., and Lindsley, D.H., 1988, Internally consistent solution models for Fe-Mg-Mn-Ti oxides: Fe-Ti oxides: American Mineralogist, v. 73, p. 714-726.

- Anderson, D., Lindsley, D.H., and Davidson, P., 1993, QUILF: A Pascal program to assess equilibria among the Fe-Mg-Mn-Ti oxides, pyroxenes, olivine, and quartz: Computers and Geosciences, v. 19, p. 1333-1350.
- Annen, C., Blundy, J.D., and Sparks, R.S.J., 2006, The genesis of intermediate and silicic magmas in deep crustal hot zones: Journal of Petrology, v. 47, p. 505-539.
- Armstrong, R.L., 1968, A model for the evolution of strontium and lead isotopes in a dynamic earth: Reviews of Geophysics, v. 6, p. 175-199.
- Asimow, P.D., and Ghiorso, M.S., 1998, Algorithmic modifications extending MELTS to calculate subsolidus phase relations: American Mineralogist, v. 83, p. 1127-1131.
- Atherton, M.P., and Petford, N., 1993, Generation of sodium-rich magmas from newly underplated basaltic crust: Nature, v. 362, p. 144-146.
- Aubouin, J., Bourgois, J., Azema, J., and von Huene, R., 1985, Guatemala margin: A model of convergent extensional margin?: Initial reports of the Deep Sea Drilling Project covering Leg 84 of the cruises of the Drilling Vessel Glomar Challenger; Balboa, Panama, to Manzanillo, Mexico, January-February 1982, v. 84, p. 911-917.
- Audetat, A., and Keppler, H., 2005, Solubility of rutile in subduction zone fluids, as determined by experiments in the hydrothermal diamond anvil cell: Earth and Planetary Science Letters, v. 232, p. 393-402.
- Bacon, C.R., and Druitt, T.H., 1988, Compositional evolution of the zoned calcalkaline magma chamber of Mount-Mazama, Crater Lake: Contributions to Mineralogy and Petrology, v. 98, p. 224-256.
- Baker, M.C.W., 1981, The nature and distribution of upper Cenozoic ignimbrite centres in the Central Andes: Journal of Volcanology and Geothermal Research, v. 11, p. 293-315.
- Baldwin, A.K., and Marrett, R.A., 2004, Evidence for a releasing bend at the southern margin of the Puna plateau, Argentine Andes, GSA Annual Meeting, abstract: Denver, CO.

- Barazangi, M., and Isacks, B.L., 1976, Spatial distribution of earthquakes and subduction of the Nazca Plate beneath South America: Geology, v. 4, p. 686-692.
- Barker, F., and Arth, J.G., 1976, Generation of trondhjemitic-tonalitic liquids and Archean bimodal trondhjemite-basalt suites: Geology, v. 4, p. 596-600.
- Barth, M., McDonough, W.F., and Rudnick, R.L., 2000, Tracking the budget of Nb and Ta in the continental crust: Chemical Geology, v. 165, p. 197-213.
- Bea, F., 1996, Residence of the REE, Y, Th, and U in granites and crustal protoliths; Implications for the chemistry of crustal melts: Journal of Petrology, v. 37, p. 521-552.
- Becchio, R., Lucassen, F., Kasemann, S., Franz, G., and Viramonte, J.G., 1999, Geoquímica y sistemática isotópica de rocas metamórficas del Paleozoico inferior: Noroeste de Argentina y Norte de Chile (21°–27° S): Acta Geologica Hispanica, v. 34, p. 273-299.
- Beck, S.L., Zandt, G., Myers, S.C., Wallace, T.C., Silver, P.G., and Drake, L., 1996, Crustal-thickness variations in the Central Andes: Geology, v. 24, p. 407-410.
- Beck, S.L., and Zandt, G., 2002, The nature of orogenic crust in the Central Andes: Journal of Geophysical Research, v. 107, no. B10, doi: 10.1029/2000jb000124.
- Ben Othman, D., White, W.M., and Patchett, J., 1989, The geochemistry of marine sediments, island arc magma genesis, and crust-mantle recycling: Earth and Planetary Science Letters, v. 94, p. 1-21.
- Bindeman, I.N., Eiler, J.M., Yogodzinski, G.M., Tatsumi, Y., Stern, C.R., Grove, T.L., Portnyagin, M., Hoernle, K., and Danyushevsky, L.V., 2005, Oxygen isotope evidence for slab melting in modern and ancient subduction zones: Earth and Planetary Science Letters, v. 235, p. 480-496.
- Blundy, J., and Wood, B., 1994, Prediction of crystal-melt partition coefficients from elastic moduli: Nature, v. 372, p. 452-454.

- Bohrson, W.A., and Spera, F.J., 2001, Energy-constrained open-system magmatic processes II: Application of energy-constrained assimilation-fractional crystallization (EC-AFC) model to magmatic systems: Journal of Petrology, v. 42, p. 1019-1041.
- Bosch, D., Jamais, M., Boudier, F., Nicolas, A., Dautria, J.M., and Agrinier, P., 2004, Deep and high-temperature hydrothermal circulation in the Oman ophiolite -Petrological and isotopic evidence: Journal of Petrology, v. 45, p. 1181-1208.
- Bowen, N.L., 1928, The Evolution of Igneous Rocks: New York, NY, Dover, 332 p.
- Brenan, J.M., Shaw, H.F., Ryerson, F.J., and Phinney, D.L., 1995a, Experimental determination of trace-element partitioning between pargasite and a synthetic hydrous andesitic melt: Earth and Planetary Science Letters, v. 135, p. 1-11.
- —, 1995b, Mineral-aqueous fluid partitioning of trace elements at 900 °C and 2.0 GPa: Constraints on the trace element chemistry of mantle and deep crustal fluids: Geochimica et Cosmochimica Acta, v. 59, p. 3331-3350.
- Büchl, A., Münker, C., Mezger, K., and Hofmann, A.W., 2002, High precision Nb/Ta and Zr/Hf ratios in global MORB: Geochimica et Cosmochimica Acta, v. Suppl. 66, p. A108.
- Caffe, P.J., Trumbull, R., Coira, B., and Romer, R.L., 2002, Petrogenesis of early Neogene magmatism in the northern Puna: Implications for magma genesis and crustal processes in the Central Andean Plateau: Journal of Petrology, v. 43, p. 907-942.
- Cahill, T.A., and Isacks, B.L., 1992, Seismicity and shape of the subducted Nazca Plate: Journal of Geophysical Research, v. 97, p. 17,503-17,529.
- Caminos, R., and Fauqué, L., 2000, Carta Geológica de la Republica Argentina, Tinogasta, 2969-II, SEGEMAR Instituto de Geología y Recursos Minerales.
- Cao, X.D., Yin, M., and Wang, X.R., 2001, Elimination of the spectral interference from polyatomic ions with rare earth elements in inductively coupled plasma mass spectrometry by combining algebraic correction with chromatographic separation: Spectrochimica Acta Part B-Atomic Spectroscopy, v. 56, p. 431-441.

- Carr, M.J., 1984, Symmetrical and segmented variation of physical and geochemical characteristics of the Central American Volcanic Front: Journal of Volcanology and Geothermal Research, v. 20, p. 231-252.
- Carr, M.J., Feigenson, M.D., and Bennett, E.A., 1990, Incompatible element and isotopic evidence for tectonic control of source mixing and melt extraction along the Central-American arc: Contributions to Mineralogy and Petrology, v. 105, p. 369-380.
- Carrapa, B., Adelmann, D., Hilley, G.E., Mortimer, E., Sobel, E.R., and Strecker, M.R., 2005, Oligocene range uplift and development of plateau morphology in the southern Central Andes: Tectonics, v. 24, no 4, p. 1-19.
- Castillo, P., Batiza, R., Vanko, D., Malavassi, E., Barquero, J., and Fernandez, E., 1988, Anomalously young volcanoes on old hot-spot traces: 1. Geology and Petrology of Cocos-Island: Geological Society of America Bulletin, v. 100, p. 1400-1414.
- Christeson, G.L., McIntosh, K.D., Shipley, T.H., Flueh, E.R., and Goedde, H., 1999, Structure of the Costa Rica convergent margin, offshore Nicoya Peninsula: Journal of Geophysical Research-Solid Earth, v. 104, p. 25443-25468.
- Cigolini, C., Kudo, A.M., Brookins, D.G., and Ward, D., 1991, The petrology of Poas Volcano lavas: Basalt-andesite relationship and their petrogenesis with the magmatic arc of Costa Rica: Journal of Volcanology and Geothermal Research, v. 48, p. 367-384.
- Cigolini, C., 1998, Intracrustal origin of Arenal basaltic andesite in the light of solidmelt interactions and related compositional buffering: Journal of Volcanology and Geothermal Research, v. 86, p. 277-310.
- Clift, P., and Vannucchi, P., 2004, Controls on tectonic accretion versus erosion in subduction zones: Implications for the origin and recycling of the continental crust: Reviews of Geophysics, v. 42, doi:10.1029/2003RG000127.
- Clift, P., Chan, L.H., Blusztajn, J., Layne, G.D., Kastner, M., and Kelly, R., 2005, Pulsed subduction accretion and tectonic erosion reconstructed since 2.5 Ma from the tephra record offshore Costa Rica: Geochemistry Geophysics Geosystems, v. 6, no. 9, doi:10.1029/2005GC000963.

- Clift, P., and Hartley, A., 2007, Slow rates of subduction erosion and coastal underplating along the Andean margin of Chile and Peru: Geology, v. 35, p. 503-506.
- Cloos, M., and Shreve, R.L., 1988, Subduction-channel model of prism accretion, melange formation, sediment subduction, and subduction erosion at convergent plate margins: Part 1, Background and description: Pure and Applied Geophysics, v. 128, p. 455-500.
- Cloos, M., 1993, Lithospheric buoyancy and collisional orogenesis: Subduction of oceanic plateaus, continental margins, island arcs, spreading ridges, and seamounts: Geological Society of America Bulletin, v. 105, p. 715-737.
- Coedo, A.G., Dorado, M.T., Padilla, I., and Alguacil, F.J., 1998, Use of boric acid to improve the microwave-assisted dissolution process to determine fluoride forming elements in steels by flow injection inductively coupled plasma mass spectrometry: Journal of Analytical Atomic Spectrometry, v. 13, p. 1193-1197.
- Coira, B., Kay, S.M., and Viramonte, J.G., 1993, Upper Cenozoic magmatic evolution of the Argentine Puna - A model for changing subduction geometry: International Geology Review, v. 35, p. 677-720.
- Coira, B., Caffe, P.J., Kay, S.M., Diaz, A., and Ramirez, A., 1996, Complejo volcanico Vilama-sistema caldérico del Cenozoico superior en Puna, Jujuy, 13º Congreso Geológico Argentino, v. 13: Buenos Aires, Argentina, p. 603-620.
- Coira, B., Kay, S.M., Peréz, B., Woll, B., Hanning, M., and Flores, P., 1999, Magmatic sources and tectonic setting of Gondwana margin Ordovician magmas, northern Puna of Argentina and Chile, *in* Ramos, V.A., and Keppie, D., eds., Laurentia-Gondwana Connections before Pangea: Geological Society of America Special Paper 336, p. 147-169.
- Comte, D., Haessler, H., Dorbath, L., Pardo, M., Monfret, T., Lavenu, A., Pontoise, B., and Hello, Y., 2002, Seismicity and stress distribution in the Copiapo, northern Chile subduction zone using combined on- and off-shore seismic observations: Physics of the Earth and Planetary Interiors, v. 132, p. 197-217.
- Conrey, R.M., Hooper, P.R., Larson, P.B., Chesley, J., and Ruiz, J., 2001, Trace element and isotopic evidence for two types of crustal melting beneath a High

Cascade volcanic center, Mt. Jefferson, Oregon: Contributions to Mineralogy and Petrology, v. 141, p. 710-732.

- Cornejo, P., Mpodozis, C., Raimírez, C.F., and Tomlinson, A., 1993, Estudio geológico de la región de El Salvador y Potrerillos, Servicio Nacional de Geología y Minería-CODELCO, Open File Report: Santiago, Chile, p. 1-258.
- Cruciani, C., Carminati, E., and Doglioni, C., 2005, Slab dip vs. lithosphere age: No direct function: Earth and Planetary Science Letters, v. 238, p. 298-310.
- Davidson, J.P., 1996, Deciphering mantle and crustal signatures in subduction zone magmas, *in* Bebout, G.E., Scholl, D., Kirby, S.H., and Platt, J.P., eds., Subduction: Top to Bottom, v. 96, American Geophysical Union, p. 251-262.
- de Boer, J., Drummond, M.S., Bordelon, M.J., Defant, M.J., Bellon, H., and Maury, R.C., 1995, Cenozoic magmatic phases of the Costa Rican island arc (Cordillera de Talamanca), *in* Mann, P., ed., Geologic and Tectonic Development of the Caribbean Plate Boundary in Southern Central America: Geological Society of America Special Paper 295, p. 35-55.
- de Boer, J.Z., Defant, M.J., Stewart, R.H., and Bellon, H., 1991, Evidence for active subduction below western Panama: Geology, v. 19, p. 649-652.
- de Silva, S.L., 1989a, Geochronology and stratigraphy of the ignimbrites from the 21° 30'S to 23° 30'S portion of the central Andes of northern Chile: Journal of Volcanology and Geothermal Research, v. 37, p. 93-131.
- —, 1989b, Altiplano-Puna volcanic complex of the Central Andes: Geology, v. 17, p. 1102-1106.
- —, 1991, Styles of zoning in central Andean ignimbrites: Insights into magma chamber processes, *in* Harmon, R.S., and Rapela, C.W., eds., Geological Society of America centennial meeting, 7th Latin America geological congress, v. 265, Geological Society of America, p. 217-232.
- de Silva, S.L., and Francis, P.W., 1991, Volcanoes of the Central Andes: Berlin, Springer-Verlag, 216 p.

- de Silva, S.L., Self, S., Francis, P.W., Drake, R.E., and Ramirez, C.R., 1994, Effusive siliceous volcanism in the Central Andes: The Chao dacite and other young lavas of the Altiplano-Puna Volcanic Complex: Journal of Geophysical Research, v. 99, p. 17805-17825.
- de Silva, S.L., and Gosnold, W.D., 2007, Episodic construction of batholiths: Insights from the spatiotemporal development of an ignimbrite flare-up: Journal of Volcanology and Geothermal Research, doi:10.1016/j.jvolgeores.2007.07.015.
- Defant, M.J., and Drummond, M.S., 1990, Derivation of some modern arc magmas by melting of young subducted lithosphere: Nature, v. 347, p. 662-665.
- Defant, M.J., Clark, L.F., Stewart, R.H., Drummond, M.S., de Boer, J.Z., Maury, R.C., Bellon, H., Jackson, T.E., and Restrepo, J.F., 1991a, Andesite and dacite genesis via contrasting processes: The geology and geochemistry of El Valle Volcano, Panama: Contributions to Mineralogy and Petrology, v. 106, p. 309-324.
- Defant, M.J., Richerson, P.M., de Boer, J.Z., Stewart, R.H., Maury, R.C., Bellon, H., Drummond, M.S., Feigenson, M.D., and Jackson, T.E., 1991b, Dacite genesis via both slab melting and differentiation: Petrogenesis of La Yeguada volcanic complex, Panama: Journal of Petrology, p. 1101-1142.
- Defant, M.J., Jackson, T.E., Drummond, M.S., de Boer, J.Z., Bellon, H., Feigenson, M.D., Maury, R.C., and Stewart, R.H., 1992, The geochemistry of young volcanism throughout western Panama and southeastern Costa-Rica: An overview: Journal of the Geological Society of London, v. 149, p. 569-579.
- DeMets, C., Gordon, R.G., Argus, D.F., and Stein, S., 1990, Current plate motions: Geophysical Journal International, v. 101, p. 425-478.
- DeMets, C., 2001, A new estimate for present-day Cocos-Caribbean Plate motion: Implications for slip along the Central American volcanic arc: Geophysical Research Letters, v. 28, p. 4043-4046.
- DePaolo, D.J., 1981, Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization: Earth and Planetary Science Letters, v. 53, p. 189-202.

- Droop, G.T.R., 1987, A general equation for estimating Fe³⁺ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria: Mineralogical Magazine, v. 51, p. 431-435.
- Drummond, M.S., and Defant, M.J., 1990, A model for trondhjemite-tonalite-dacite genesis and crustal growth via slab melting: Archean to modern comparisons: Journal of Geophysical Research, v. 95, p. 21,503-21,521.
- Eggins, S.M., Woodhead, J.D., Kinsley, L.P.J., Mortimer, G.E., Sylvester, P., McCulloch, M.T., Hergt, J.M., and Handler, M.R., 1997, A simple method for the precise determination of ≥ 40 trace elements in geological samples by ICPMS using enriched isotope internal standardization: Chemical Geology, v. 134, p. 311-326.
- Eichelberger, J.C., Carrigan, C.R., Westrich, H.R., and Price, R.H., 1986, Nonexplosive silicic volcanism: Nature, v. 323, p. 598-602.
- Elliott, T., Plank, T., Zindler, A., White, W., and Bourdon, B., 1997, Element transport from slab to volcanic front at the Mariana Arc: Journal of Geophysical Research, v. 102, p. 14,991-15,019.
- Ewart, A., and Griffin, W.L., 1994, Application of proton-microprobe data to traceelement partitioning in volcanic-rocks: Chemical Geology, v. 117, p. 251-284.
- Fauqué, L., 2000, Carta Geológica de la Republica Argentina, Pastillos, 2969-I, SEGEMAR Instituto de Geología y Recursos Minerales.
- Feigenson, M.D., and Carr, M.J., 1986, Positively correlated Nd and Sr isotope ratios of lavas from the Central American volcanic front: Geology, v. 14, p. 79-82.
- Feigenson, M.D., Carr, M.J., V., M.S., Juliano, S., and L., B.L., 2004, Lead isotope composition of Central American volcanoes: Influence of the Galapagos plume: Geochemistry, Geophysics, Geosystems, v. 5, no 6, doi:10.1029/2003gc000621.
- Fiebig, J., Wiechert, U., Rumble, D., III, and Hoefs, J., 1999, High-precision in situ oxygen isotope analysis of quartz using an ArF laser: Geochimica et Cosmochimica Acta, v. 63, p. 687-702.

- Fisher, D.M., Gardner, T.W., Marshall, J.S., Sak, P.B., and Protti, M., 1998, Effect of subducting sea-floor roughness on fore-arc kinematics, Pacific Coast, Costa Rica: Geology, v. 26, p. 467-470.
- Folch, A., and Marti, J., 1998, The generation of overpressure in felsic magma chambers by replenishment: Earth and Planetary Science Letters, v. 163, p. 301-314.
- Foley, S., Tiepolo, M., and Vannucci, R., 2002, Growth of early continental crust controlled by melting of amphibolite in subduction zones: Nature, v. 417, p. 837-840.
- Foley, S.F., Barth, M.G., and Jenner, G.A., 2000, Rutile/melt partition coefficients for trace elements and an assessment of the influence of rutile on the trace element characteristics of subduction zone magmas: Geochimica et Cosmochimica Acta, v. 64, p. 933-938.
- Francis, P.W., and Baker, M.C.W., 1978, Sources of two large ignimbrites in the central Andes: Some Landsat evidence: Journal of Volcanology and Geothermal Research, v. 4, p. 81-87.
- Francis, P.W., Sparks, R.S.J., Hawkesworth, C.J., Thorpe, R.S., Pyle, D.M., Tait, S.R., Mantovani, M.S.M., and McDermott, F., 1989, Petrology and geochemistry of volcanic rocks of the Cerro Galán Caldera, Northwest Argentina: Geological Magazine, v. 126, p. 515-547.
- Freundt, A., 1998, The formation of high-grade ignimbrites, I: Experiments on highand low-concentration transport systems containing sticky particles: Bulletin of Volcanology, v. 59, p. 414-435.
- —, 1999, Formation of high-grade ignimbrites, II: A pyroclastic suspension current model with implications also for low-grade ignimbrites: Bulletin of Volcanology, v. 60, p. 545-567.
- Frisch, W., Meschede, M., and Sick, M., 1992, Origin of the Central-American ophiolites - evidence from paleomagnetic results: Geological Society of America Bulletin, v. 104, p. 1301-1314.

- Fromm, R., Zandt, G., and Beck, S.L., 2004, Crustal thickness beneath the Andes and Sierras Pampeanas at 30 °S inferred from Pn apparent phase velocities: Geophysical Research Letters, v. 31, no. 6, doi:10.1029/2003GL019231.
- Gardeweg, M., and Ramírez, C.F., 1987, La Pacana caldera and the Atana ignimbrite -A major ash-flow and resurgent caldera complex in the Andes of northern Chile: Bulletin of Volcanology, v. 49, p. 547-566.
- Gardeweg, M., Mpodozis, C., Clavero, J., and Cuitiño, L., 1998, The Ojos del Salado complex: The highest active volcano in the world, Volcanoes and their Roots -IAVCEI, abstracts: Cape Town, South Africa, p. 21.
- Gardeweg, M., Clavero, J., Mpodozis, C., Pérez de Arce, C., and Villeneuve, M., 2000, El Macizo Tres Cruces: Un complejo volcánico longevo y potencialmente activo en la Alta Cordillera de Copiapó, Chile, 9° Congreso Geológico Chileno, Actas: Puerto Varas, Chile, p. 191-195.
- Gardner, T.W., Verdonck, D., Pinter, N.M., Slingerland, R.L., Furlong, K.P., Bullard, T.F., and Wells, S.G., 1992, Quaternary uplift astride the aseismic Cocos Ridge, Pacific Coast, Costa Rica: Geological Society of America Bulletin, v. 104, p. 219-232.
- Garrido, C.J., Bodinier, J.L., Burg, J.P., Zeilinger, G., Hussain, S.S., Dawood, H., Chaudhry, M.N., and Gervilla, F., 2006, Petrogenesis of mafic garnet granulite in the lower crust of the Kohistan paleo-arc complex (Northern Pakistan): Implications for intra-crustal differentiation of island arcs and generation of continental crust: Journal of Petrology, v. 47, p. 1873-1914.
- Garrison, J.M., and Davidson, J.P., 2003, Dubious case for slab melting in the Northern volcanic zone of the Andes: Geology, v. 31, p. 565-568.
- Garzione, C.N., Molnar, P., Libarkin, J.C., and MacFadden, B.J., 2006, Rapid late Miocene rise of the Bolivian Altiplano: Evidence for removal of mantle lithosphere: Earth and Planetary Science Letters, v. 241, p. 543-556.
- Geist, D., White, W.M., Albarede, F., Harpp, K., Reynolds, R., Blichert-Toft, J., and Kurz, M.D., 2002, Volcanic evolution in the Galapagos: The dissected shield of Volcan Ecuador: Geochemistry, Geophysics, Geosystems, v. 3, no. 10, doi:10.1029/2002GC000355.

- Gelcich, S., Spooner, E.T.C., and Davis, D.W., 2005, Tracking the basement of the early Andean magmatism: U-Pb ages of zircon xenocrysts of the La Negra Formation in the Coastal Cordillera near Chañaral (~ 26° S), Northern Chile, 6th International Symposium on Andean Geodynamics (2005): Barcelona, p. 308-311.
- Ghiorso, M.S., and Carmichael, I.S.E., 1981, A Fortran-IV computer program for evaluating temperatures and oxygen fugacities from the compositions of coexisting iron-titanium oxides: Computers & Geosciences, v. 7, p. 123-129.
- Ghiorso, M.S., and Sack, R.O., 1995, Chemical mass transfer in magmatic processes IV: A revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and pressures: Contributions to Mineralogy and Petrology, v. 119, p. 197-212.
- Gilbert, H.J., Beck, S., and Zandt, G., 2006, Lithospheric and upper mantle structure of central Chile and Argentina: Geophysical Journal International, v. 165, p. 383-398.
- Gorring, M.L., and Kay, S.M., 2000, Carbonatite metasomatized peridotite xenoliths from southern Patagonia: Implications for lithospheric processes and Neogene plateau magmatism: Contributions to Mineralogy and Petrology, v. 140, p. 55-72.
- Goss, A., Kay, S.M., and Mpodozis, C., 2003, Subduction erosion controlled adakites: Examples from the Bonete/Incapillo-Andean and Middle American Margins, 10° Congreso Geológico Chileno, Actas: Concepción, Chile.
- Goss, A.R., and Kay, S.M., 2006a, Steep REE patterns and enriched Pb isotopes in southern Central American arc magmas: Evidence for forearc subduction erosion?: Geochemistry Geophysics Geosystems, v. 7, doi: 10.1029/2005GC001163.
- —, 2006b, Adakitic volcanism within an unstable Andean arc: The Pircas Negras and Dos Hermanos andesites, Chile/Argentina (~27° S, ~68° W), Backbone of the Americas, abstracts: Mendoza, Argentina.

- Goss, A.R., Kay, R.W., and Mpodozis, C., Chapter 2, Central Andean adakites from the northern edge of the Chilean flatslab (27°-28.5° S) associated with arc migration and forearc subduction: Ithaca, NY, Ph.D thesis, Cornell University.
- Goss, A.R., and Kay, S.M., Chapter 3, Extreme High Field Strength element (HFSE) depletion and near-chondritic Nb/Ta ratios in Central Andean adakite-like lavas (~ 28° S, 68° W) Ithaca, NY, Ph.D. thesis, Cornell University.
- Goss, A.R., Kay, S.M., and Mpodozis, C., Chapter 4, The Incapillo Caldera (~ 28° S): A stranded magma chamber over a dying Andean arc: Ithaca, NY, Ph.D. thesis, Cornell University.
- Götze, H.-J., Lahmeyer, B., Schmidt, S., and Strunk, S., 1994, The lithospheric structure of the Central Andes (20°-26° S) as inferred from interpretation of regional gravity, *in* Reutter, K.J., Scheuber, E., and Wigger, P.J., eds., Tectonics of the Southern Central Andes: Structure and Evolution of an Active Continental Margin: Berlin, Springer-Verlag, p. 1349-1343.
- Govindaraju, K., 1989, 1989 compilation of working values and sample description of 272 geostandards: Geostandards Newsletter, v. 13, p. 1-113.
- ---, 1994, 1994 compilation of working values and descriptions for 383 geostandards: Geostandards Newsletter, v. 18, p. 1-158.
- Green, T.H., and Ringwood, A.E., 1968, Genesis of the calc-alkaline igneous rock suite: Contributions to Mineralogy and Petrology, v. 18, p. 105-162.
- Green, T.H., 1982, Anatexis of mafic crust and high pressure crystallization of andesite, *in* Thorpe, R.S., ed., Andesites: Orogenic Andesites and Related Rocks: New York, John Wiley and Sons, p. 465-487.
- Green, T.H., and Pearson, N.J., 1986, Ti-rich accessory phase saturation in hydrous mafic-felsic compositions at high PT: Chemical Geology, v. 54, p. 185-201.
- —, 1987, An experimental study of Nb and Ta partitioning between Ti-rich minerals and silicate minerals at high pressure and temperature: Geochimica et Cosmochimica Acta, v. 51, p. 55-62.

- Green, T.H., Blundy, J.D., Adam, J., and Yaxley, G.M., 2000, SIMS determination of trace element partition coefficients between garnet, clinopyroxene and hydrous basaltic liquids at 2-7.5 GPa and 1080-1200 °C: Lithos, v. 53, p. 165-187.
- Gregory, R.T., and Taylor, H.P., 1981, An oxygen isotope profile in a section of Cretaceous oceanic-crust, Samail Ophiolite, Oman evidence for δ^{18} O buffering of the oceans by deep (> 5 km) seawater-hydrothermal circulation at mid-ocean ridges: Journal of Geophysical Research, v. 86, p. 2737-2755.
- Gromet, L.P., and Silver, L.T., 1983, Rare earth element distribution among minerals in a granodiorite and their petrogenetic implications: Geochimica et Cosmochimica Acta, v. 47, p. 925-940.
- —, 1987, REE variations across the Peninsular Ranges batholith: Implications for batholithic petrogenesis and crustal growth in magmatic arcs: Journal of Petrology, v. 28, p. 75-125.
- Grove, T.L., Parman, S.W., Bowring, S.A., Price, R.C., and Baker, M.B., 2002, The role of an H₂O-rich fluid component in the generation of primitive basaltic andesites and andesites from the Mt. Shasta region, N. California: Contributions to Mineralogy and Petrology, v. 142, p. 375-396.
- Grove, T.L., Elkins-Tanton, L.T., Parman, S.W., Chatterjee, N., Muentener, O., and Gaetani, G.A., 2003, Fractional crystallization and mantle-melting controls on calc-alkaline differentiation trends: Contributions to Mineralogy and Petrology, v. 145, p. 515-533.
- Grove, T.L., Chatterjee, N., Parman, S.W., and Medard, E., 2006, The influence of H₂O on mantle wedge melting: Earth and Planetary Science Letters, v. 249, p. 74-89.
- Guerrero, M.A., Lanadaio, E., and Marcos, O., 1993, Mapa geológico de la provincia de La Rioja, Republica Argentina, Secretaria de Minería, Dirección Nacional del Servicio Geológico.
- Gutscher, M.-A., Maury, R.C., Eissen, J.-P., and Bourdon, B., 2000a, Can slab melting be caused by flat subduction?: Geology, v. 28, p. 535-538.

- Gutscher, M.-A., Spakman, W., Bijwaard, H., and Engdahl, E.R., 2000b, Geodynamics of flat subduction: Seismicity and tomographic constraints from the Andean margin: Tectonics, v. 19, p. 814-833.
- Gutscher, M.-A., 2002, Andean subduction styles and their effect on thermal structure and interplate coupling: Journal of South American Earth Sciences, v. 15, p. 3-10.
- Hacker, B.R., Abers, G.A., and Peacock, S.M., 2003a, Subduction factory: 1, Theoretical mineralogy, densities, seismic wave speeds, and H₂O contents: Journal of Geophysical Research, v. 108.
- Hacker, B.R., Peacock, S.M., Abers, G.A., and Holloway, S.D., 2003b, Subduction factory: 2, Are intermediate-depth earthquakes in subducting slabs linked to metamorphic dehydration reactions?: Journal of Geophysical Research, v. 108, no. B1.
- Harmon, R.S., and Hoefs, J., 1995, Oxygen isotope heterogeneity of the mantle deduced from global ¹⁸O systematics of basalts from different geotectonic settings: Contributions to Mineralogy and Petrology, v. 120, p. 95-114.
- Harpp, K.S., Wanless, V.D., Otto, R.H., Hoernle, K., and Werner, R., 2005, The Cocos and Carnegie aseismic ridges: A trace element record of long-term plumespreading center interaction: Journal of Petrology, v. 46, p. 109-133.
- Hart, S., and Dunn, T., 1993, Experimental cpx/melt partitioning of 24 trace elements: Contributions to Mineralogy and Petrology, v. 113, p. 1-8.
- Hauff, F., Hoernle, K., Tilton, G., Graham, D.W., and Kerr, A.C., 2000a, Large volume recycling of oceanic lithosphere over short time scales: Geochemical constraints from the Caribbean Large Igneous Province: Earth and Planetary Science Letters, v. 174, p. 247-263.
- Hauff, F., Hoernle, K., van den Bogaard, P., Alvarado, G., and Garbe-Schoenberg, D., 2000b, Age and geochemistry of basaltic complexes in western Costa Rica: Contributions to the geotectonic evolution of Central America: Geochemistry, Geophysics, Geosystems, v. 1, paper number 1999GC000020.

- Hawkesworth, C.J., Hergt, J.M., Ellam, R.M., and Mcdermott, F., 1991, Element fluxes associated with subduction related magmatism: Philosophical Transactions of the Royal Society of London Series A - Mathematical, Physical, and Engineering Sciences, v. 335, p. 393-405.
- Heit, B., 2005, Teleseismic tomographic images of the Central Andes at 21° S and 25.5° S: An inside look at the Altiplano and Puna plateaus: Potsdam, Germany, Ph.D. thesis, GeoForschungsZentrum (GFZ).
- Hey, R., 1977, Tectonic evolution of the Cocos-Nazca spreading center: Geological Society of America Bulletin, v. 88, p. 1404-1420.
- Hildreth, W., and Moorbath, S., 1988, Crustal contributions to arc magmatism in the Andes of central Chile: Contributions to Mineralogy and Petrology, v. 98, p. 455-489.
- Hildreth, W., 1991, The timing of caldera collapse at Mount Katmai in response to magma withdrawal toward Novarupta: Geophysical Research Letters, v. 18, p. 1541-1544.
- Hilyard, M., Nielsen, R.L., Beard, J.S., Patino-Douce, and Blencoe, J., 2000, Experimental determination of the partitioning behavior of rare earth and high field strength elements between pargasitic amphibole and natural silicate melts: Geochimica et Cosmochimica Acta, v. 64, p. 1103-1120.
- Hoernle, K., Werner, R., Jason, P.M., Garbe-Schoenberg, D., Bryce, J., and Mrazek, J., 2000, Existence of complex spatial zonation in the Galapagos Plume for at least 14 m.y: Geology, v. 28, p. 435-438.
- Hoernle, K., van den Bogaard, P., Werner, R., Lissinna, B., Hauff, F., Alvarado, G., and Garbe-Schoenberg, D., 2002, Missing history (16-71 Ma) of the Galapagos hotspot: Implications for the tectonic and biological evolution of the Americas: Geology, v. 30, p. 795-798.
- Hoernle, K., Hauff, F., and van den Bogaard, P., 2004, 70 m.y. history (139-69 Ma) for the Caribbean large igneous province: Geology, v. 32, p. 697-700.

- Hofmann, A.W., 1988, Chemical differentiation of the Earth: The relationship between mantle, continental crust, and oceanic crust: Earth and Planetary Science Letters, v. 90, p. 297-314.
- Hora, J.M., Singer, B.S., and Wörner, G., 2007, Volcano evolution and eruptive flux on the thick crust of the Andean Central Volcanic Zone: ⁴⁰Ar³⁹Ar constraints from Volcán Parinacota, Chile: Geological Society of America Bulletin, v. 119, p. 343-362.
- Huang, W.-L., and Wyllie, P.J., 1986, Phase relationships of gabbro-tonalite-granitewater at 15 kb with applications to differentiation and anatexis: American Mineralogist, v. 71, p. 301-316
- Ionov, D.A., and Hofmann, A.W., 1995, Nb-Ta-rich mantle amphiboles and micas: Implications for subduction-related metasomatic trace element fractionations: Earth and Planetary Science Letters, v. 131, p. 341-356.
- Isacks, B., Oliver, J., and Sykes, L.R., 1968, Seismology and the new global tectonics: Journal of Geophysical Research, v. 73, p. 5855-5899.
- Isacks, B.L., 1988, Uplift of the Central Andean Plateau and bending of the Bolivian Orocline: Journal of Geophysical Research, v. 93, p. 3211-3231.
- Ito, K., and Kennedy, G.C., 1968, Melting and phase relations in the plane tholeiitelherzolite-nepheline basanite to 40 kilobars with geological implications: Contributions to Mineralogy and Petrology, v. 19, p. 177-211.
- James, D.E., 1971, Andean crustal and upper mantle structure: Journal of Geophysical Research, v. 76, p. 3246-3271.
- —, 1981, The combined use of oxygen and radiogenic isotopes as indicators of crustal contamination: Annual Review of Earth and Planetary Sciences, v. 9, p. 311-344.
- Jarosewich, E., Nelen, J.A., and Norberg, J.A., 1980, Reference samples for electron microprobe analysis: Geostandards Newsletter, v. 4, p. 43-47.

- Jenner, G.A., Foley, S.F., Jackson, S.E., Green, T.H., Fryer, B.J., and Longerich, H.P., 1993, Determination of partition coefficients for trace elements in high pressure-temperature experimental run products by laser ablation microprobeinductively coupled plasma-mass spectrometry (LAM-ICP-MS): Geochimica et Cosmochimica Acta, v. 57, p. 5099-5103.
- Jochum, K.P., 1997, Nb/Ta in mantle and crust, EOS (Transactions American Geophysical Union), v. 78, p. 804.
- Jochum, K.P., and Hofmann, A.W., 1998, Nb/Ta in MORB and continental crust: Implications for a superchondritic Nb/Ta reservoir in the mantle, EOS (Transactions American Geophysical Union), v. 79, p. S354.
- Johnson, K.T.M., 1998, Experimental determination of partition coefficients for rare earth and high-field-strength elements between clinopyroxene, garnet, and basaltic melt at high pressures: Contributions to Mineralogy and Petrology, v. 133, p. 60-68.
- Johnston, S.T., and Thorkelson, D.J., 1997, Cocos-Nazca slab window beneath Central America: Earth and Planetary Science Letters, v. 146, p. 465-474.
- Jordan, T.E., Isacks, B.L., Allmendinger, R.W., Brewer, J.A., Ramos, V.A., and Ando, C.J., 1983, Andean tectonics related to geometry of subducted Nazca Plate: Geological Society of America Bulletin, v. 94, p. 341-361.
- Jull, M., and Kelemen, P.B., 2001, On the conditions for lower crustal convective instability: Journal of Geophysical Research, v. 106, p. 6423-6446.
- Kamenov, G.D., Mueller, P., and Perfit, M.R., 2004, Optimization of mixed Pb-Tl solutions for high precision isotopic analyses by MC-ICP-MS: Journal of Analytical Atomic Spectrometry, v. 19, p. 1262-1267.
- Kamenov, G.D., Perfit, M.R., Mueller, P.A., and Jonasson, I.R., 2007, Controls on magmatism in an island arc environment: Study of lavas and sub-arc xenoliths from the Tabar-Lihir-Tanga-Feni island chain: Contributions to Mineralogy and Petrology, submitted.
- Kay, R.W., 1978, Aleutian magnesian andesite: Melts from subducted Pacific Ocean crust: Journal of Volcanology and Geothermal Research, v. 4, p. 117-132.

- Kay, R.W., Sun, S.S., and Lee-Hu, C.N., 1978, Pb and Sr isotopes in volcanic rocks from the Aleutian Islands and Pribilof Islands, Alaska: Geochimica et Cosmochimica Acta, v. 42, p. 263-274.
- Kay, R.W., 1980, Volcanic arc magmas: Implications of a melting-mixing model for element recycling in the crust-upper mantle system: Journal of Geology, v. 88, p. 497-522.
- Kay, R.W., and Kay, S.M., 1991, Creation and destruction of lower continental-crust: Geologische Rundschau, v. 80, p. 259-278.
- ---, 1993, Delamination and delamination magmatism: Tectonophysics, v. 219, p. 177-189.
- Kay, R.W., 2006, Subduction erosion and recycled crust at convergent margins: The Adak adakite example, Backbone of the Americas, abstract: Mendoza, Argentina.
- Kay, S.M., and Kay, R.W., 1983, Thermal history of the deep crust inferred from granulite xenoliths, Queensland, Australia: American Journal of Science, v. 283a, p. 486-513.
- Kay, S.M., Maksaev, V., Moscoso, R., Mpodozis, C., and Nasi, C., 1987, Probing the evolving Andean lithosphere: Mid-late Tertiary magmatism in Chile (29° 30° 30') over the modern zone of subhorizontal subduction: Journal of Geophysical Research, v. 92, p. 6173-6189.
- Kay, S.M., Ramos, V.A., Mpodozis, C., and Sruoga, P., 1989, Late Paleozoic to Jurassic silicic magmatism at the Gondwana margin: Analogy of the middle Proterozoic in North America?: Geology, v. 17, p. 324-328.
- Kay, S.M., Mpodozis, C., Ramos, V.A., and Munizaga, F., 1991, Magma source variations for mid-late Tertiary magmatic rocks associated with a shallowing subduction zone and a thickening crust in the Central Andes (28 to 33 ° S), *in* Harmon, R.S., and Rapela, C.W., eds., Andean Magmatism and its Tectonic Setting: Boulder, Colorado, Geological Society of America Special Paper 265, p. 113-137.

- Kay, S.M., Ramos, V.A., and Marquez, M., 1993, Evidence in Cerro Pampa volcanic rocks for slab-melting prior to ridge-trench collision in southern South America: Journal of Geology, v. 101, p. 703-714.
- Kay, S.M., Coira, B., and Viramonte, J., 1994a, Young mafic back arc volcanic rocks as indicators of continental lithospheric delamination beneath the Argentine Puna Plateau, Central Andes: Journal of Geophysical Research, v. 99, p. 24,323-24,339.
- Kay, S.M., and Kay, R.W., 1994, Aleutian magmas in space and time, *in* Plafker, G., and Jones, D.L., eds., The Geology of Alaska, v. G-11: Boulder, CO, Geological Society of America, p. 687-722.
- Kay, S.M., Mpodozis, C., Tittler, A., and Cornejo, P., 1994b, Tertiary magmatic evolution of the Maricunga mineral belt in Chile: International Geology Review, v. 36, p. 1079-1112.
- Kay, S.M., and Abbruzzi, J.M., 1996, Magmatic evidence for Neogene lithospheric evolution of the central Andean "flat-slab" between 30° S and 32° S: Tectonophysics, v. 259, p. 15-28.
- Kay, S.M., Mpodozis, C., and Coira, B., 1999, Neogene magmatism, tectonism, and mineral deposits of the Central Andes (22° to 33°S latitude), *in* Skinner, B.J., ed., Geology and Ore Deposits of the Central Andes, v. Society of Economic Geology Special Publication 7, p. 27-59.
- Kay, S.M., and Mpodozis, C., 2000, Chemical signatures from magmas at the southern termination of the central Andean Volcanic Zone: The Incapillo/Bonete and surrounding regions, 9° Congreso Geológico Chileno, v. 1: Puerto Varas, Chile, p. 626-629.
- —, 2002, Magmatism as a probe to the Neogene shallowing of the Nazca Plate beneath the modern Chilean flat-slab: Journal of South American Earth Sciences, v. 15, p. 39-57.
- Kay, S.M., Godoy, E., and Kurtz, A., 2005, Episodic arc migration, crustal thickening, subduction erosion, and magmatism in the south-central Andes: Geological Society of America Bulletin, v. 117, p. 67-88.

- Kay, S.M., Burns, W.M., Copeland, P., and Mancilla, O., 2006, Upper Cretaceous to Holocene magmatism and evidence for transient Miocene shallowing of the Andean subduction zone under the northern Neuquén Basin, *in* Kay, S.M., and Ramos, V., eds., Evolution of an Andean margin: A Tectonic and Magmatic View from the Andes to the Neuquén Basin (35°-39° S lat), Geological Society of America Special Paper 407, p. 19-60, doi: 10.1130/2006.2407(02).
- Kay, S.M., and Coira, B., in prep., Chemistry, evolution, and origin of the Neogene ignimbrites of the Central Andean Puna Volcanic Complex.
- Kay, S.M., Mpodozis, C., and Woerner, G., in prep., Chemical and isotopic evidence for modification of the Central Andean arc mantle by crust removed by forearc subduction erosion
- Kelemen, P.B., 1995, Genesis of high Mg-andesites and the continental crust: Contributions to Mineralogy and Petrology, v. 120, p. 1-19.
- Kelemen, P.B., Hart, S.R., and Bernstein, S., 1998, Silica enrichment in the continental upper mantle via melt/rock reaction: Earth and Planetary Science Letters, v. 164, p. 387-406.
- Kelemen, P.B., Hanghøj, K., and Green, A.R., 2003a, One view of the geochemistry of subduction-related magmatic arcs, with emphasis on primitive andesite and the lower crust, *in* Holland, H.D., and Turekian, K.K., eds., Treatise on Geochemistry, v. 3: Amsterdam, Elsevier, p. 593-659.
- Kelemen, P.B., Yogodzinski, G.M., and Scholl, D.W., 2003b, Along-strike variation in the Aleutian island arc: Genesis of high Mg# andesite and implications for continental crust, *in* Eiler, J., ed., Inside the subduction factory, v. 138, American Geophysical Union - Geophysical Monograph Series, p. 223-276.
- Kepezhinskas, P.K., McDermott, F., Defant, M.J., Hochstaedter, A.G., Drummond, M.S., Hawkesworth, C.J., Koloskov, A.V., Maury, R.C., and Bellon, H., 1997, Trace element and Sr-Nd-Pb isotopic constraints on a three-component model of Kamchatka Arc petrogenesis: Geochimica et Cosmochimica Acta, v. 61, p. 577-600.
- Klein, M., Stosch, H.G., and Seck, H.A., 1997, Partitioning of high field-strength elements and rare-earth elements between amphibole and quartz-dioritic to tonalitic melts: An experimental study: Chemical Geology, v. 138, p. 257-271.

- Klein, M., Stosch, H.G., Seck, H.A., and Shimizu, N., 2000, Experimental partitioning of high field strength and rare earth elements between clinopyroxene and garnet in andesitic to tonalitic systems: Geochimica et Cosmochimica Acta, v. 64, p. 99-115.
- Klemme, S., Blundy, J.D., and Wood, B.J., 2002, Experimental constraints on major and trace element partitioning during partial melting of eclogite: Geochimica et Cosmochimica Acta, v. 66, p. 3109-3123.
- Kolarsky, R.A., Mann, P., and Montero, W., 1995, Island arc response to shallow subduction of the Cocos Ridge, Costa Rica, *in* Mann, P., ed., Geologic and Tectonic Development of the Caribbean Plate Boundary in Southern Central America: Geological Society of America Special Paper 295, p. 235-262.
- Koppers, A.A.P., 2002, ArArCALC-Software for ⁴⁰Ar/³⁹Ar age calculations: Computers and Geosciences, v. 28, p. 141-148.
- Lallemand, S., 1995, High rates of arc consumption by subduction processes: Some consequences: Geology, v. 23, p. 551-554.
- Lallemand, S., Heuret, A., and Boutelier, D., 2005, On the relationships between slab dip, back-arc stress, upper plate absolute motion, and crustal nature in subduction zones: Geochemistry Geophysics Geosystems, v. 6, doi: 10.1029/2005GC000917.
- Lallemand, S.E., Schnurle, P., and Manoussis, S., 1992, Reconstruction of subduction zone paleogeometries and quantification of upper plate material losses caused by tectonic erosion: Journal of Geophysical Research, v. 97, p. 217-239.
- Lamb, S., and Davis, P., 2003, Cenozoic climate change as a possible cause for the rise of the Andes: Nature, v. 425, p. 792-797.
- Laursen, J., Scholl, D.W., and von Huene, R., 2002, Neotectonic deformation of the central Chile margin: Deepwater forearc basin formation in response to hot spot ridge and seamount subduction: Tectonics, v. 21, no. 5, p. 1-27.
- Le Maitre, R.W., Bateman, R., Dudek, A., Keller, J., Lameyre, J., *et al.*, 1989, A Classification of Igneous Rocks and Glossary of Terms: Oxford, Blackwell.

- Leake, B.E., Woolley, A.R., Arps, C.E.S., Birch, W.D., Gilbert, M.C., et al., 1997, Nomenclature of amphiboles: Report of the Subcommittee on Amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names: American Mineralogist, v. 82, p. 1019-1037.
- Lindsay, J.M., de Silva, S.L., Trumbull, R., Emmermann, R., and Wemmer, K., 2001, La Pacana caldera, N. Chile: A re-evaluation of the stratigraphy and volcanology of one of the world's largest resurgent calderas: Journal of Volcanology and Geothermal Research, v. 106, p. 145-173.
- Lindsley, D.H., 1983, Pyroxene thermometry: American Mineralogist, v. 68, p. 477-493.
- Lipman, P.W., 1997, Subsidence of ash-flow calderas: Relation to caldera size and magma-chamber geometry: Bulletin of Volcanology, v. 59, p. 198-218.
- Lissinna, B., Hoernle, K., van den Bogaard, P., and Werner, R., 2002, Northern migration of arc volcanism in western Panama: Evidence for subduction erosion, EOS (Transactions American Geophysical Union), v. 83, p. V11-A1368.
- Lucassen, F., and Thirlwall, M.F., 1998, Sm-Nd ages of mafic rocks from the Coastal Cordillera at 24° S, northern Chile: Geologische Rundschau, v. 86, p. 767-774.
- Lucassen, F., Franz, G., Thirlwall, M.F., and Mezger, K., 1999, Late Paleozoic granites of the Chilean Coast Range and Precordillera at ~22° S: Journal of Petrology, v. 40, p. 1527–1551.
- Lucassen, F., Becchio, R., Harmon, R., Kasemann, S., Franz, G., Trumbull, R., Wilke, H.G., Romer, R.L., and Dulski, P., 2001, Composition and density model of the continental crust at an active continental margin: The Central Andes between 21° and 27° S: Tectonophysics, v. 341, p. 195-223.
- Lucassen, F., Escayola, M., Romer, R.L., Viramonte, J., Koch, K., and Franz, G., 2002, Isotopic composition of late Mesozoic basic and ultrabasic rocks from the Andes (23°-32° S): Implications for the Andean mantle: Contributions to Mineralogy and Petrology, v. 143, p. 336-349.

- Lundstrom, C.C., Shaw, H.F., Ryerson, F.J., Williams, Q., and Gill, J., 1998, Crystal chemical control of clinopyroxene-melt partitioning in the Di-Ab-An system: Implications for elemental fractionations in the depleted mantle: Geochimica et Cosmochimica Acta, v. 65, p. 2849-2862.
- Macfarlane, A.W., Marcet, P., LeHuray, A.P., and Peterson, U., 1990, Lead isotope provinces of the central Andes inferred from ores and crustal rocks: Economic Geology, v. 85, p. 1857-1880.
- MacPherson, C., Dreher, S.T., and Thirlwall, M.F., 2006, Adakites without slab melting: High pressure differentiation of island arc magma, Mindinao, the Philippines: Earth and Planetary Science Letters, v. 243, p. 581-593.
- Magaritz, M., Whitford, D.J., and James, D.E., 1978, Oxygen isotopes and origin of high ⁸⁷Sr/⁸⁶Sr andesites: Earth and Planetary Science Letters, v. 40, p. 220-230.
- Mahood, G., and Hildreth, W., 1983, Large partition-coefficients for trace-elements in high-silica rhyolites: Geochimica et Cosmochimica Acta, v. 47, p. 11-30.
- Mahood, G.A., 1984, Pyroclastic rocks and calderas associated with strongly peralkaline magmatism: Journal of Geophysical Research, v. 89, p. 8540-8552.
- Maksaev, V., Moscoso, R., Mpodozis, C.M., and Nasi, C., 1984, Las unidades volcanicas y plutonicas del Cenozoico superior en la Alta Cordillera del Norte Chico (29° -31° S): Geología, alteración hidrotermal y mineralización: Revista Geológica de Chile, v. 21, p. 11-51.
- Markham, B.L., and Barker, J.L., 1986, Landsat MSS and TM post-calibration dynamic ranges, exoatmospheric reflectances and at-satellite temperatures: EOSAT Tech. Notes, v. 1, p. 3-8.
- Marshall, J.S., and Anderson, R.S., 1995, Quaternary uplift and seismic cycle deformation, Peninsula de Nicoya, Costa Rica: Geological Society of America Bulletin, v. 107, p. 463-473.
- Marshall, J.S., Idleman, B.D., Gardner, T.W., and Fisher, D.M., 2003, Landscape evolution within a retreating volcanic arc, Costa Rica, Central America: Geology, v. 31, p. 419-422.

- Martin, H., 1987, Petrogenesis of Archaean trondhjemites, tonalites and granodiorites from eastern Finland: Major and trace element geochemistry: Journal of Petrology, v. 28, p. 921-953.
- ---, 1999, Adakitic magmas: Modern analogues of Archaean granitoids: Lithos, v. 46, p. 411-429.
- Martin, M.W., Clavero, J., and Mpodozis, C., 1997, Eocene to Late Miocene magmatic development of the El Indio belt, 30° S, north central Chile, 8° Congreso Geológico Chileno, Actas, v. 1: Antofagasta, Chile, p. 149-153.
- Masuda, A., Nakamura, N., and Tanaka, T., 1973, Fine structures of mutually normalized rare-earth patterns of chondrites: Geochimica et Cosmochimica Acta, v. 37, p. 239-248.
- McCulloch, M.T., and Gamble, J.A., 1991, Geochemical and geodynamical constraints on subduction zone magmatism: Earth and Planetary Science Letters, v. 102, p. 358-374.
- McDonough, W.F., and Sun, S.S., 1995, The composition of the Earth: Chemical Geology, v. 120, p. 223-253.
- McGlashan, N., Brown, L.D., and Kay, S.M., 2007, Crustal thickness in the central Andes from teleseismically recorded pmP depth phase precursors: Geophysical Journal International, accepted.
- McKee, E., Robinson, A.C., Rybuta, J.J., Cuitiño, L., and Moscoso, R., 1994, Age and Sr-isotopic composition of volcanic rocks in the Maricunga Belt, Chile: Implications for magma sources: Journal of South American Earth Sciences, v. 7, p. 167-177.
- McNulty, B.A., Farber, D.L., Wallace, G.S., Lopez, R., and Palacios, O., 1998, Role of plate kinematics and plate-slip-vector partitioning in continental magmatic arcs: Evidence from the Cordillera Blanca, Peru: Geology, v. 26, p. 827-830.
- Meschede, M., Zweigel, P., and Kiefer, E., 1999a, Subsidence and extension at a convergent plate margin: Evidence for tectonic erosion off Costa Rica: Terra Nova, v. 11, p. 112-117.

- Meschede, M., Zweigel, P., Frisch, W., and Voelker, D., 1999b, Mélange formation by subduction erosion: The case of the Osa mélange in southern Costa Rica: Terra Nova, v. 11, p. 141-148.
- Mickus, K., 2003, Gravity constraints on the crustal structure of Central America: AAPG Memoir 79, p. 638-655.
- Miller, C.F., and Mittlefehldt, D.W., 1982, Light rare earth element depletion in felsic magmas: Geology, v. 10, p. 129-133.
- Moore, G., and Carmichael, I.S.E., 1998, The hydrous phase equilibria (to 3 kbar) of an andesite and basaltic andesite from western Mexico: Constraints on water content and conditions of phenocryst growth: Contributions to Mineralogy and Petrology, v. 130, p. 304-319.
- Morris, J., Valentine, R., and Harrison, T., 2002, ¹⁰Be imaging of sediment accretion and subduction along the Northeast Japan and Costa Rica convergent margins: Geology, v. 30, p. 59-62.
- Moscoso, R., Maksaev, V., Cuituno, L., Diaz, F., Koeper, R., Tosdal, R., Cunningham, C., McKee, E., and Rytuba, J., 1993, El Complejo Cerros Bravos, Region de Maricunga, Chile: Geología, Alteración Hidrotermal y Mineralización, Investigación de Metales Preciosos en los Andes Centrales: Projecto BID/PC 88-02-32-spi63-8.
- Mpodozis, C., Kay, S.M., and Nasi, C., 1988, Las sequencias volcánicas terciarias de la Alta Cordillera entre los ríos Copiapó y Huasco (27° 30'-29° S): Cambios geoquímicos ligados a la disminuación del ángulo de subducción, 5° Congreso Geólogico Chileno, actas: Santiago, Chile, p. 267.
- Mpodozis, C., and Ramos, V.A., 1989, The Andes of Chile and Argentina, *in* Ericksen, G.E., ed., Geology of the Andes and its Relation to Hydrocarbon and Mineral Resources, Circum-Pacific Council for Energy and Mineral Resources, p. 59-90.
- Mpodozis, C., and Kay, S.M., 1992, Late Paleozoic to Triassic evolution of the Gondwana margin: Evidence from Chilean Frontal Cordilleran batholiths (28° S to 31° S): Geological Society of America Bulletin, v. 104, p. 999-1014.

- Mpodozis, C., 1995, Evolución magmática terciaria de la región de transición entre la CVZ y la zona de subducción subhorizontal de los Andes Chilenos, Final Report of FONDECYT Project 149/92: Santiago, Chile, Servicio Nacional de Geología y Minería, Open File Report.
- Mpodozis, C., Kay, S., Cornejo, P., and Tittler, A., 1995, La Franja de Maricunga: síntesis de la evolución del frente volcánico oligoceno-mioceno de la zona sur de los Andes Centrales: Revista Geológica de Chile, v. 22, p. 273-313.
- Mpodozis, C., Kay, S.M., Gardeweg, M.P., and Coira, B., 1996, Geología de la region de Ojos del Salado (Andes centrales, 27° S): Implicancias de la migración hacia el este del frente volcanico Cenozoico superior, 13° Congreso Geólogico Argentino, v. 13: Buenos Aires, Argentina, p. 539-548.
- Mpodozis, C., Kay, S.M., Gardeweg, M., and Coira, B., 1997, Geología de la region de Valle-Ancho-Laguna Verde (Catamarca, Argentina): Una ventana al basamento del extremo sur de la zona volcánica de los Andes Centrales, 8° Congreso Geológico Chileno, Actas: Antofagasta, Chile, p. 1689-1693.

Mpodozis, C., unpublished, Mapa geológica del region Valle-Ancho y Cerro Bonete.

- Münker, C., 1998, Nb/Ta fractionation in a Cambrian arc back arc system, New Zealand: Source constraints and application of refined ICPMS techniques: Chemical Geology, v. 144, p. 23-45.
- Münker, C., Pfander, J.A., Weyer, S., Buchl, A., Kleine, T., and Mezger, K., 2003, Evolution of planetary cores and the earth-moon system from Nb/Ta systematics: Science, v. 301, p. 84-87.
- Münker, C., Polat, A., and Yogodzinski, G., 2004a, The influence of slab melting processes on the global Nb-Ta budget: Geochimica et Cosmochimica Acta, v. 68, p. A751-a751.
- Münker, C., Wörner, G., Yogodzinski, G., and Churikova, T., 2004b, Behaviour of high field strength elements in subduction zones: Constraints from Kamchatka-Aleutian arc lavas: Earth and Planetary Science Letters, v. 224, p. 275-293.
- Müntener, O., Kelemen, P.B., and Grove, T.L., 2001, The role of H₂O during crystallization of primitive arc magmas under uppermost mantle conditions and

genesis of igneous pyroxenites: An experimental study: Contributions to Mineralogy and Petrology, v. 141, p. 643-658.

- Nash, W.P., and Crecraft, H.R., 1985, Partition-coefficients for trace-elements in silicic magmas: Geochimica et Cosmochimica Acta, v. 49, p. 2309-2322.
- Nicholls, I.A., and Ringwood, A.E., 1973, Effect of water on olivine stability in tholeiites and the production of silica saturated magmas in the island arc environment: Journal of Geology, v. 81, p. 285-300.
- Nichols, H.J., Hoernle, K., and Bogaard, P., 2003, What is the origin of the OIB-like signature in Pliocene-Recent Costa Rican arc volcanic rocks?, Geological Society of America, abstracts: Seattle, Washington, p. 323.
- Ort, M.H., 1993, Eruptive processes and caldera formation in a nested downsagcollapse caldera: Cerro Panizos, central Andes: Journal of Volcanology and Geothermal Research, v. 56, p. 221-252.
- Pardo-Casas, F., and Molnar, P., 1987, Relative motion of the Nazca (Farallon) and South American plates since Late Cretaceous time: Tectonics, v. 6, p. 233-248.
- Pardo, M., Comte, D., and Monfret, T., 2002, Seismotectonic and stress distribution in the central Chile subduction zone: Journal of South American Earth Sciences, v. 15, p. 11-22.
- Pardo, M., Monfret, T., Vera, E.E., Eisenberg, A., and Yañez, G., 2003, Morfología de la subduccion utilizando datos locales: Sismotectonica de Chile Central, 10° Congreso Geológico Chileno, Actas: Concepción, Chile.

Peacock, S.M., 1990, Fluid processes in subduction zones: Science, v. 248, p. 329-337.

- Peacock, S.M., Rushmer, T., and Thompson, G., 1994, Partial melting of subducting oceanic crust: Earth and Planetary Science Letters, v. 121, p. 227-244.
- Peacock, S.M., van Keken, P.E., Holloway, S.D., Hacker, B.R., Abers, G.A., and Fergason, R.L., 2005, Thermal structure of the Costa Rica Nicaragua subduction zone: Physics of the Earth and Planetary Interiors, v. 149, p. 187-200.

- Pearce, J., and Peate, D.W., 1995, Tectonic implications of the composition of volcanic arc magmas: Annual Review of Earth and Planetary Sciences, v. 23, p. 251-285.
- Pearce, J.A., Baker, P.E., Harvey, P.K., and Luff, I.W., 1995, Geochemical evidence for subduction fluxes, mantle melting and fractional crystallization beneath the South Sandwich-Island Arc: Journal of Petrology, v. 36, p. 1073-1109.
- Pearce, J.A., Kempton, P.D., and Gill, J.B., 2002, Behaviour of high field strength elements in subduction systems: Geochimica et Cosmochimica Acta, v. 66, p. A584-a584.
- Pearce, J.A., 2003, Quantifying element transfer from slab to mantle at subduction zones: Geochimica et Cosmochimica Acta, v. 67, p. A377-a377.
- Pertermann, M., and Hirschmann, M.M., 2003, Anhydrous partial melting experiments on MORB-like eclogite: Phase relations, phase compositions and mineral-melt partitioning of major elements at 2-3 GPa: Journal of Petrology, v. 44, p. 2173-2201.
- Petford, N., and Atherton, M.P., 1996, Na-rich partial melts from newly underplated basaltic crust: The Cordillera Blanca batholith, Peru: Journal of Petrology, v. 37, p. 1491-1591.
- Pfänder, J.A., Muenker, C., Mezger, K., and Hofmann, A.W., 2002, In search of a superchondritic Nb/Ta reservoir: High-precision Nb/Ta and Zr/Hf ratios in ocean island and intraplate basalts: Geochimica et Cosmochimica Acta, v. Suppl. 66 (S1), p. A597.
- Pichowiak, S., Buchelt, M., and Damm, K.W., 1990, Magmatic activity and tectonic setting of the early stages of the Andean cycle in northern Chile, *in* Kay, S.M., and Rapela, C.W., eds., Plutonism from Antarctica to Alaska, v. Geological Society of America Special Paper 241: Boulder, Colorado, p. 127-144.
- Pilger, R.H., 1984, Cenozoic plate kinematics, subduction and magmatism: South American Andes: Journal of the Geological Society of London, v. 141, p. 793-802.

- Plank, T., and Langmuir, C.H., 1993, Tracing trace elements from sediment input to volcanic output at subduction zones: Nature, v. 362, p. 739-743.
- Plank, T., and White, W.M., 1995, Nb and Ta in arc and mid-ocean ridge basalts, EOS (Transactions American Geophysical Union), v. 76, p. 655.
- Plank, T., and Langmuir, C.H., 1998, The chemical composition of subducting sediment and its consequences for the crust and mantle: Chemical Geology, v. 145, p. 325-394.
- Poli, S., and Schmidt, M.W., 1995, H₂O transport and release in subduction zones: Experimental constraints on basaltic and andesitic systems: Journal of Geophysical Research-Solid Earth, v. 100, p. 22299-22314.
- Prezzi, C., Götze, H.-J., and Schmidt, S., 2005, Density structure of the Central Andes from 3D integrated gravity modeling, 6th International Symposium on Andean Geodynamics, Extended abstracts: Barcelona, Spain, p. 574-577.
- Protti, M., Guendel, F., and McNally, K., 1995, Correlation between the age of the subducting Cocos Plate and the geometry of the Wadati-Benioff zone under Nicaragua and Costa Rica, *in* Mann, P., ed., Geologic and Tectonic Development of the Caribbean Plate Boundary in Southern Central America: Geological Society of America Special Paper 295: Boulder, CO, p. 309-326.
- Ranero, C.R., and von Huene, R., 2000, Subduction erosion along the Middle America convergent margin: Nature, v. 404, p. 748-755.
- Rapp, R.P., Watson, E.B., and Miller, C.F., 1991, Partial melting of amphibolite/eclogite and the origin of Archean trondhjemites and tonalites: Precambrian Research, v. 51, p. 1-25.
- Rapp, R.P., and Watson, E.B., 1995, Dehydration melting of a metabasalt at 8-32 kbar: Implications for continental growth and crust-mantle recycling: Journal of Petrology, v. 36, p. 891-931.
- Rapp, R.P., Shimizu, N., Norman, M.D., and Applegate, G.S., 1999, Reaction between slab-derived melts and peridotite in the mantle wedge: Experimental constraints at 3.8 GPa: Chemical Geology, v. 160, p. 335-356.

- Rapp, R.P., Laporte, D., and Martin, H., 2007, Primary high magnesian andesites from adakite-metasomatized peridotite: Insights from melting-hybridizationassimilation experiments at 1.5-4.0 GPa, State of the Arc, Extended abstracts: Puyehue, Chile, p. 194-197.
- Rea, D.K., and Ruff, L.J., 1996, Composition and mass flux of sediment entering the world's subduction zones: Implications for global sediment budgets, great earthquakes, and volcanism.: Earth and Planetary Science Letters, v. 140, p. 1-12.
- Rech, J.A., Currie, B.S., Michalski, G., and Cowan, A.M., 2006, Neogene climate change and uplift in the Atacama Desert, Chile: Geology, v. 34, p. 761-764.
- Rehkaemper, M., and Hofmann, A.W., 1997, Recycled ocean crust and sediment in Indian Ocean MORB: Earth and Planetary Science Letters, v. 147, p. 93-106.
- Renne, P.R., Swisher, C.C., Deino, A.L., Karner, D.B., Owens, T.L., and DePaolo, D.J., 1998, Intercalibration of standards, absolute ages and uncertainties in ⁴⁰Ar/³⁹Ar dating: Chemical Geology, v. 145, p. 117-152.
- Richardson, S.W., and England, P.C., 1979, Metamorphic consequences of crustal eclogite production in overthrust orogenic zones: Earth and Planetary Science Letters, v. 42, p. 183-190.
- Ringwood, A.E., 1972, Phase transformations and mantle dynamics: Earth and Planetary Science Letters, v. 14, p. 233-241.
- Rodine, J.D., and Johnson, A.M., 1976, Ability of debris, heavily freighted with coarse clastic materials, to flow on gentle slopes: Sedimentology, v. 23, p. 213-234.
- Rubiolo, D., Zappettini, E., Lizuain, A., and Hickson, C., 2002, Regional aspects of the southern end of the central volcanic zone (between 27° and 28° S), Argentina, 5th International Symposium on Andean Geodynamics: Toulouse, France, p. 560-557.
- Rudnick, R.L., and Taylor, S.R., 1991, Petrology and geochemistry of lower crustal xenoliths from northern Queensland and inferences on lower crustal composition, *in* Drummond, B., ed., The Australian Lithosphere v. 17, Special Publication of the Geological Society of Australia p. 189-208.

Rudnick, R.L., 1995, Making continental crust: Nature, v. 378, p. 571-578.

- Rudnick, R.L., and Fountain, D.M., 1995, Nature and composition of the continental crust: A lower crustal perspective: Reviews of Geophysics, v. 33, p. 267-309.
- Rudnick, R.L., Barth, M., Horn, I., and McDonough, W.F., 2000, Rutile-bearing refractory eclogites: Missing link between continents and depleted mantle: Science, v. 287, p. 278-281.
- Rutland, R.W.R., 1971, Andean orogeny and ocean floor spreading: Nature, v. 233, p. 252-255.
- Ryerson, F.J., and Watson, E.B., 1987, Rutile saturation in magmas: Implications for Ti-Nb-Ta depletion in island-arc basalts: Earth and Planetary Science Letters, v. 86, p. 225-239.
- Sacks, I.S., 1983, The subduction of young lithosphere: Journal of Geophysical Research, v. 88, p. 3355-3366.
- Sajona, F.G., Bellon, H., Maury, R.C., Pubellier, M., Cotten, J., and Rangin, C., 1994, Magmatic response to abrupt changes in geodynamic settings: Pliocene Quaternary calc-alkaline and Nb-enriched lavas from Mindanao (Philippines): Tectonophysics, v. 237, p. 47-72.
- Sallarès, V., Danobeitia, J.J., Flueh, E.R., and Leandro, G., 1999, Seismic velocity structure across the middle American landbridge in northern Costa Rica: Journal of Geodynamics, v. 27, p. 327-344.
- Sallarès, V., Danobeitia, J.J., and Flueh, E.R., 2001, Lithospheric structure of the Costa Rican Isthmus: Effects of subduction zone magmatism on an oceanic plateau: Journal of Geophysical Research, v. 106, p. 621-642.
- Salters, V., and Stracke, A., 2004, Composition of the depleted mantle: Geochemistry, Geophysics, Geosystems, v. 5, doi: 10.1029/2003GC000597.
- Scheuber, E., 1994, Tektonische Entwicklung des nordchilenischen aktiven Kontinentalrandes: Der Einfluâ von Plattenkonvergenz und Rheologie: Geotektonische Forchungen, v. 81, p. 1-131.

- Scheuber, E., and Geise, P., 1999, Architecture of the Central Andes A compilation of geoscientific data along a transect at 21° S: Journal of South American Earth Sciences, v. 12, p. 103-107.
- Schmidt, M.W., Dardon, A., Chazot, G., and Vannucci, R., 2004, The dependence of Nb and Ta rutile-melt partitioning on melt composition and Nb-Ta fractionation during subduction processes: Earth and Planetary Science Letters, v. 226, p. 415-432.
- Schmincke, H.U., 1974, Volcanological aspects of peralkaline silicic welded ash-flow tuffs: Bulletin of Volcanology, v. 38, p. 594–636.
- Schmitt, A.K., 2001, Gas-saturated crystallization and degassing in large-volume, crystal-rich dacitic magmas from the Altiplano-Puna, northern Chile: Journal of Geophysical Research, v. 106, no B12, p. 30,561–30578.
- Schmitz, M., Lessel, K., Giese, P., Wigger, P., Araneda, M., *et al.*, 1999, The crustal structure beneath the Central Andean forearc and magmatic arc as derived from seismic studies: The PISCO 94 experiment in northern Chile (21°-23° S): Journal of South American Earth Sciences, v. 12, p. 237-260.
- Schnurr, W.B.W., Trumbull, R., Clavero, J., Hahne, K., Siebel, W., and Gardeweg, M., 2007, Twenty-five million years of silicic volcanism in the southern central volcanic zone of the Andes: Geochemistry and magma genesis of ignimbrites from 25 to 27 °S, 67 to 72 °W: Journal of Volcanology and Geothermal Research, v. 166, p. 17-46.
- Schweller, W.J., Kulm, L.D., and Prince, R.A., 1981, Tectonics, structure, and sedimentary framework of the Peru-Chile Trench, *in* Kulm, L.D., Dasch, E.J., and Hussong, D.M., eds., Submarine Fans and Related Turbidite Systems, v. 154: New York, Springer Verlag, p. 23-28.
- Seggiaro, R.E., 1994, Petrología, geoquímica y mecanismos de erupción del complejo volcánico Coranzulí: Salta, Argentina, Ph.D. thesis, Universidad Nacional de Salta.
- Sen, C., and Dunn, T., 1994, Dehydration melting of a basaltic composition amphibolite at 1.5 and 2.0 GPa: Implications for the origin of adakites: Contributions to Mineralogy and Petrology, v. 117, p. 394-409.
- SERNAGEOMIN, 2003, Mapa Geológico de Chile: versión digital: Santiago, Servicio Nacional de Geología y Minería, Publicación Geológica Digital, no. 4.
- Seyfried, H., Astorga, A., Amann, H., Calvo, C., Kolb, W., Schmidt, H., and Winsemann, J., 1991, Anatomy of an evolving island arc: Tectonic and eustatic control in the South Central American forearc area, *in* Macdonald, D.I.M., ed., Sea-level Changes at Active Plate Margins: Processes and Products, International Association of Sedimentologists Special Publication 12, p. 217-240.
- Shannon, R.D., 1976, Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides: Acta Crystallographica Section A, v. 32, p. 751-767.
- Shimoda, G., Tatsumi, Y., Nohda, S., Ishizaka, K., and Jahn, B.M., 1998, Setouchi high-Mg andesites revisited: Geochemical evidence for melting of subducting sediments: Earth and Planetary Science Letters, v. 160, p. 479-492.
- Shipley, T.H., McIntosh, K.D., Silver, E.A., and Stoffa, P.L., 1992, Three-dimensional seismic imaging of the Costa Rica accretionary prism: Structural diversity in a small volume of the lower slope: Journal of Geophysical Research, v. 97, p. 4439-4459.
- Siebel, W., Schnurr, W.B.W., Hahne, K., Kraemer, B., Trumbull, R., van der Bogaard, P., and Emmermann, R., 2001, Geochemistry and isotope systematics of smallto medium-volume Neogene–Quaternary ignimbrites in the southern central Andes: Evidence for derivation from andesitic magma sources: Chemical Geology, v. 171, p. 213-237.
- Singer, B.S., Ackert, R.P., and Guilllou, H., 2004, ⁴⁰Ar/³⁹Ar and K-Ar chronology of Pleistocene glaciations in Patagonia: Geological Society of America Bulletin, v. 116, p. 434-450.
- Smalley, R., Jr., and Isacks, B.L., 1990, Seismotectonics of thin- and thick-skinned deformation in the Andean foreland from local network data: Evidence for a seismogenic lower crust: Journal of Geophysical Research, v. 95, p. 12,487-12,498.
- Soler, M.M., Caffe, P.J., Coira, B.L., Onoe, A.T., and Kay, S.M., 2007, Geology of the Vilama caldera: A new interpretation of a large-scale explosive event in the

Central Andean plateau during the Upper Miocene: Journal of Volcanology and Geothermal Research, v. 164, p. 27-53.

- Somoza, R., 1998, Updated Nazca (Farallon)-South America relative motions during the last 40 My: Implications for mountain building in the Central Andean region: Journal of South American Earth Sciences, v. 11, p. 211-215.
- Sparks, R.S.J., Sigurdsson, H., and Wilson, L., 1977, Magma mixing: A mechanism for triggering acid explosive eruptions: Nature, v. 267, p. 315-318.
- Sparks, R.S.J., Francis, P.W., Hamer, R.D., Pankhurst, R.J., O'Callaghan, L.O., Thorpe, R.S., and Page, R., 1985, Ignimbrites of the Cerro Galán Caldera, NW Argentina: Journal of Volcanology and Geothermal Research, v. 24, p. 205-248.
- Spera, F.J., and Bohrson, W.A., 2001, Energy-constrained open-system magmatic processes I: General model and energy-constrained assimilation and fractional crystallization (EC-AFC) formulation: Journal of Petrology, v. 42, p. 999-1018.
- Stalder, R., Foley, S.F., Brey, G.P., and Horn, I., 1998, Mineral-aqueous fluid partitioning of trace elements at 900-1200 °C and 3.0-5.7 GPa: New experimental data for garnet, clinopyroxene, and rutile, and implications for mantle metasomatism: Geochimica et Cosmochimica Acta, v. 62, p. 1781-1801.
- Steiger, R.H., and Jaeger, E., 1977, Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology: Earth and Planetary Science Letters, v. 36, p. 359-362.
- Stern, C.R., 1991, Role of subduction erosion in the generation of Andean magmas: Geology, v. 19, p. 78-81.
- Stern, C.R., and Skewes, M.A., 1995, Miocene to present magmatic evolution at the northern end of the Andean Southern Volcanic Zone, Central Chile: Revista Geológica de Chile, v. 22, p. 261-271.
- Stern, C.R., and Killian, R., 1996, Role of the subducted slab, mantle wedge and continental crust in the generation of adakites from the Andean Austral Volcanic Zone: Contributions to Mineralogy and Petrology, v. 123, p. 263-281.

- Stern, R.J., Kohut, E., Bloomer, S.H., Leybourne, M., Fouch, M., and Vervoort, J., 2006, Subduction factory processes beneath the Guguan cross-chain, Mariana Arc: No role for sediments, are serpentinites important?: Contributions to Mineralogy and Petrology, v. 151, p. 202-221.
- Stevenson, D.J., and Turner, J.S., 1977, Angle of subduction: Nature, v. 270, p. 334-336.
- Stolper, E., and Newman, S., 1992, The role of water in the petrogenesis of Mariana Trough magmas: Earth and Planetary Science Letters, v. 121, p. 293-325.
- Stolz, A.J., Jochum, K.P., Spettel, B., and Hofmann, A.W., 1996, Fluid and meltrelated enrichment in the subarc mantle: Evidence from Nb/Ta variations in island arc basalts: Geology, v. 24, p. 587-590.
- Sun, S.S., and McDonough, W.F., 1989, Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes, *in* Saunders, A.D., and Norry, M.J., eds., Magmatism in the Ocean Basins, Geological Society of London Special Publication No. 42, p. 313-345.
- Tassara, A., Gotze, H.J., Schmidt, S., and Hackney, R., 2006, Three-dimensional density model of the Nazca plate and the Andean continental margin: Journal of Geophysical Research, v. 111, doi:10.1029/2005JB003976.
- Tatsumi, Y., 1982, Origin of high-magnesian andesites in the Setouchi volcanic belt, Southwest Japan: II, Melting phase relations at high pressures: Earth and Planetary Science Letters, v. 60, p. 305-317.
- Tatsumi, Y., and Ishizaka, K., 1982, Origin of high-magnesian andesites in the Setouchi volcanic belt, Southwest Japan: I, Petrographical and chemical characteristics: Earth and Planetary Science Letters, v. 60, p. 293-404.
- Tatsumi, Y., Hamilton, D.L., and Nesbitt, R.W., 1986, Chemical characteristics of fluid phase released from a subducted lithosphere and origin of arc magmas: Evidence from high-pressure experiments and natural rocks: Journal of Volcanology and Geothermal Research, v. 29, p. 293-309.
- Tatsumi, Y., and Kogiso, T., 2002, The subduction factory: Its role in the evolution of the mantle reservoirs: Geochimica et Cosmochimica Acta, v. 66, p. A764-A764.

- Taylor, H.P., 1980, The effects of assimilation of country rock by magmas on ¹⁸O/¹⁶O and ⁸⁷Sr/⁸⁶Sr systematics in igneous rocks: Earth and Planetary Science Letters, v. 47, p. 243-254.
- Taylor, H.P., and Sheppard, S.M.P., 1986, Igneous Rocks: I. Processes of isotopic fractionation and isotopic systematics, *in* Valley, J.W., Taylor, H.P., and O'Neil, J.R., eds., Stable Isotopes in High Temperature Geological Processes, v. 16: Washington, American Mineralogical Society, p. 227-271.
- Taylor, S.R., and McLennan, S.M., 1985, The Continental Crust: Its Composition and Evolution: An Examination of the Geochemical Record Preserved in Sedimentary Rocks: Oxford, Blackwell Scientific, 312 p.
- Tebbens, S.F., and Cande, S.C., 1997, Southeast Pacific tectonic evolution from early Oligocene to Present: Journal of Geophysical Research, v. 102, p. 12061-12084.
- Thorkelson, D.J., and Breitsprecher, K., 2005, Partial melting of slab window margins: Genesis of adakitic and non-adakitic magmas: Lithos, v. 79, p. 25-41.
- Tiepolo, M., Vannucci, R., Oberti, R., Foley, S., Bottazzi, P., and Zanetti, A., 2000, Nb and Ta incorporation and fractionation in titanian pargasite and kaersutite: Crystal-chemical constraints and implications for natural systems: Earth and Planetary Science Letters, v. 176, p. 185-201.
- Tiepolo, M., Oberti, R., and Vannucchi, P., 2002, Trace-element incorporation in titanite: Constraints from experimentally determined solid/liquid partition coefficients: Chemical Geology, v. 191, p. 105-119.
- Tittler, A., 1995, The chemistry of Miocene Andean volcanic rocks from the "flatslab" to Central Volcanic Zone transition, Chile, 26° to 28°: Ithaca, NY, M.S. thesis, Cornell University.
- Tomascak, P.B., Ryan, J.G., and Defant, M.J., 2000, Lithium isotope evidence for light element decoupling in the Panama subarc mantle: Geology, v. 28, p. 507-510.
- Tosdal, R., 1996, The Amazon-Laurentian connection as viewed from the Middle Proterozoic rocks in the central Andes, western Bolivia, and northern Chile: Tectonics, v. 15, p. 827-842.

- Tovish, A., Schubert, G., and Luyendyk, B.P., 1978, Mantle flow pressure and the angle of subduction: Non-Newtonian corner flows: Journal of Geophysical Research, v. 83, p. 5892-5898.
- Ulmer, P., Müntener, O., and Alonzo-Pérez, R., 2003, Potential role of garnet fractionation in H₂O-understurated andesite liquids at high pressure: An experimental study and a comparison with the Kohistan arc: Geophysical Research Abstract, v. 5, 08308.
- van Westrenen, W., Wood, B.J., and Blundy, J.D., 2001, A predictive thermodynamic model of garnet-melt trace element partitioning: Contributions to Mineralogy and Petrology, v. 142, p. 219-234.
- Vandervoort, D.S., Jordan, T.E., Zeitler, P.K., and Alonso, R.N., 1995, Chronology of internal drainage development and uplift, southern Puna plateau, Argentine central Andes: Geology, v. 23, p. 145-148.
- Vannucchi, P., Scholl, D.W., Meschede, M., and McDougall-Reid, K., 2001, Tectonic erosion and consequent collapse of the Pacific margin of Costa Rica: Combined implications from ODP Leg 170, seismic offshore data, and regional geology of the Nicoya Peninsula: Tectonics, v. 20, p. 649-668.
- Vannucchi, P., Ranero, C.R., Galeotti, S., Straub, S.M., Scholl, D.W., and McDougall-Ried, K., 2003, Fast rates of subduction erosion along the Costa Rica Pacific margin: Implications for nonsteady rates of crustal recycling at subduction zones: Journal of Geophysical Research, v. 108, doi: 10.1029/2002JB002207.
- Vannucchi, P., Galeotti, S., Clift, P.D., Ranero, C.R., and von Huene, R., 2004, Longterm subduction-erosion along the Guatemalan margin of the Middle America Trench: Geology, v. 32, p. 617-620.
- von Huene, R., Friesen, W., and Blome, C., 1985, Igneous and sedimentary-rocks recovered during Deep-Sea Drilling Project site surveys off Guatemala: Initial Reports of the Deep Sea Drilling Project, v. 84, p. 619-624.
- von Huene, R., and Lallemand, S., 1990, Tectonic erosion along the Japan and Peru convergent margins: Geological Society of America Bulletin, v. 102, p. 704-720.

- von Huene, R., and Scholl, D.W., 1991, Observations at convergent margins concerning sediment subduction, subduction erosion, and the growth of continental crust: Reviews of Geophysics, v. 29, p. 279-316.
- -, 1993, The return of sialic material to the mantle indicated by terrigeneous material subducted at convergent margins: Tectonophysics, v. 219, p. 163-175.
- von Huene, R., and Flueh, E.R., 1994, A review of marine geophysical studies along the Middle America Trench off Costa Rica and the problematic seaward terminus of continental crust: Profil, v. 7, p. 143-159.
- von Huene, R., Corvalan, J., Flueh, E.R., Hinz, K., Korstgard, J., *et al.*, 1997, Tectonic control of the subducting Juan Fernandez Ridge on the Andean margin near Valparaiso, Chile: Tectonics, v. 16, p. 474-488.
- von Huene, R., Weinrebe, W., and Heeren, F., 1999, Subduction erosion along the North Chile margin: Journal of Geodynamics, v. 27, p. 345-358.
- von Huene, R., and Ranero, C.R., 2003, Subduction erosion and basal friction along the sediment-starved convergent margin off Antofagasta, Chile: Journal of Geophysical Research, v. 108, no. B2, doi: 10.1029/2001JB001569.
- von Huene, R., Ranero, C.R., and Vannucchi, P., 2004, Generic model of subduction erosion: Geology, v. 32, p. 913-916.
- Wade, J., and Wood, B.J., 2001, The Earth's "missing" niobium may be in the core: Nature, v. 409, p. 75-78.
- Walker, J.A., 1984, Volcanic rocks from the Nejapa and Granada cinder cone alignments, Nicaragua, Central America: Journal of Petrology, v. 25, p. 299-342.
- Walker, J.A., Patino, L.C., Carr, M.J., and Feigenson, M.D., 2001, Slab control over HFSE depletions in central Nicaragua: Earth and Planetary Science Letters, v. 192, p. 533-543.

- Wang, Q., McDermott, F., Xu, J., Bellon, H., and Zhu, Y., 2005, Cenozoic K-rich adakitic volcanic rocks in the Hohxil area, northern Tibet: Lower-crustal melting in an intracontinental setting: Geology, v. 33, p. 465-468.
- Werner, R., Hoernle, K., Barckhausen, U., and Hauff, F., 2003, Geodynamic evolution of the Galapagos hot spot system (Central East Pacific) over the past 20 m.y.: Constraints from morphology, geochemistry, and magnetic anomalies: Geochemistry Geophysics Geosystems, v. 4, doi:10.1029/2003GC000576.
- White, W.M., and Dupré, B., 1986, Sediment subduction and magma genesis in the Lesser Antilles: Isotopic and trace element constraints: Journal of Geophysical Research, v. 91, p. 5927-5941.
- White, W.M., 1989, Geochemical evidence for crust-to-mantle recycling in subduction zones, *in* Hart, S.R., and Gulen, L., eds., Crust/Mantle Recycling at Convergence Zones: Dordrecht, Kluwer Academic Publishers, p. 43-58.
- White, W.M., McBirney, A.R., and Duncan, R.A., 1993, Petrology and geochemistry of the Galapagos Islands: Portrait of a pathological mantle plume: Journal of Geophysical Research, v. 98, B11, p. 19533-19563.
- White, W.M., and Duncan, R.A., 1996, Geochemistry and geochronology of the Society Islands: New evidence for deep mantle recycling, *in* Basu, A., and Hart, S., eds., Earth Processes: Reading the Isotopic Code, v. 95, AGU Geophysical Monograph, p. 183-206.
- Whitman, D., Isacks, B.L., and Kay, S.M., 1996, Lithospheric structure and alongstrike segmentation of the central Andean Plateau: Topography, tectonics, and timing: Tectonophysics, v. 259, p. 29-40.
- Wigger, P.J., Schmitz, M., Araneda, M., Asch, G., Baldzuhn, S., *et al.*, 1994, Variation in the crustal structure of the southern Central Andes deduced from seismic refraction investigations, *in* Reutter, K.J., Scheuber, E., and Wigger, P.J., eds., Tectonics of the Southern Central Andes: Structure and Evolution of an Active Continental Margin: Berlin, Springer-Verlag, p. 23-48.
- Willbold, M., and Jochum, K.P., 2005, Multi-element isotope dilution sector field ICP-MS: A precise technique for the analysis of geological materials and its application to geological reference materials: Geostandards and Geoanalytical Research, v. 29, p. 63-82.

- Woerner, G., Moorbath, S., and Harmon, R.S., 1992, Andean Cenozoic volcanic centers reflect basement isotopic domains: Geology, v. 20, p. 1103-1106.
- Wolf, M.B., and Wyllie, P.J., 1994, Dehydration-melting of amphibolite at 10 kbar: The effects of temperature and time: Contributions to Mineralogy and Petrology, v. 115, p. 369-383.
- Wortel, M., and Vlaar, N.J., 1978, Age-dependent subduction of oceanic lithosphere beneath western South America: Physics of the Earth and Planetary Interiors, v. 17, p. 201-208.
- Wyllie, P.J., 1984, Constraints imposed by experimental petrology on possible and impossible magma sources and products: Philosophical Transactions of the Royal Society of London, v. A310, p. 439-456.
- Wyllie, P.J., and Wolf, M.B., 1993, Amphibolite dehydration-melting: Sorting out the solidus, *in* Pritchard, H.M., Alabaster, T., Harris, N.B.W., Neary, C.R., ed., Magmatic Processes and Plate Tectonics, Geological Society Special Paper 76, p. 405-416.
- Xiong, X.L., Adam, J., and Green, T.H., 2005, Rutile stability and rutile/melt HFSE partitioning during partial melting of hydrous basalt: Implications for TTG genesis: Chemical Geology, v. 218, p. 339-359.
- Yañez, G.A., Ranero, C., von Huene, R., and Diaz, J., 2001, Magnetic anomaly interpretation across the southern Central Andes (32°-34° S): The role of the Juan Fernandez Ridge in the late Tertiary evolution of the margin: Journal of Geophysical Research, v. 106, p. 6325-6345.
- Ye, S., Bialas, J., Flueh, E.R., Stavenhagen, A., von Huene, R., Leandro, G., and Hinz, K., 1996, Crustal structure of the middle American trench off Costa Rica from wide-angle seismic data: Tectonics, v. 15, p. 1006-1021.
- Yogodzinski, G.M., Volynets, O.N., Koloskov, A.V., Seliverstov, N.I., and Matvenkov, V.V., 1994, Magnesian andesites and the subduction component in a strongly calc-alkaline series at Piip Volcano, far western Aleutians: Journal of Petrology, v. 35, p. 163-204.

- Yogodzinski, G.M., Kay, R.W., Volynets, O.N., Koloskov, A.V., and Kay, S.M., 1995, Magnesian andesite in the western Aleutian Komandorsky region: Implications for slab melting and processes in the mantle wedge: Geological Society of America Bulletin, v. 107, p. 505-519.
- Yogodzinski, G.M., Lees, J.M., Churikova, T.G., Dorendorf, F., Woerner, G., and Volynets, O.N., 2001, Geochemical evidence for the melting of subducting oceanic lithosphere at plate edges: Nature, v. 409, p. 500-504.
- Yuan, X., Sobolev, S.V., and Kind, R., 2002, Moho topography in the Central Andes and its geodynamic implications: Earth and Planetary Science Letters, v. 199, p. 389-402.
- Zack, T., Kronz, A., Foley, S., and Rivers, T., 2002, Trace element abundances in rutiles from eclogites an associated garnet mica schists: Chemical Geology, v. 184, p. 97-122.
- Ziegler, A.M., Barrett, S.F., and Scotese, C.R., 1971, Paleoclimate, sedimentation and continental accretion: Philosophical Transactions of the Royal Society of London, Series A, v. 301, p. 253-264.
- Zindler, A., and Hart, S., 1986, Chemical geodynamics: Annual Review of Earth and Planetary Sciences, v. 14, p. 493-571.