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Description of calculations of chemistry of stream and lake samples.

David Bouldin, Emeritus Professor Cornell University.

#### ABSTRACT

The chemistry of the waters of Cayuga Lake and its watersheds are described as a calcium-carbonate-phosphate system. The calcium and carbonate are the predominant ions and phosphate is the chemical factor limiting photosynthetic activity where and when temperature and light are favorable. And photosynthesis is a major source of energy for the non- photosynthetic organisms.

The calcium carbonate and phosphate are the three constituents which are involved in the precipitation and biological immobilization reactions that are likely to have a major impact on solution chemistry.

The inputs for the calculations are temperature, alkalinity, calcium, pH and dissolved reactive phosphate (MRP, SRP). The outputs are the activities of all of the carbonate, orthophosphate and water ions, the partial pressure of CO<sub>2</sub>, total inorganic carbon and ion activity products of selected calcium carbonate and calcium phosphate minerals.

Illustrated are aspects of the water chemistry and two graphs which summarize several hundred analyses of streams and Cayuga Lake, 1927-2008.

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The inorganic chemistry model is visualized as a **solution** of all of the several ions but without, at this stage, interactions with biological activity, solid phases (such as precipitates) or the atmosphere. This is also predicated on the assumption that all of the ions / molecules in the solution are in equilibrium with each other: suppose an addition of some inorganic ions via a solution; within a period of perhaps an arbitrary time of 5 minutes (again no precipitates, no biological input/output no interaction with the atmosphere) the solution is again in equilibrium because the kinetics of these within- solution reactions are rapid enough they will reestablish equilibrium within a very few minutes. BUT there is no assumption about equilibrium between the idealized solution and solid or the atmosphere – this will be discussed later.

The essence of this procedure is discussed by G Evelyn Hutchinson in his “A Treatise on Limnology” and in Garrels and Christ in “Solutions, Minerals, and Equilibrium” and many others. They do indeed go through the above framework but never really compare it with much data. My innovations are a) to develop an excel spreadsheet making temperature adjustments, activity adjustments and ion pairs and b) to utilize this spreadsheet to summarize the mass of data on Cayuga Lake, 1927, 1969-74, 1998-2008 and stream data for Cayuga Lake watersheds, 1972-2008 and other data for central NY watersheds and groundwater.

One rationale for the solution model is the limnology – based - procedure which separates solution from solid phase by filtration and determination of “molybdate reactive phosphorus” (MRP, SRP) without any further treatment to determine the organic forms of phosphate . Thus the model here is an extension of the concept that there is a solution phase which is separated from biomass and particulate inorganics (precipitates?) by filtration / centrifugation.

Another concept is that the ionic composition of the solution phase can be compared with the solubility of possible mineral forms of calcium – carbonates-phosphates with the expectation that this is one way to identify solution – solid phase interactions or biological interactions. This concept is common to expectations of limnologists, soil scientists, bone and teeth medical specialists, ocean chemists etc. and all are usually disappointed to find this not very useful. So why bother?

The first rationale is to compare stream and lake water chemistry. The second is to provide a framework for describing effects of biological activity. The third is to provide a framework for describing effects of inorganic solid phase on solutions- there is an effect but we just don't know how to describe it.

The inputs to the model are temperature, alkalinity, calcium, pH and MRP. The model then calculates the activity of carbonate ions, phosphate ions, the partial pressure of CO<sub>2</sub>, total inorganic carbon (tic) and activity product of selected calcium carbonates and phosphates. The latter are useful in judging the probability of precipitation of calcium carbonates and phosphates. In reality, the pH and total inorganic carbon maintain electrical neutrality.

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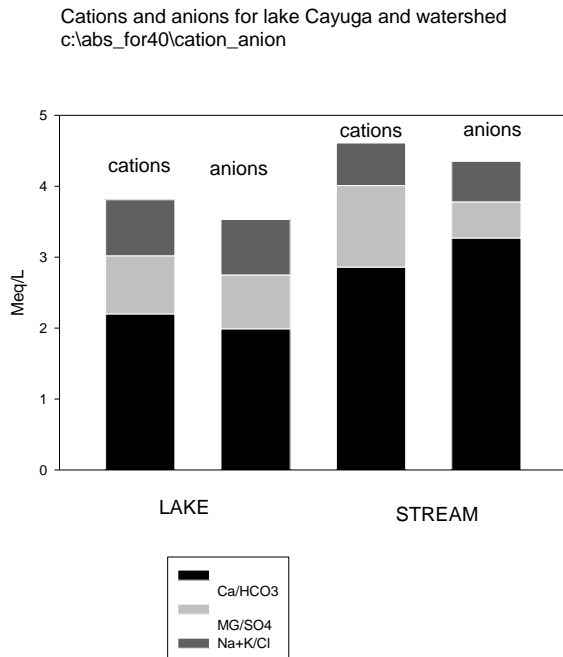
Most of the data for the calculations of the solution equilibria were taken from: Norstrum et al, Revised chemical equilibrium data for major water – mineral reactions and their limitations., Chapter 31, in ed D.C Melchoir Chemical modeling of aqueous systems II. American Chemical Society. 1990. This includes temperature effects for the carbonate solid phases and equilibrium among the inorganic carbon species.

The publication by Ito et al (J.biomed mater res 36:522-528.1997) furnished guidance on solubility of apatite-like calcium phosphate minerals and influence of solution composition on solubility.

The calculations are carried out by an excel spreadsheet. A master page is devoted to a source of the input data and summaries of the calculations carried out in two additional pages. One page receives the temperature, Ca, alkalinity and pH data and carries out all of the details of the ionic activities associated with these components and furnishes the summary for the master page. Likewise another page is devoted to all of the phosphate ionic activities.

A macro takes a list of input data and transforms it into a printout of results.

The major anions and cations in Cayuga Lake and streams in the Cayuga Lake watersheds. Note that the Ca and carbonate anions are the major ions in both systems.

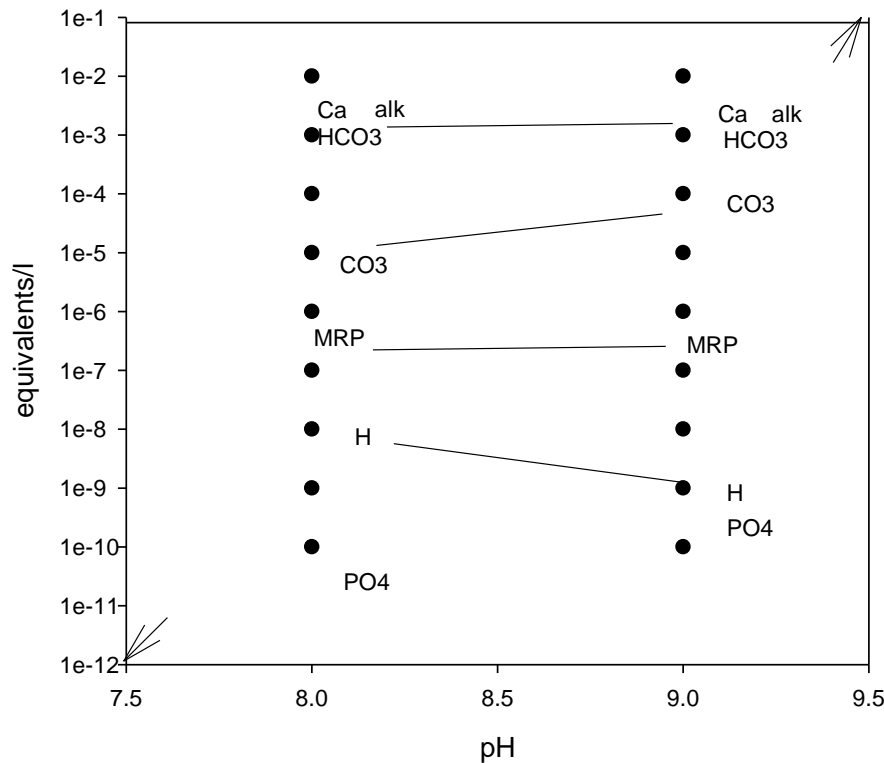


The concentrations of most ions in the lake/ stream system illustrated in the diagram are very nearly constant over days and even years -They are buffered by the very large volume of the lake and are not subject to major interactions with biological activity or chemical reaction (precipitation). The most reactive are calcium, carbonates and phosphates and they do vary as the pH changes. In fact in the pH range from about 7.5 to 9 the solubility of calcium carbonates and phosphates changes from very soluble to very insoluble.

# Model calculations of ions for calcium-carbonate-phosphate system at pH 8 and 9

Constant alkalinity and  $\text{Ca}=2\text{e-}3$  equivalents/l,  $\text{MRP}= 15 \text{ PPB}$ ,  $\text{T}=24\text{C}$

ion plot



Note Y axis decreases by factor of 1 billion!

Note the changes in ion concentration between pH 8 and 9:

H decrease by factor of 10

CO<sub>3</sub> increase ~ factor of 10

PO<sub>4</sub> increase ~ factor of 10

PO<sub>4</sub> is less than MRP by a factor

1000 to 10000!

MRP less than Ca by ~1000

PO<sub>4</sub> very low concentration



## Review: The total inorganic carbon (TIC) story

A birds eye view of the components of the TIC story. Fortunately we can concentrate on the pH range of 7.5 to 9. But it is important to see that all three pieces (H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) are present in amounts that must be accounted for in this pH range. The equations can be manipulated so as to estimate, from pH, alkalinity, and temperature, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, TIC and partial pressure of CO<sub>2</sub> in the solution and compare it with atmospheric CO<sub>2</sub>. Probably within a few minutes after some change, all of the solution parts are in equilibrium with each other but seldom are the solutions in equilibrium with either calcite or atmospheric CO<sub>2</sub>.

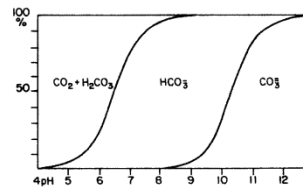


FIGURE 186. Proportions of CO<sub>2</sub> (and H<sub>2</sub>CO<sub>3</sub>), HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> in solution at different pH values (Buch).

$$\frac{[\text{Ca}^{++}][\text{CO}_3^{2-}]}{[\text{CaCO}_3]} = K_{\text{CaCO}_3} = 10^{-8.3} \quad (3.1)$$

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_{\text{H}_2\text{CO}_3} = 10^{-6.4} \quad (3.2)^1$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_{\text{HCO}_3^-} = 10^{-10.3} \quad (3.3)$$

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K_{\text{H}_2\text{O}} = 10^{-14.0} \quad (3.4)$$

$$\frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}} = K_{\text{CO}_2} = 10^{-1.47} \quad (3.5)$$

**The only components of the solutions that have any realistic effect on cation-anion balance are those associated with TIC and pH.**

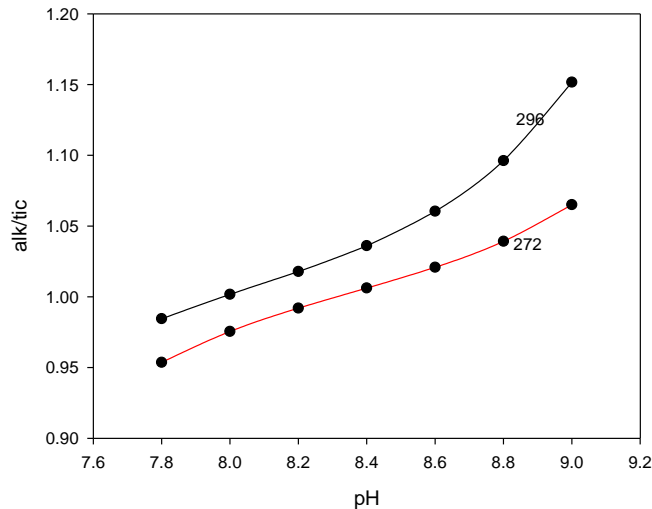
For our purposes we define the permanent ions as all those except carbonates. Examples are Na, K, Ca, Mg, Cl, SO<sub>4</sub>, NO<sub>3</sub> etc. For the most part the sum of the charges of these ions are nearly constant and suppose we call the this difference (sum cationic charges – sum charges anions) =X. Thus this difference must be equal to the alkalinity (HCO<sub>3</sub>+2\*CO<sub>3</sub>).

The following is an illustration of cation-anion balance . A 2e-3 mol/liter of KHCO<sub>3</sub> is prepared and maintained in the absence of any atmosphere. The ratio of K to HCO<sub>3</sub> is necessarily 1. But in the presence of an N<sub>2</sub> atmosphere some of the HCO<sub>3</sub> will form H<sub>2</sub>CO<sub>3</sub> and CO<sub>2</sub> will escape to the atmosphere. Now the sum of HCO<sub>3</sub> + 2\*CO<sub>3</sub> is equal to 2e-3 equivalents per liter of K. Next in the presence of the normal atmosphere, after several days the solution comes to equilibrium with the atmosphere and the HCO<sub>3</sub> + 2\*CO<sub>3</sub> is equal to 2e-3 equivalents and the calculated and measured pH is about 8.5.

In the lake/ stream model the pH, alkalinity and temperature calculate the partial pressure of CO<sub>2</sub> and the total inorganic carbon consistent with these inputs, given that these are parameters of a true solution. **And seldom are the stream and Lake samples at equilibrium with atmospheric CO<sub>2</sub>.**

In lake/stream solutions, the all important cation-anion balance is maintained by interaction among TIC, alkalinity and pH. The figure below illustrates that as pH increases, the alkalinity per unit of inorganic carbon increases. Or as the pH increases a given amount of total carbon balances increasing excesses of cations relative to anions. Note also the effects of temperature.

ALK/TIC VS pH  
tran12\alktic21712  
alk/tic@296=6.26 - 1.37\*pH +0.897\*pH^2 r2=0.99 n=6  
alk/tic@272=0.27=0.0875\*pH r2=0.00 n=6



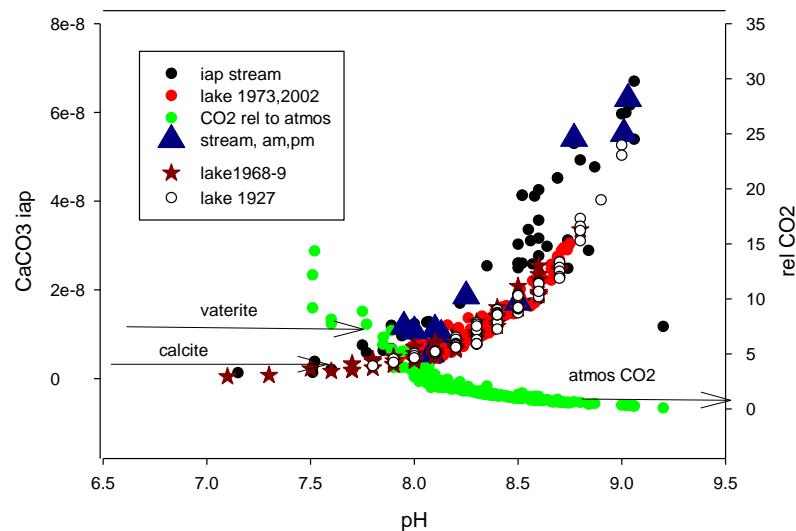
Commonly Fall Creek samples were brought to the laboratory in a sealed thermos. The pH and temperature were determined immediately and samples for Ca and alkalinity titrated. After several days of exposure to atmospheric air they were reanalysed. Most samples were not in equilibrium with the atmosphere when taken so changes with time were a measure of the model calculations; namely were the observed changes in pH consistent with expectations based on model calculations for laboratory conditions? The following examples of 2 samples, one cold and over saturated with atmospheric CO<sub>2</sub> and one at warm temperatures and undersaturated with atmospheric CO<sub>2</sub>.

Effect of c equilibration of Fall Creek samples with laboratory conditions						
-----measured-----					calculated	total
temp, C	alk, eq/L	Ca m/l	pH	SRP, PPB	rel Pco2	inorg c
original sample 0745 on 3/4/09 on very cold day in the early morning						
4	2.44E-03	1.26E-03	7.66	32	6.94	2.583E-03
storage in 5 gal bucket, samples on 4/2/09						
24	2.44E-03	1.26E-03	8.50	22	1.20	2.300E-03
model chemistry: temperature 24 C and rel pco2 = 1						
24	2.44E-03	1.26E-03	8.57	32	1.01	2.276E-03
original sample 8/17/09 taken 1515 on bright sunny warm day						
28	2.38E-03	9.75E-04	9.02	25	0.32	1.993E-03
storage in 5 gal bucket anal on 9/28/09						
24	2.38E-03	9.85E-04	8.57	25	1.00	2.250E-03

Note the PCO<sub>2</sub> and TIC in cold sample decreases with time and with warmer sample PCO<sub>2</sub> and Tic increase. Almost invariably other stored samples changed to pH 8.60 +/- 0.05 as they come to equilibrium with atmospheric CO<sub>2</sub> (and evaporation loss corrected by water addition)

Combined summary of several hundred lake and stream samples. Inputs are temperature, alkalinity, calcium, pH; output calcium carbonate ion product and solution partial pressure of CO<sub>2</sub> relative to atmosphere. Note that most samples are oversaturated with respect to vaterite and calcite, two common calcium carbonate species (left axis) and with respect to atmospheric CO<sub>2</sub> (right axis). The large blue triangles were stream samples taken on consecutive days during summer bloom pH~8 at 7am and pH~9 at 4 pm.

combined lake and stream CaCO<sub>3</sub> iap vs pH  
com\_iap\_lake\_stream.jnb  
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Continuing part 2. Details of ions for calcium-carbonate-phosphate system at pH 8 and 9

Constant alkalinity and  $\text{Ca}=2\text{e-}3$  equivalents/l, MRP= 15 PPB, T=24C

Effects on ion activity products for possible precipitates, equilibrium with atmosphere.

Calcite is one of 3 possible calcium carbonate minerals

Solubility product =  $k_{sp}=3.4\text{e-}9$

$iap= (\text{Ca})\cdot(\text{CO}_3)$  product calculated from previous slide

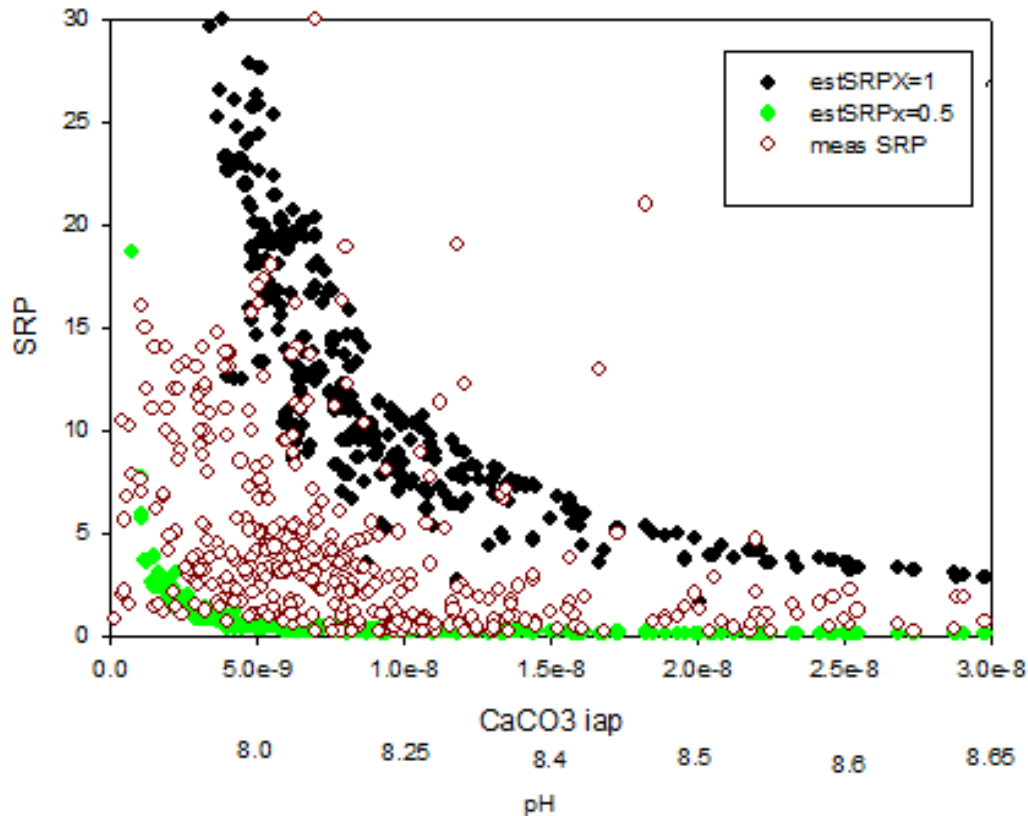
$iap/k_{sp}$  pH 8 =1.96

$iap/k_{sp}$  pH 9= 15.8

Most lake and stream samples are very far from equilibrium with any calcium carbonate mineral

Most solutions have Ca and  $\text{CO}_3$  products indicating solutions much higher than expected for equilibrium with calcium carbonate minerals except deep lake samples discussed later

Comparison of SRP (=MRP) and calcium phosphate solubility with observed SRP in lake samples 1968-2006. Note x-axis both CaCO<sub>3</sub> and pH. Black symbols of expected SRP with observed Ca and CO<sub>3</sub> in equilibrium with  $(Ca^{10}) \cdot (PO_4^6) \cdot (CO_3)$ , open circles observed SRP, green with half of OH replaced with CO<sub>3</sub>. Note that observed SRP is mostly less than expected for  $(Ca^{10}) \cdot (PO_4^6) \cdot (CO_3)$  and the observed SRP decreases as pH increases.



Continuing part 3. Details of ions for calcium-carbonate-phosphate system at pH 8 and 9

Constant alkalinity and  $\text{Ca} = 2 \times 10^{-3}$  equivalents/l, MRP = 15 PPB,  $T = 24^\circ\text{C}$   
Effects on ion activity products for possible precipitates, equilibrium with atmosphere.

There are several calcium phosphate minerals which are possible precipitates, all variations on hydroxyapatite mineral structures. Hydroxyapatite  $[(\text{Ca}^{10}) \cdot (\text{PO}_4^6) \cdot (\text{OH}^2)]$  is usually far too insoluble but a carbo-apatite with  $\text{CO}_3$  substituted for OH is more nearly consistent with observed phosphate concentrations. (Ito et al)

The  $k_{sp} = (\text{Ca}^{10}) \cdot (\text{PO}_4^6) \cdot (\text{CO}_3) = 1.6 \times 10^{-103}$

$\text{Iap}/k_{sp}$  pH 8 = 0.42

$\text{Iap}/k_{sp}$  pH 9 =  $5.3 \times 10^6$

But all of this seems a bit imaginary since  $\text{PO}_4 \sim 1.0 \times 10^{-10}$  m/l, how can activity or rates of precipitation be estimated? Despite this comment the observed MRP is within the estimated concentrations between hydroxyapatite and carbo apatite.



S14

Comments on observed discrepancy between ion activity products and solubility products of least soluble minerals.

First, the 2 figures which summarize both lake and stream samples indicate some important relations between solution properties and hypothesized mineral phases; these are **NOT** random numbers in my view. Some hypotheses follow

First, the kinetics of precipitation of well formed crystals may well be slow enough so that solid phases are amorphous and simply have no well defined solubility products. However in Cayuga Lake the temperature gradients isolate the deeper portions for several months of the year which would favor crystallization. The data collected during the 1968-1974 period from the 60+ meter depth was consistent with equilibrium with Calcite or Vaterite; a pH of about 8.0,  $\text{CaCO}_3$  ion product close to calcite or vaterite ion product and partial pressure of  $\text{CO}_2$  substantially higher than atmospheric. (Slide 12). However, during the 2000 -2008 period the Lake source cooling data reports reduction in turbidity following acid treatment – presumably due to  $\text{CaCO}_3$  precipitates yet the  $\text{CaCO}_3$  ion products are higher than expected for either Calcite or Vaterite in these samples.

S15

Another issue is incongruent dissolution; that is the ion composition of the solution is far different from the ratio of the solid phase. For example the Ca/CO<sub>3</sub> ionic ratio is on the order of ten to 100 in most solutions; for solid phases with small particle size, this probably means a surface composition very different from the bulk composition.

Another issue is the effect of seed crystals/ surfaces capable of initiating seed crystal formation such as bone formation.

And finally alkalinity and Ca determinations may include some very finely divided particles (less than 0.2 micron).