Lecture 16

Guest Lecturer this week. Prof. Greg Ravizza

General Concepts for Natural Controls on Fresh Water Composition

1. **Generalizations about freshwater compositions**
2. **Conservative/non-conservative ions in water**
3. **Inorganic solubility and chemical reactions**

General Considerations

Today's discussion builds on topics we have already discussed this semester, including:

- ✓ **Solubility**
- ✓ **pH and Bjerrum plots**
- ✓ **Mineral stability diagrams**
- ✓ **Redox and E_H-pH diagrams**
- ✓ **Weathering reactions**

Generalizations about freshwater compositions

The natural sources of solutes and their pathways into the environment involve a complex interplay of **many processes:**

Inorganic	Biological/Organic
✶ acid-base reactions ✶ mineral dissolution ✶ salt dissolution/precipitation ✶ gas solubility ✶ surface reactions on particles	✶ photosynthesis-respiration ✶ OM complexation/chelation ✶ Redox **Physical** ✶ flow regime ✶ particle content ✶ reservoir size ✶ temperature/pressure

Generalizations about freshwater compositions

TDS composition: The types and proportions of inorganic chemicals reflect the solids that the water has interacted with and chemical exchanges between water and the solids.

1. **extent of dissolution** of is governed by solubility (e.g., of a mineral, organic substance, or manmade solid) and texture of that material (e.g., porosity, grain size, etc..).

2. **extent to which ions stay in water** or create precipitation minerals is governed by both the mineral stability in water and the solute stability in the presence of solubility enhancing ligands, especially from DOC)

(see our prior discussions of *Ionic Potential*)

Generalizations about freshwater compositions

Integrated Compositions

Water compositions provide a record of natural and anthropogenic processes occurring in an environment.

Compositional variations and solute budgets can be studied at the watershed, regional or continent-scale depending upon what it is you want to learn.

Residence Time Reminder:
Natural Waters tend to gain ***higher TDS*** and ***more variable compositions*** with **longer residence time** in a reservoir.

Inorganic compositions reflect ***local inputs*** from ***solids*** and ***gasses*** that are present.

Organic compositions reflect the ***local biosphere***

Generalizations about Inorganic compositions

Conservative and Non-Conservative Ions

A useful distinction can be made between two categories of aqueous ions:

conservative and ***non-conservative***

The distinction is based on whether or not their concentrations in aqueous solutions are affected by changes in

✶ pH ✶ T ✶ P (and ✶ pe)

at relatively low concentration.

Generalizations about Inorganic compositions

See the discussion in the first half of White Ch 6, which you read for week 3

This working definition works well for natural waters in the exogenic hydrologic cycle, which rarely become saturated in the salts of the principal conservative ions:

Conservative ions:
fully dissociated from their conjugate acids and bases over the normal range of pH of natural waters.

They come from high solubility salts.

Here are a few common examples

Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-

When no organisms are around

Generalizations about Inorganic compositions

Non-conservative ions: the proton and hydroxide ion, plus those that associate/dissociate with H^+ or OH^- in this pH range. The principal high solubility non-conservative ions are:

HCO_3^-	CO_3^{2-}	$B(OH)_4^-$	HS^-	NH^{4+}
phosphate species (conjugate bases of $H_3PO_4^-$)		many organic anions (especially conjugate bases of many carboxylic acid anions)		

An important lower solubility non-conservative ion is $H_3SiO_4^-$

Virtually all the non-conservative species are *anions*, the two principle exceptions being H^+ and NH_4^+.

Generalizations about Inorganic compositions

Recall our discussion of conservative/non-conservative ions of last time.

Material and Charge Balance is another useful concept when looking at the interaction of water and solids. It *requires*:

a. solutes “i” follow the stoichiometry of solubility reactions

b. electrical neutrality is retain in solution: $\Sigma\ m_i z_i = 0$

[or Σ (moles cation charge) = Σ (mole anion charge)]

These concepts allow us to track compositional variations in natural waters as a function of specific minerals dissolving or specific salts becoming saturated.

Generalizations about Inorganic compositions

Material and Charge Balance.

Let’s examine these in a simple solution of Na_2CO_3 in water (unsaturated). Important reactions are

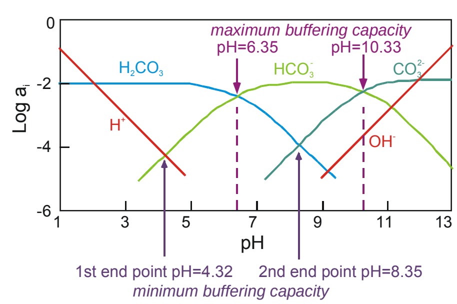
$Na_2CO_3 \leftrightarrow 2Na^+ + CO_3^{2-}$

$CO_3^{2-} + H_2O \leftrightarrow HCO_3^{2-} + OH^-$

$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-$

and $H_2O \leftrightarrow H^+ + OH^-$

recall from an earlier lecture…



Bjerrum plot, activities of different species in the aqueous carbonate system as a function of pH, for $\Sigma CO_2 = 10^{-2}$, T = 25°C.

1. The charge balance equation is:

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

2. The Material Balance Equations:

a. conservation of carbonate species:

$$\Sigma CO = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$$

where $\Sigma CO = Na_2CO_3$ originally dissolved

at saturation ΣCO is fixed.

b. H^+ balance equation:

$$[H^+] + [HCO_3^-] + 2[H_2CO_3] = [OH^-]$$

This one considers the dissociation of water $[H^+] = [OH^-]$ and the fact that each mole of HCO_3^- formed produces one OH^-, and that each H_2CO_3 formed produces two OH^-.

Alkalinity Revisited

Let's use the material and charge balance concepts we have just discussed to look at Alkalinity again in more detail.

Alkalinity is the *acid neutralizing capacity of a solution titrated to the CO_2 equivalence point* (where $[H^+] = [HCO_3^-]$).

Alkalinity derives from the combined effects of all the bases and acids in a solution.

The Na_2CO_2 solution we just discussed is an analogous to a solution of $CaCO_3$ in water in some ways, in that both produce carbonate alkalinity in the water.

► Because we made our solution from Sodium carbonate and water, the total alkalinity is a "carbonate alkalinity" (i.e., it depends only upon ions of the carbonate system in water).

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

(i.e., the sum of all non-conservative anions in this solution).

►because the charge balance equation for this situation is

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

► With a little algebra we see that alkalinity in *this solution* is:

$$[Alk] = [H^+] + [Na^+]$$

GG325 L16, F2013

► In more realistic natural solutions, the *Total Alkalinity* also includes contributions from the major non conservative ions in solution. A more realistic general expression is:

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] - [H^+]$$

► We can also express alkalinity in terms of conservative and non-conservative ions in solution using a charge balance equation. In general:

$$\Sigma eq_{cations} - \Sigma\, eq_{anions} = 0$$

(recall that eq are "equivalents" = mole charge per liter).

GG325 L16, F2013

This charge balance equation can the be expanded to:

$$\Sigma eq_{\text{conservative cations}} - \Sigma eq_{\text{conservative anions}} + \Sigma eq_{\text{non-conservative cations}} - \Sigma eq_{\text{non-conservative anions}} = 0$$

Rearranging...

$$\Sigma eq_{\text{conservative cations}} - \Sigma eq_{\text{conservative anions}} = \Sigma eq_{\text{non-conservative anions}} - \Sigma eq_{\text{non-conservative cations}}$$

The right hand side of the above is equal to the *Total alkalinity* for natural waters:

$$Alk = \Sigma eq_{\text{non-conservative anions}} - \Sigma eq_{\text{non-conservative cations}}$$

Thus:

$$Alk = \Sigma eq_{\text{conservative cations}} - \Sigma eq_{\text{conservative anions}}$$

$$\boxed{Alk = \Sigma eq_{\text{conservative cations}} - \Sigma eq_{\text{conservative anions}}}$$

This last equation emphasizes an important point:

alkalinity is a conservative property of an aqueous solution because the difference of the sum of two conservative properties (conservative anions and cations) must also be conservative property.

So perhaps non-intuitively, *Alkalinity is independent of pH, pressure or temperature*.

Total alkalinity is conservative, although the concentrations of individual species are not.

Inorganic Carbon in Natural Waters

How much DIC ("dissolved inorganic carbon") do we expect to find in a natural waters?

We need to consider

- CO_2 from the atmosphere
- CO_3^{2-} from weathering of rocks
- carbon from the biosphere

- CO_2 from the atmosphere:

Using equations we discussed earlier this semester...
we can calculate that the pH of liquid atmosphere water in equilibrium with atmospheric CO_2 (see lecture 3):

At a P_{CO2} = 384 ppm, the atmospheric value in the 2008, equilibrium pH ~5.5 at 25°C.

Because $CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$,
$[HCO_3^-] = [H^+] = 10^{-5.5} = 3.2$ µM/L at equilibrium

Generalizations about Inorganic Carbon

- CO_3^{2-} from weathering of rocks

As water interacts with surface rocks it dissolved inorganic carbon concentrations increase from the following types of reactions:

<u>Carbonate Rocks:</u>
$CO_2 + CaCO_3 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$
(notice that 1 mole HCO_3^- comes from the rock and 1 from the atmosphere).

<u>Silicate Rocks:</u>
The "Urey reaction"
$CO_2 + \boxed{CaSiO_3} + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + SiO_2(aq) \leftrightarrow CaCO_3 + SiO_2$
[*reaction intermediates*]
(notice that 1 mole HCO_3^- comes from the atmosphere: all HCO_3^- is "non-rock").

$CaSiO_3$ can be thought of as representing "silicate rock" (i.e., similar reactions can be written for all the primary rock forming silicate minerals)

Generalizations about Inorganic Carbon

❖ carbon from the biosphere

As we have discussed already this semester, respiration of organic matter produces inorganic carbon.

$CH_2O + O_2 \leftrightarrow CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$

(for aerobic respiration notice that 1 mole HCO3- comes from organic matter).

Other Inorganic solutes.

- ❖ Highly soluble materials (especially salts) dissolve readily at almost any naturally-occurring pH.
- ❖ Solutes derived from terrigenous materials have highly pH dependent solubilities (e.g., Si and Al oxides).

Important chemical reactions:

A. Congruent rxns: dissolution/precipitation

$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^-$

$CaSO_4 \leftrightarrow Ca^{2+} + SO_4^{2-}$

notice that.. $\Sigma(Ca^{2+})_{liberated} = \Sigma(HCO_3^-)_{liberated}$ -or- $\Sigma(Ca^{2+})_{liberated} = \Sigma(SO_4^{2-})_{liberated}$

B. incongruent reactions: such as leaching and mineral transformation.

For instance, Feldspars ↔ clays:

$2NaAlSi_3O_8 + 2H^+ + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4SiO_2(aq)$

$2KAlSi_3O_8 + 2H^+ + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4SiO_2(aq)$

notice that.. $\Sigma(Na^+ + K^+)_{liberated} = 1/2\Sigma(SiO_2)_{liberated}$

C. Surface reactions (discussed last week)

Recall that there are many different reactions involving complexing agents and the surfaces of inorganic and organic solids

Watershed Water Chemical Classification Schemes

Let's first look at some Chemical Classification schemes based on the sorts of solubility reactions we just discussed.

Chemical Classification of Watershed Water

The above relationships lead to several different approaches to providing genetic information from dissolved composition, which we will look at next time; we won't go into details.

4 factors play the largest role:

1. evaporation
2. precipitation
3. rock dissolution
4. rock type

Simple indicators include TDS and ionic composition.

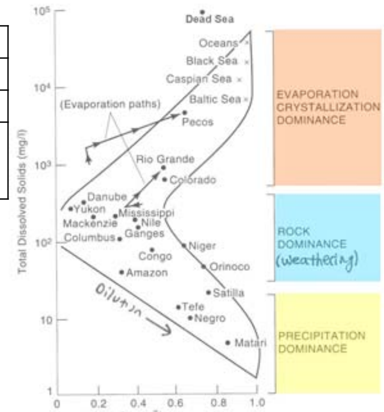
Let's look at a few of the most common river classification schemes.

► "Gibbs Scheme"

	TDS	$Na^+/(Na^+ + Ca^{2+})$
rain-dominated	Low	high -- ($[Ca]_{rain}$ is low)
rock-dominated	moderate	low
evaporation-dominated	high	high -- ($CaCO_3$ is one of first salts to precipitate out of solution with evaporation.

Note: The sea water evaporation sequence, first noted by 19th century scientist Usiglio is:
Fe_2O_3 and $CaCO_3 \rightarrow CaSO_4$ and $NaCl \rightarrow (MgSO_4, MgCl_2, NaBr, KCl)$

the last phases are rarely seen during large-scale natural evaporation. Although Fe is an early precipitate, we do not use it to classify rivers in the Gibbs scheme because it is so dependent on pH, pe and DOC.



Berner and Berner, "Global Environment"

Ionic composition of rivers in the central part of a Gibbs diagram reflect rock weathering input onto a marine salt composition.

- ❖ Mg, K and SiO_2 also generally increase as $Na^+/(Na^+ + Ca^{2+})$ decreases
- ❖ Cl- (and to a lesser extent SO_4^{2-}) will decrease as HCO_3^- increases in rock-dominated rivers. In fact, some people suggest that it is better to classify rivers using $Cl^-/(Cl^- + HCO_3^-)$ instead of $Na^+/(Na^+ + Ca^{2+})$.

► The "Stallard and Edmond" scheme uses more chemical elements and also considers rock types. It incorporates elemental ratios from congruent and incongruent dissolution reactions.

Table 5.8 Stallard and Edmond's River Classification

source: Berner and Berner, Global Environment (1996)

Total Cationic Charge (μeq/l)	TDS (mg/l)	Predominant Source-Rock Type	Characteristic Water Chemistry (molar)	Examples	Gibbs Category
<200	<20	Intensely weathered (cation-poor) siliceous rocks and soild (thick regolith)	Si-enriched; low pH $Si/(Na + K) = 2$ $Na/(Na + Ca)$ = high	Amazon tributaries (Matari, Tefe, Negro)	rain-dominated
200-450	20-40	Siliceous (cation-rich); igneous rocks and shales (sedimentary silicates)	More Si-enriched $Si/(Na + K) = 2$ $Na/(Na + Ca)$ = intermediate	Lower Amazon, Orinoco, Zaire	between rain-dominated and rock-dominated
450-3000	40-250	Marine sediments; carbonates, pyrite; minor evaporites	$Na/Cl = 1$ $\frac{(Ca + Mg)}{(0.5\ HCO_3 + SO_4)} = 1$ $Na/(Na + Ca)$ = low	Most major rivers	rock-dominated
>3000	>250	Evaporites; $CaSO_4$ and NaCl	$Na/Cl = 1$ $\frac{(Ca + Mg)}{(0.5\ HCO_3 + SO_4)} = 1$ $Na/(Na + Ca)$ = high	Rio Grande, Colorado	Evaporation-crystallization

Notice these stoichiometries from our discussion of a few slides ago

► The "Extended Stallard Scheme" is plotted on a ternary diagram. TDS increases clockwise around the diagram.

Most rivers plot in the HCO_3 > Cl + SO_4 part of the diagram (with variable SiO_2), reflecting the greater relative inputs to TDS from sedimentary rocks compared to crystalline rocks.

Both schemes have limitations, particularly for some low-TDS rivers.

Some low TDS and HCO_3^- Amazon basin rivers do not resemble their watershed rain because:

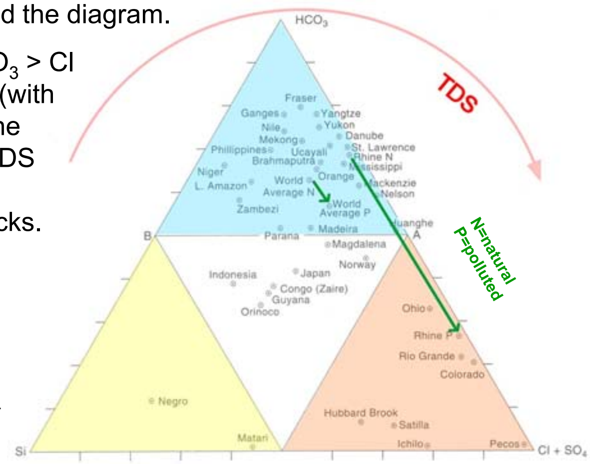


Figure 5.5. Major rivers: Percentage of Si (μmol/l); HCO_3^- (μEq/l); and sum of $Cl^- + SO_4^{2-}$ (μEq/l). For example, 100% HCO_3^- plots at the HCO_3^- vertex; 50% HCO_3^- and 50% Si plots at point *B*; and 50% HCO_3^- and 50% ($Cl^- + SO_4^{2-}$) plots at point *A*. River TDS increases from Si vertex to HCO_3^- vertex to ($Cl^- + SO_4^{2-}$) vertex. (Data from Tables 5.7 and 5.14.) *Berner and Berner, "Global Environment"*

A. intensely weathered soils have little remaining soluble ion-content

B low pH rivers (high conce. of dissolved organic acids) have low HCO_3^-

What about anthropogenic effects?

"Evaporation" is enhanced by human activities such as agriculture by distributing water across the landscape, resulting in enhanced evaporation and more saline soil waters.

(e.g., see green arrows extending from "natural" to "polluted" on the preceding slide).

These saline waters re-enter local waters with increased TDS.

Extreme cases of human enhanced evaporation cause salts to build up in cultivated soils, which periodically wash into rivers or groundwaters.