

Lecture 17

- General Concepts for Natural Controls on Fresh Water Composition
 - a. Conservative behavior
 - b. Charge and material balance
 - c. Alkalinity
 - d. Inorganic carbon
 - e. Other solutes

GG325 L17, F2009

General Considerations

Today we discuss the main variables that control water compositions in the hydrosphere as a prelude to our tour through aspects of the hydrologic cycle over the coming weeks.

Over the next 2 weeks we will build 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
- ❖ Surface chemistry (particle charge, ion exchange, sorption)

GG325 L17, F2009

Generalizations about freshwater compositions

They 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 the what it is you want to learn.

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

<p>Inorganic</p> <ul style="list-style-type: none"> * acid-base reactions * mineral dissolution * salt dissolution/precipitation * gas solubility * surface reactions on particles 	<p>Biological/Organic</p> <ul style="list-style-type: none"> * photosynthesis-respiration * OM complexation/chelation * Redox <p>Physical</p> <ul style="list-style-type: none"> * flow regime * particle content * reservoir size * temperature/pressure
--	--

GG325 L17, F2009

Generalizations about freshwater compositions

The types and proportions of chemicals that make up the TDS reflect the solids that the water has interacted with and chemical exchanges between water and the solids.

1. **extent of dissolution** is governed by mineral solubility and rock texture.
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* and *mineral stability diagrams*)

GG325 L17, F2009

Generalizations about Inorganic compositions

Conservative and Non-Conservative Ions

One useful distinction we have not yet made this semester is between what geochemists call **conservative** and **non-conservative** categories of aqueous ions. The distinction is based on whether or not their concentrations in aqueous solutions are affected by changes in

 pH

 T

 P (and  pE)

at concentrations less than the saturation point for their least soluble salt.

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:

GG325 L17, F2009

Generalizations about Inorganic compositions

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.

Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
-----------------	----------------	------------------	------------------	-----------------	-------------------------------	------------------------------

(Ca²⁺ is not truly conservative in some waters; e.g., in seawater, where precipitation of CaCO₃ by organisms can occur at concentrations below saturation.)

GG325 L17, F2009

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^+ .

GG325 L17, F2009

Generalizations about Inorganic compositions

another useful concept is **Material and Charge Balance**. It requires that:

- solute "i" follow the stoichiometry of the main solubility reactions
- to retain electric neutrality $\sum m_i z_i = 0$

[or $\sum (\text{moles cation charge}) = \sum (\text{mole anion charge})$].

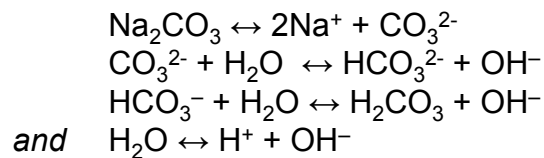
Equations of this sort allow one to track compositional variations in natural waters as a function of specific minerals dissolving or specific salts becoming saturated.

GG325 L17, F2009

Generalizations about Inorganic compositions

Material and Charge Balance.

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



1. The charge balance equation is:

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

GG325 L17, F2009

Generalizations about Inorganic compositions

Material Balance Equations:

2. We can also write an equation for **the conservation of carbonate species**:

$$\begin{aligned} \Sigma\text{CO} &= [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] \\ \text{where } \Sigma\text{CO} &= \text{Na}_2\text{CO}_3 \text{ originally dissolved} \\ &\text{at saturation } \Sigma\text{CO} \text{ is fixed.} \end{aligned}$$

3. We can also write **a H⁺ balance equation**:

$$[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] = [\text{OH}^-]$$

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

GG325 L17, F2009

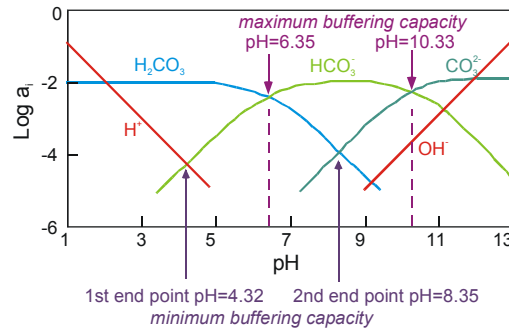
Alkalinity

Alkalinity is the *acid neutralizing capacity of a solution titrated to the CO₂ equivalence point* (where $[H^+] = [HCO_3^-]$).

Alkalinity derives from the combined effects of all the bases and acids in a solution (see discussion in lecture 7).

Let's use the material and charge balance concepts just discussed to look at this in more detail.

In the Na₂CO₂ solution we just discussed (or for an analogous solution of CaCO₃ in water), the following Bjerrum plot applies (see also lecture 7)



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

GG325 L17, F2009

- ☛ The total **alkalinity** is a “**carbonate alkalinity**” because it depends only upon members of the carbonate system and the dissociation products of water.

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

Because we made our solution from Sodium carbonate and water, and 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 also:

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

GG325 L17, F2009

☛ 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:

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{B}(\text{OH})_4^-] + [\text{H}_3\text{SiO}_4^-] + [\text{HS}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] - [\text{H}^+]$$

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

$$\sum \text{eq}_{\text{cations}} - \sum \text{eq}_{\text{anions}} = 0$$

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

GG325 L17, F2009

This **charge balance equation** can be expanded to:

$$\begin{aligned} \sum \text{eq}_{\text{conservative cations}} - \sum \text{eq}_{\text{conservative anions}} + \\ \sum \text{eq}_{\text{non-conservative cations}} - \sum \text{eq}_{\text{non-conservative anions}} = 0 \end{aligned}$$

Rearranging...

$$\begin{aligned} \sum \text{eq}_{\text{conservative cations}} - \sum \text{eq}_{\text{conservative anions}} = \\ \sum \text{eq}_{\text{non-conservative anions}} - \sum \text{eq}_{\text{non-conservative cations}} \end{aligned}$$

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

$$\text{Alk} = \sum \text{eq}_{\text{non-conservative anions}} - \sum \text{eq}_{\text{non-conservative cations}}$$

Thus:

$$\text{Alk} = \sum \text{eq}_{\text{conservative cations}} - \sum \text{eq}_{\text{conservative anions}}$$

GG325 L17, F2009

$$\text{Alk} = \sum e q_{\text{conservative cations}} - \sum e q_{\text{conservative anions}}$$

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 Alkalinity is independent of pH, pressure or temperature.

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

GG325 L17, F2009

Generalizations about Inorganic Carbon

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

We need to consider

- * CO₂ from the atmosphere
- * CO₃²⁻ from weathering of rocks
- * carbon from the biosphere

* CO₂ from the atmosphere:

Using equations we discussed earlier this semester...

we can calculate that the pH of liquid atmosphere water in equilibrium with atmospheric CO₂ (see lecture 3):

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

Because CO₂ + H₂O ↔ HCO₃⁻ + H⁺ ,
[HCO₃⁻] = [H⁺] = 10^{-5.5} = 3.2 μM/L at equilibrium

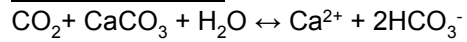
GG325 L17, F2009

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:

Carbonate Rocks:



(notice that 1 mole HCO_3^- comes from the rock and 1 from the atmosphere).

Silicate Rocks:

The "Urey reaction"



(notice that 1 mole HCO_3^- comes from the atmosphere: all HCO_3^- is "non-rock").

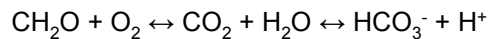
CaSiO₃ can be thought of as representing "silicate rock" (i.e., similar reactions can be written for all the primary rock forming silicate minerals)

GG325 L17, F2009

Generalizations about Inorganic Carbon

* carbon from the biosphere

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



(for aerobic respiration notice that 1 mole HCO_3^- comes from organic matter).

GG325 L17, F2009

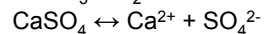
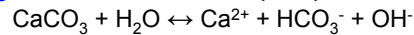
Other Inorganic solutes.

* 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:

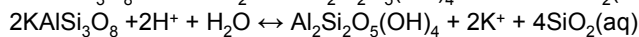
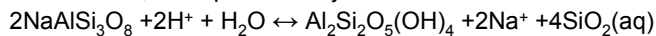
A. Congruent rxns: dissolution/precipitation



notice that.. $\Sigma(\text{Ca}^{2+})_{\text{liberated}} = \Sigma(\text{HCO}_3^-)_{\text{liberated}}$ -or- $\Sigma(\text{Ca}^{2+})_{\text{liberated}} = \Sigma(\text{SO}_4^{2-})_{\text{liberated}}$

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

For instance, Feldspars \leftrightarrow clays:



notice that.. $\Sigma(\text{Na}^+ + \text{K}^+)_{\text{liberated}} = 1/2\Sigma(\text{SiO}_2)_{\text{liberated}}$

C. Surface reactions (discussed last week)

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

GG325 L17, F2009

Chemical Classification of Watershed Water

Many different approaches to providing genetic information from dissolved composition; 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.

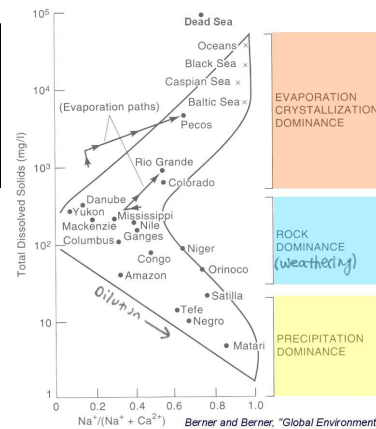
GG325 L17, F2009

❖ "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.



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

❖ Mg, K and SiO₂ also generally increase as $Na^+/(Na^++Ca^{2+})$ decreases

❖ Cl⁻ (and to a lesser extent SO₄²⁻) will decrease as HCO₃⁻ increases in rock-dominated rivers. In fact, some people suggest that it is better to classify rivers using $Cl^-/(Cl^- + HCO_3^-)$ instead of $Na^+/(Na^++Ca^{2+})$.

GG325 L17, F2009

❖ 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 soil (thick regolith)	Si-enriched; low pH $Si/(Na + K) = 2$ $Na/(Na + Ca) = \text{high}$	Amazon tributaries (Matari, Tefe, Negro)	rain-dominated
200-450	20-40	Siliceous (cation-rich); igneous rocks and shales (sedimentary silicates)	More Si-enriched $Si/(Na + K) = 2$ $Na/(Na + Ca) = \text{intermediate}$	Lower Amazon, Orinoco, Zaire	between rain-dominated and rock-dominated
450-3000	40-250	Marine sediments; carbonates, pyrite; minor evaporites	$Na/Cl = 1$ $(Ca + Mg) / (0.5 HCO_3 + SO_4) = 1$ $Na/(Na + Ca) = \text{low}$	Most major rivers	rock-dominated
>3000	>250	Evaporites; CaSO ₄ and NaCl	$Na/Cl = 1$ $(Ca + Mg) / (0.5 HCO_3 + SO_4) = 1$ $Na/(Na + Ca) = \text{high}$	Rio Grande, Colorado	Evaporation-crystallization

Notice these stoichiometries from our discussion of a few slides ago

GG325 L17, F2009

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

Most rivers world-wide plot in the $\text{HCO}_3^- > \text{Cl}^- + \text{SO}_4^{2-}$ 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:

- ❶ they flow through intensely weathered soils with little remaining soluble ion-content
- ❷ low pH rivers (high concentration of dissolved organic acids lowers HCO_3^-)

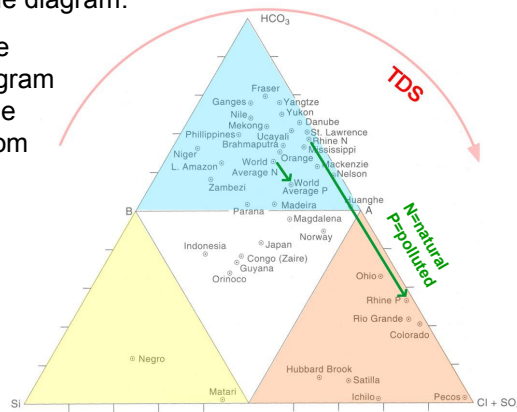


Figure 5.5. Major rivers: Percentage of Si ($\mu\text{mol/l}$); HCO_3^- ($\mu\text{Eq/l}$); and sum of $\text{Cl}^- + \text{SO}_4^{2-}$ ($\mu\text{Eq/l}$). For example, 100% HCO_3^- plots at the HCO_3^- vertex; 50% HCO_3^- and 50% Si plots at point B; and 50% HCO_3^- and 50% ($\text{Cl}^- + \text{SO}_4^{2-}$) plots at point A. River TDS increases from Si vertex to HCO_3^- vertex to ($\text{Cl}^- + \text{SO}_4^{2-}$) vertex. (Data from Tables 5.7 and 5.14.) Berner and Berner, "Global Environment"

GG325 L17, F2009

! What about anthropogenic effects? !

"Evaporation" is enhanced by human activities such as agriculture (e.g., see green arrows extending from "natural" to "polluted" on the preceding slide).

This distributes water across the landscape, resulting in enhanced evaporation and more saline soil waters.

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.

GG325 L17, F2009