

**Chapter 7 What Controls the Composition of River water and Seawater:
Equilibrium versus Kinetic Ocean**

(10/14/04)

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We have covered how to calculate the equilibrium chemical composition of natural water systems. You have learned how to set up simple box models to learn about controls on ocean chemistry. Lets now tie this up with the final question in this section: What controls the chemical composition of riverwater and seawater? Some of this material will be your responsibility in the group study project #1.

In Chapter 2 we learned that to a first approximation the input to the ocean from rivers is balanced by removal to the sediments with adjustments for inputs and removal from hydrothermal circulation at mid-ocean ridges. In the early days of chemical oceanography it was thought that, because of the long residence times, the major ion composition of seawater had been approximately constant over geological time and that chemical equilibrium might explain the composition. With the growth of paleoceanography it has become clear that there have probably been significant excursions in the composition of the ocean-atmosphere system (Berner et al., 1983; Berner, 1991) and that a kinetic or dynamic flux balance model is more appropriate.

I. The Chemical Inflow from Rivers

Ions transported by rivers are the most important source of most elements to the ocean. The composition of river water is significantly different from seawater. The concentrations are compared in **Table 7-1**. Some characteristic ratios are also compared. To a first approximation seawater is mainly a Na⁺ and Cl⁻ solution while river water is a Ca²⁺ and HCO₃⁻ solution. It is pretty clear that we can not make seawater simply by evaporation of river water. Other factors must be involved and significant chemical reactions and modifications must take place.

Table 7-1 The composition of average seawater and river water in mmol kg⁻¹.

<u>Element</u>	<u>Seawater (mmol kg⁻¹)</u>	<u>River water (mmol kg⁻¹)</u>		
Na	468.0	0.26		
Mg	53.1	0.17		
Ca	10.3	0.38		
K	10.2	0.07		
Sr	0.09	----		
Cl	546.0	0.22		
SO ₄	28.2	0.11		
HCO ₃	2.39	0.96		
Br	0.84	----		
	mainly Na ⁺ and Cl ⁻	mainly Ca ²⁺ and HCO ₃ ⁻		
	<u>RATIOS</u>			
	Na/K	Mg/Ca	Na/Ca	(Ca+Mg)/HCO ₃
Oceans	45.6	5.22	45.9	26.64
Rivers	6.0	0.42	0.8	0.59

There is significant variability in the composition of rivers between continents. The average compositions for different continents are shown in **Table 7-2** (from Holland, 1978).

Table 7-2 The mean composition of rivers on different continents (in ppm). The concentrations for anions and cations are given in meq l⁻¹ in the bottom two rows. Data from Livingston (1963). Table from Holland, 1978.

Mean Composition of River Waters of the World ^a											
Continent	HCO ₃ ⁻	SO ₄ ²⁺	Cl ⁻	NO ₃ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Fe	SiO ₂	Sum
North America	68	20	8	1	21	5	9	1.4	0.16	9	142
South America	31	4.8	4.9	0.7	7.2	1.5	4	2	1.4	11.9	69
Europe	95	24	6.9	3.7	31.1	5.6	5.4	1.7	0.8	7.5	182
Asia	79	8.4	8.7	0.7	18.4	5.6	9.3		0.01	11.7	142
Africa	43	13.5	12.1	0.8	12.5	3.8	11		1.3	23.2	121
Australia	31.6	2.6	10	0.05	3.9	2.7	2.9	1.4	0.3	3.9	59
World	58.4	11.2	7.8	1	15	4.1	6.3	2.3	0.67	13.1	120
Anions ^b	0.958	0.233	0.220	0.017							1.428
Cations ^b					0.750	0.342	0.274	0.059			1.425

^aLivingstone (1963); concentrations in ppm.

^bMillequivalents of strongly ionized components.

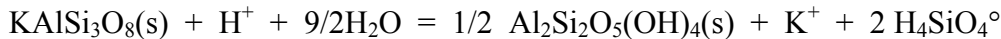
In general the weathering reaction on continents can be written as **congruent** or **incongruent** reactions (see Table 14.1 of Libes, 1992). In congruent reactions the total mineral goes into solution. In incongruent reactions the initial mineral is leached and modified and converted into a secondary mineral. Weathering of CaCO₃ is considered a congruent reaction.



Weathering of aluminosilicate minerals to clay minerals are examples of incongruent reactions.



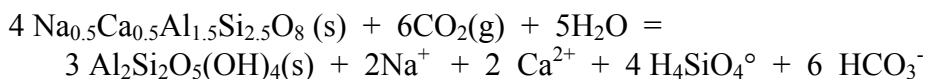
We can write these weathering reactions in terms of H⁺, CO₂(g) or H₂CO₃. For example the weathering of the potassium feldspar mineral called orthoclase (KAlSi₃O₈(s)) to the clay mineral called kaolinite (Al₂Si₂O₅(OH)₄(s)) is an important reaction in soils from humid climates. We can write the reaction in terms of H⁺ as follows:



The same reaction written in terms of atmospheric CO₂(g) would be:



For a different feldspar called plagioclase which contains an equal mole fraction Na and Ca, we can write:



You can see that in general, during weathering, a structured aluminosilicate (feldspar) is converted into a cation-poor, degraded aluminosilicate (clay), cations and silicic acid go into solution, $\text{CO}_2(\text{g})$ is consumed and HCO_3^- is produced. The bicarbonate concentration released is equivalent to the cations released according to the stoichiometry of the reaction.

There are many different minerals in rocks and they weather with different susceptibilities. The stability of minerals with respect to weathering (Goldrich's "mineral stability series") is shown in **Table 7-3** (Goldich, 1938). Among the mafic minerals (those with Mg and Fe), olivine weathers much faster than biotite. Quartz and K-feldspar are more resistant to weathering than the plagioclase minerals. Such weathering susceptibilities are clear when you look at rocks in the field.

Table 7-3 (from Goldich, 1938) **Mineral Stability Series in Weathering (the minerals are arranged according to decreasing rate of decomposition)***

<i>Mafic minerals</i>	<i>Felsic minerals</i>
Olivine	Ca-plagioclase
Pyroxene	Ca-Na plagioclase
Amphibole	Na-Ca plagioclase
Biotite	Na-plagioclase
	K-feldspar, muscovite
	Quartz

Weathering of carbonate minerals consumes one CO_2 from the atmosphere and produces one CO_3^{2-} (which can be expressed as two HCO_3^-) from the mineral thus there should be about twice as much HCO_3^- as Ca^{2+} . In a plot of HCO_3^- versus Ca^{2+} (**Fig. 7-1**, from Holland, 1978) we see that most of the world's major rivers fall close to the line of $\text{HCO}_3^- = 2\text{Ca}^{2+}$ which is consistent with weathering of carbonate minerals being a major control. Most rivers that don't fall on the line are above the line consistent with a silicate weathering source for some of the HCO_3^- . The Rio Grande is the only major river below the line because gypsum can be a major source of Ca^{2+} .

The average composition of rivers from different continents is plotted in **Fig 8-2** (from Garrels and Mackenzie, 1971). You can see that most of the variability in composition between different continents is due to Ca^{2+} and HCO_3^- . This is because Europe, North America and Asia have more carbonate rocks than South America and Africa. The products of silicate weathering are more uniformly distributed between continents..

Example: We can estimate the percent of CO_2 neutralized by silicate weathering using the following simple model. We assume that on average silicate minerals produce one HCO_3^- from each $\text{CO}_2(\text{g})$ consumed while releasing $2\text{H}_4\text{SiO}_4$ (e.g. silicate + $\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + 2\text{H}_4\text{SiO}_4$). All the Ca^{2+} and Mg^{2+} comes from carbonate minerals except that required to balance SO_4^{2-} (e.g. gypsum). Each $\text{CO}_2(\text{g})$ neutralized by carbonate minerals produces two HCO_3^- . The results for this calculation for different continents are shown in **Table 7-4**. The columns show the bicarbonate produced from weathering carbonate and silicate rocks and the total. The last column shows the percent of the total $\text{CO}_2(\text{g})$ consumed by weathering which is neutralized by silicate rocks. The values vary from 7% for Europe to 38% for Africa.

Fig. 7-1 HCO_3^- (bicarbonate) versus Ca^{2+} in a collection of the world's rivers. The diagonal line marked $m_{\text{HCO}_3^-} = 2m_{\text{Ca}^{2+}}$ shows the composition in equilibrium with $\text{CaCO}_3(\text{s})$ solubility. Calcite solubility at different values of P_{CO_2} are shown. Atmospheric P_{CO_2} is $10^{-3.5}$. (Data from Livingston, 1963 and the Figure is from Holland, 1978).

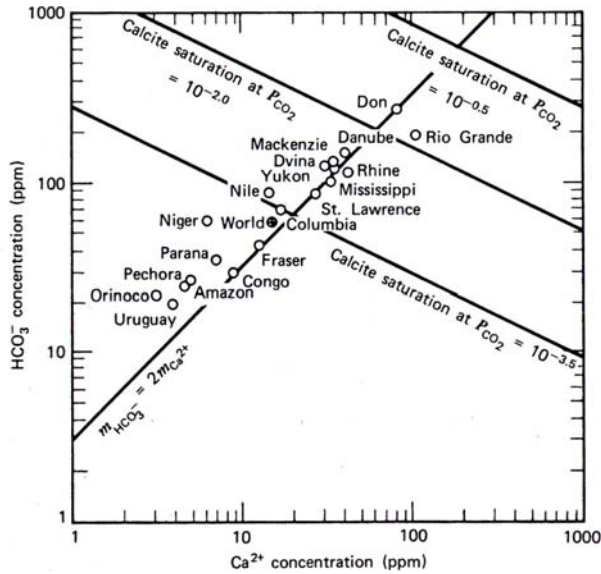


Fig 7-2 The average composition of rivers on different continents (from Garrels and Mackenzie, 1971).

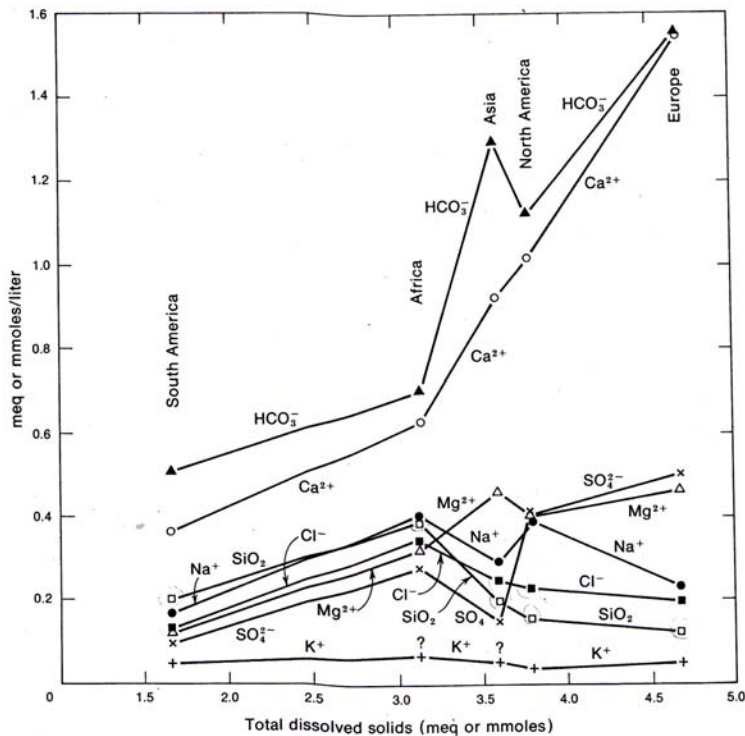


Table 7-4: Example calculations showing the CO₂ consumed during weathering by carbonate and silicate minerals (from Garrels and Mackenzie, 1971). Remember 1 mol Ca²⁺ = 2 meq Ca²⁺.

Continent	Limestone bicarbonate (meq Ca ²⁺ + meq Mg ²⁺ - meq SO ₄ ²⁻)		Silica bicarbonate (% mmoles SiO ₂)	
	HCO ₃ ⁻	CO ₂ neutralized	HCO ₃ ⁻	CO ₂ neutralized
Europe	1.49	0.75	0.06	0.06
Asia	1.10	0.55	0.10	0.10
North America	1.06	0.53	0.07	0.07
Africa	0.65	0.33	0.20	0.20
South America	0.38	0.19	0.10	0.10
World average	0.85	0.42	0.11	0.11

Total A + B (meq)	Observed bicarbonate (meq)	Percent CO ₂ neutralized by silicates
1.54	1.54	7
1.20	1.20	15
1.13	1.11	12
0.85	0.72	38
0.48	0.51	35
0.96	0.96	19

In addition to weathering of carbonate and silicate rocks, weathering of salt deposits which contain halite (NaCl) and gypsum (CaSO₄), weathering of sulfide deposits and weathering of organic carbon also need to be considered as sources to river water composition.

For some ions the atmosphere is a significant source. This is especially true for HCO₃⁻ which comes from atmospheric CO₂(g). Significant fluxes of Cl⁻ and SO₄²⁻ originate from the ocean as sea-salt aerosols which are transported over land where they are washed out by the rain. Sea-salt aerosols decrease from the edge of continents into the interior (Fig 7-3 from Junge and Werby, 1958).

The importance of these different sources for average river water is summarized in **Table 7-5** (from Holland, 1978) (also see Table 21.2 in Libes)

The Provenance of Solutes in Average River Water

Source	Anions (meq/kg)			Cations (meq/kg)				Neutral Species (mmol/kg)
	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SiO ₂
Atmosphere ^c	0.58 ^a	0.09 ^b	0.06	0.01	<0.01	0.05	<0.01	<0.01
Weathering or solution of								
Silicates	0	0	0	0.14	0.20	0.10	0.05	0.21
Carbonates	0.31	0	0	0.50	0.13	0	0	0
Sulfates	0	0.07	0	0.07	0	0	0	0
Sulfides	0	0.07	0	0	0	0	0	0
Chlorides	0	0	0.16	0.03	<0.01	0.11	0.01	0
Organic Carbon	0.07	0	0	0	0	0	0	0
Sum	0.96	0.23	0.22	0.75	0.35	0.26	0.07	0.22

^aLargely as atmospheric CO₂.

^bMuch of this is apparently balanced by H⁺.

^cThese figures do not include soil-derived material.

anions are generally from the atmosphere

cations are from rock weathering

The composition of endmember hydrothermal vent solutions at 350°C is also very different from seawater. Table 7-6 summarizes data from several vents from Von Damm et al (1985). Average seawater is in the right column. Especially note the concentrations of Mg, Ca, SO₄ and Alkalinity.

Table 7-6

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TABLE 7-6 ENDMEMBER CONCENTRATIONS

	NGS	21° OBS	NORTH SW	HG	GSC ¹	SEAWATER
The Alkalies						
Li μ^2	1033	891	899	1322	689-1142	28
Na ³ m	510	432	439	443	+	484
K m	25.8	23.2	23.2	23.9	18.7-18.8	9.79
Rb μ	31	28	27	33	13.4-21.3	1.3
NH ₄ m	<0.01	<0.01	<0.01	<0.01	n.a.	<0.01
The Alkaline Earths						
Be n	37	15	10	13	11-37	0.02
Mg m	0	0	0	0	0	52.7
Ca m	30.8	15.8	16.6	11.7	24.6-40.3	10.3
Sr μ	87	81	83	85	87	87
Ba μ	>15	>7	>9	>10	17.2-42.8	0.14
Y ₈₇ μ	>16	>8	>10	>11		
⁸⁷ Sr/ ⁸⁶ Sr	.703019 ±68	.703171 ±32	.703345 ±103	.703026 ±120	n.a.	.7091
pH	3.8	3.4	3.6	3.3		7.8
Alk meq	-0.19	-0.40	-0.30	-0.50	0	3.3
Cl m	579	489	496	496	+	541
SiO ₂ m	19.5	17.8	17.3	15.8	21.9	0.16
Al μ	4.0	3.2	4.7	4.5	n.a.	0.005
Trace Metals						
Mn μ	1002	960	899	878	360-1140	<0.001 ⁷
Fe μ	871	1864	750	2429	+	<0.001
Fe/Mn	0.9	1.8	1.0	2.9		
Co m	22	213	66	227	n.a.	0.03
Cu μ	<0.02	35	9.7	44	0	0.007
Zn μ	40	106	89	104	n.a.	0.01
Ag m	<1	38	26	37	n.a.	0.02
Cd m	17	155	144	180	0	1
Pb n	183	308	194	359	n.a.	0.01

TABLE 5: SULFUR, ARSENIC AND SELENIUM

	NGS	21° OBS	NORTH SW	HG	GSC ¹	SEA WATER
Endmember Concentrations						
SO ₄ m ²	0	0.5 ³	0.6	0.4	0	27.9
H ₂ S m	8.57	7.30	7.45	8.37	+	0
As m	<30	247	214	452	n.a. ⁴	27

II. Equilibrium Approaches

Rivers transport chemicals to the ocean. Then what happens to them? What role does this play in determining the composition of seawater?

The first approaches to this problem were attempts to explain the composition of seawater in terms of equilibrium chemistry.

A. **Goldschmidt** (1933) proposed that a general reaction of the following type controlled the composition of the atmosphere, ocean and sediments. He suggested that for each liter of seawater, about 600 grams of igneous rock had reacted with about 1 kg of volatile substances from inside the earth (e.g., H₂O, HCl, CO₂) to form seawater, 600 grams of sediments and 3 liters of atmosphere. This one-way weathering type reaction was written as:

igneous rock (0.6kg) + volatiles (1kg) \rightleftharpoons seawater (1 L) + sediments (0.6kg) + air (3 L)

B. **Lars Gunnar Sillén** was a Swedish inorganic chemist who specialized in solution chemistry. In 1959, Sillén was asked as "an outsider" to give a lecture on the physical chemistry of seawater to the International Oceanographic Congress (IOC) in New York (Sillén, 1961). Sillén proposed that the ionic composition of seawater might be controlled by equilibrium reactions between the dissolved ions and various minerals occurring in marine sediments. Sillén argued that Goldschmidt's reaction could go both directions. The reverse reaction would be called reverse weathering.

The framework for constructing such multicomponent equilibrium models is the **Gibbs Phase Rule**. This rule is valid for a system that has reached equilibrium and it states that:

$$f = c + 2 - p$$

The number of degrees of freedom or independent variables is represented by f . These are chosen from the list of all quantitatively related aspects of a system that can change. This includes T , P and the concentrations of c components in each phase. c is the minimum number of components necessary to reproduce the system (ingredients), and p is the number of phases present at equilibrium. A phase is a domain with uniform composition and properties. Examples are gas, liquid solution, solid solution and solid phases.

In a mathematical sense f represents the difference between the number of independent variables (including T , P) and the number of constraints (equations). If the number of equations equals the number of unknown variables, we can solve for all the concentrations using equilibrium equations. If a system is at equilibrium and one adds a new component ($\Delta c = 1$), either a new phase is formed ($\Delta p = 1$) or a new free concentration variable is added ($\Delta f = 1$). For more discussion of the phase rule see Findlay (1951) or Stumm and Morgan (1996). Sillén's approach was to mix components, pick a reasonable set of phases that might be present and then see how many degrees of freedom there are to be fixed.

Sillén constructed his models in a stepwise fashion starting with a simplified ocean model of five components (HCl, H₂O, KOH, Al(OH)₃ and SiO₂) and five phases (gas, liquid, quartz, kaolinite and potassium mica) (Sillén, 1967).

Sillen's (al)most complete ocean model was composed of nine components ($c = 9$): HCl, H₂O and CO₂ which represent acid volatiles from inside the earth and KOH, CaO, SiO₂, NaOH, MgO and Al(OH)₃ which corresponded to the bases of the rocks. The ocean was treated as one giant acid-base titration. Sillen argued that if the ocean contained an assemblage of nine phases in equilibrium with each other ($p = 9$) then the chemistry of seawater and atmosphere (including SW pH and Atmospheric P_{CO2}) would be fixed by knowing the value for two independent variables. He argued that these were T and Cl⁻. The value of T would fix the equilibrium constants and Cl⁻ does not enter into any chemical reactions and is thus conservative.

Here are the phases he suggested were at equilibrium:

1. gas phase (atmosphere)
2. solution phase (seawater)
3. calcite (CaCO₃)
4. Quartz (SiO₂)
5. Kaolinite (Al₂Si₂O₅(OH)₄)
6. Illite (K_{0.59}(Al_{1.38}Fe_{0.73}Mg_{0.38})(Si_{3.41}Al_{0.59})₁₀(OH)₂)
7. Chlorite (Mg₃(OH)₆Mg₃Si₄O₁₀(OH)₁₀)
8. Montmorillonite (Na_{0.33} Al₂(Si_{3.67}Al_{0.33}) O₁₀(OH)₂)
9. Phillipsite (zeolite) M₃Al₃Si₄O₁₆(H₂O)₆ where M = Na + K + Ca + Mg)

All of these phases have been identified in marine sediments. The problem is in identifying whether they have formed in place by reverse weathering reactions or have detrital sources.

C. The Chemical Mass Balance for Seawater by **Mackenzie and Garrels, (1966)**(See also Libes Table 21.8)

Evaporation of river water will not make seawater. Instead, evaporation of the nearly neutral Na⁺-Ca²⁺-HCO₃⁻ river water produces a highly alkaline Na-HCO⁻-CO₃²⁻ water such as found in the evaporitic lake beds of eastern California and Nevada (Garrels and Mackenzie, 1967). In addition, comparison of the amount of material supplied to the ocean by rivers with the amount in the ocean, it is clear that most of the elements have been replaced many times. Thus some chemical reactions must be occurring in the ocean to consume the river flux.

Mackenzie and Garrels (1966) approached this problem by constructing a model based on a river balance. They first calculated the mass of ions added to the ocean by rivers over 10⁸ years. This time period was chosen because geological evidence suggests that the chemical composition of seawater has remained constant over that period and this is the time scale of building mountain ranges. They assumed that the river input is balanced only by sediment removal. The results of this balance are shown in Table 7-7.

In this balance SO₄ is removed by CaSO₄ and FeS₂ in proportion to their abundance in the sedimentary record (50/50). Ca is removed as CaCO₃ with enough Mg to correspond to the natural proportions. Chloride is removed as NaCl, and enough H₄SiO₄ is removed to make the correct amount of opal sediments. Some Na⁺ is taken up and Ca²⁺ released during ion exchange reactions in estuaries. At this point they still had to account for removal of 15% of the initial Na, 90% of the Mg, 100% of the K, 90% of the SiO₂ and 43% of the HCO₃⁻.

Fig. 7-3 The chloride composition of rain (after Junge and Werby, 1958)

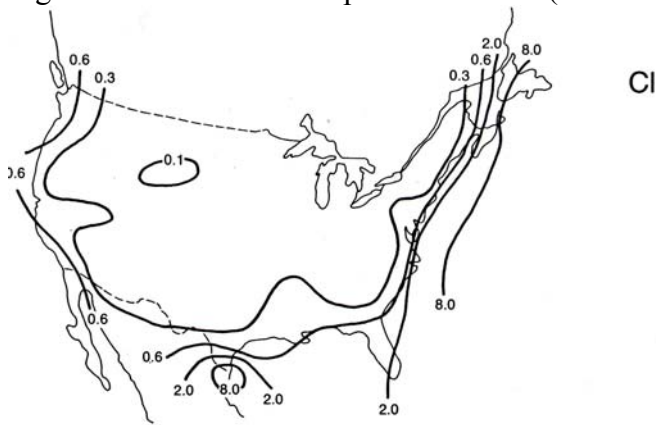


Fig. 7-4 a) The distribution of chlorite in the $<2\mu\text{m}$ fraction of deep-sea sediments (from Griffin et al., 1968), b) The distribution of illite in the $<2\mu\text{m}$ fraction.

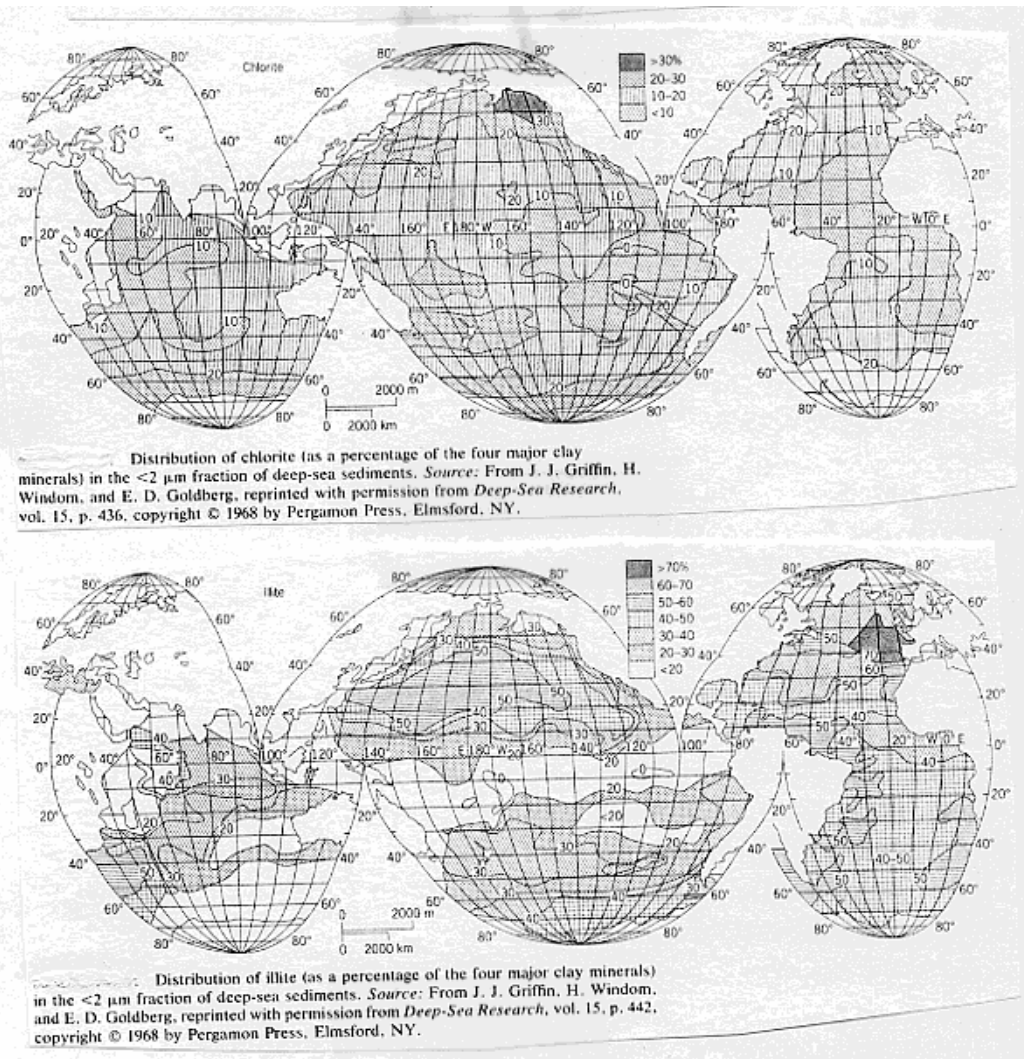


Table 7-7 Mass Balance of River Inflow according to Mackenzie and Garrels (1966).

Common minerals containing major ions:

Halite	(NaCl)
Calcite	(CaCO ₃)
Gypsum	(CaSO ₄ ·2H ₂ O)
Pyrite	(FeS ₂)
Opal, Quartz	(SiO ₂)

Reaction	SO ₄	Ca	Cl	Na	Mg	K	SiO ₂	HCO ₃	Product
Total amt to remove in 10 ⁸ yrs (x 10 ¹⁸ moles)	500	1680	1040	1360	740	240	710	4160	
Pyrite (a)	250	1680	1040	1360	740	240	710	4160	125 FeS ₂
Gypsum (b)	0	1430	1040	1360	740	240	710	4160	250 CaSO ₄
Calcite (c)	0	0	1040	1360	740	240	710	1300	1430 CaCO ₃
Halite (d)	0	0	0	320	740	240	710	1300	1040 NaCl
Opal (e)	0	0	0	320	740	240	639*	1300	71 SiO ₂

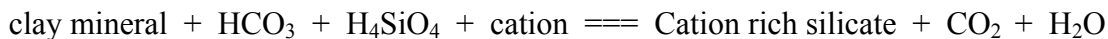
*The amount of opal formed is based on the knowledge of the sedimentary record

Known Reactions

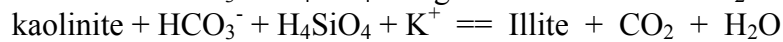
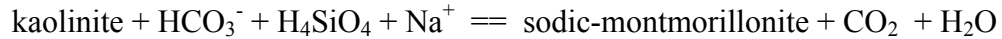
- a) $SO_4^{2-} + 2 CH_2O(s) \rightleftharpoons S^{2-} + 2 CO_2 + 2 H_2O$
 $Fe^{2+} + S^{2-} + S^0 \rightleftharpoons FeS_2(s)$
- b) $Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4(s)$
- c) $Ca^{2+} + 2 HCO_3^- \rightleftharpoons CaCO_3 (s) + CO_2 + H_2O$
- d) $Na^+ + Cl^- \rightleftharpoons NaCl (s)$
- e) $H_4SiO_4 \rightleftharpoons SiO_2 (s) + 2 H_2O$

Mackenzie and Garrels (1966) first removed the major ions necessary to form these common minerals. SO₄ was removed in equal amounts by gypsum and pyrite as is thought to be consistent with geological record. Gypsum removes some Ca as well. The rest of the Ca is removed as calcite, which also removes some HCO₃. Cl and an equal amount of Na are removed as halite (NaCl). An amount of SiO₂ is removed as opal according to the amount observed in rocks. There was still significant amounts of Na, Mg, K, SiO₂ and HCO₃ remaining to be accounted for.

Mackenzie and Garrels proposed that reverse weathering reactions in ocean sediments were the sink for the remaining ions (HCO₃, SiO₂, Mg, K, Na). These reverse reactions can be written in the general form of:



The specific reactions proposed to remove the excess ions were:



These newly formed clays would need to constitute about 7% of the sedimentary mass in order to account for the river input. The distributions of clay minerals in marine sediments do not support these reactions. See Libes Figures 14.8 to 14.10. Most clay minerals in marine sediments are of detrital origin (Drever, 1971; Kastner, 1974). The distributions of chlorite and illite are shown in **Fig. 7-4 a,b** (from Griffen et al, 1998). Chlorite comes from incomplete weathering of metamorphic rocks as occurs at high latitudes. Thus chlorite is high in the Gulf of Alaska and in the Gulf of St. Lawrence. Illite appears to originate from the continents and is transported by wind to the ocean.

A recent study has shown that authigenic minerals do form under certain circumstances. Michalopoulos and Aller (1995) recently discovered that substantial quantities of K-Fe-Mg clay minerals are forming in Amazon delta sediments. Removal in the Amazon River delta alone could account for 10% of the global river input of K^+ . This recent work needs to be explored further.

A final point to make is that the mass balance of Mackenzie and Garrels does not consider hydrothermal reactions at locations of seafloor spreading. Knowledge of these systems was lacking at that time. The composition of high-temperature hydrothermal vents is attached as **Table 7-6** (from Von Damm et al., 1985).

III. Kinetic Model of Seawater

Sillen's 1961 discussion of the physical chemistry of seawater was an important publication but we no longer ascribe to the thermodynamic view of ocean chemistry. The existence of the necessary authigenic silicates has yet to be demonstrated in marine sediments. Current models for seawater composition emphasize the balance between inputs and removals. The balance sheet has become more important than solubility relationships for explaining ocean chemistry. The difference has many important ramifications. We would expect a thermodynamic ocean to have a constant composition of the ocean and its sediments over geological time. According to the kinetic view we would expect changes in paleo ocean chemistry as inputs and removals varied in the geologic past. Broecker (1971) wrote an eloquent description of this approach in which he formed groups of elements controlled by similar processes.

The main input and removal fluxes for major seawater ions is shown below in **Table 7-7**. The main input for each of these elements is from rivers. These are calculated as the average river composition (Livingston, 1963) multiplied by the global river runoff (4.55×10^{16} L yr⁻¹). The principal uncertainty is for the average river concentrations.

Table 7-7 An input-output balance for major seawater ions and alkalinity

	Concentration (mmol/kg)	Ocean Inventory (10^{18} mol)	River Input	Atmospheric/ evaporite cycling	Ion exchange	Hydrothermal activity (10^{12} mol/y)	Low-temperature basalt weathering	Carbonate deposition	Net
Cl	545	710	10.0	(-10.0)		?			.0
Na	468	608	11.8	-9.3	-1.9	?			0.6
Mg	53	69	8.0	-0.5	-1.2	-7.8			-1.5
SO ₄	28	37	3.7	-0.5		-3.8			-0.6
K	10	13	3.2	-0.1	-0.4	+1.3	-4.0		.0
Ca	10	13	17.1	-0.1	2.6	+3.1	+2.0	-24.7	.0
Alk	2.4	3.1	47.8		0.5	-0.4		-49.4	-1.5
ΣC	2.3	3.0	43.7			+0.5		-49.4	-5.2

The elements were then grouped according to their major removal pathways.

Group Ia: (e.g., Cl-) For Chloride, the main sink over geological time is evaporite deposits. The deposition of evaporites is controlled by tectonics which controls the geometry of marginal seas which can become evaporite basins if the entry of seawater is sufficiently restricted. There are no significant evaporites forming today, and the balance for Cl is probably not at steady state. However, the residence time is so large (~100 My) that an imbalance between inputs and removals would have little influence over time scales of 10's of millions of years. Seawater cycling through aerosols is also an important sink for Cl. Other elements in seawater would also be cycled this way in their seawater proportions.

Group Ib: (e.g. Mg, SO₄, probably K) For magnesium and sulfate the main input is from rivers and the main sink is by hydrothermal circulation through ocean crust.

Thus:

$$V_r C_r = V_{\text{hydro}} (C_{\text{sw}} - C_{\text{exit fluid}})$$

$$\text{for Mg}^{2+}, C_{\text{exit fluid}} = 0$$

$$\text{thus: } C_{\text{sw}} = (V_r / V_{\text{hydro}}) C_r \\ = 300 C_r$$

The dominant control is V_{hydro} , thus tectonics.

We can do the calculation backwards by assuming that the composition of seawater and river water is known. If Mg and SO₄ share the same sinks they should give the same ratio of V_r / V_{hydro} . For Mg the ratio is $53.1/0.17 = 312$ and that for SO₄ is $28.2/0.11 = 256$. The balance given above appears to be a good approximation.

Potassium is added to seawater by hydrothermal circulation as well as river inflow. The dominant sink is less clear but appears to be low temperature scavenging by basalts on the flanks of mid-ocean ridges during low-temperature alteration.

Group II (e.g. Ca, Na) (e.g. the remaining cations with long residence times)

Consider the charge balance for seawater

$$2[\text{Ca}^{2+}] + [\text{Na}^+] + 2[\text{Mg}^{2+}] + [\text{K}^+] = [\text{HCO}_3^-] + [\text{Cl}^-] + 2[\text{SO}_4^{2-}]$$

or rearranged:

$$2[\text{Ca}^{2+}] + [\text{Na}^+] - [\text{HCO}_3^-] = [\text{Cl}^-] + 2[\text{SO}_4^{2-}] - 2[\text{Mg}^{2+}] - [\text{K}^+]$$

This side is controlled by tectonics

Therefore this sum is also controlled by tectonics

The controls on the relative proportions of elements on the left hand side are complicated but include:

- a) Ca/Na ion exchange in estuaries
- b) Ca/HCO₃ regulation by calcium carbonate equilibria

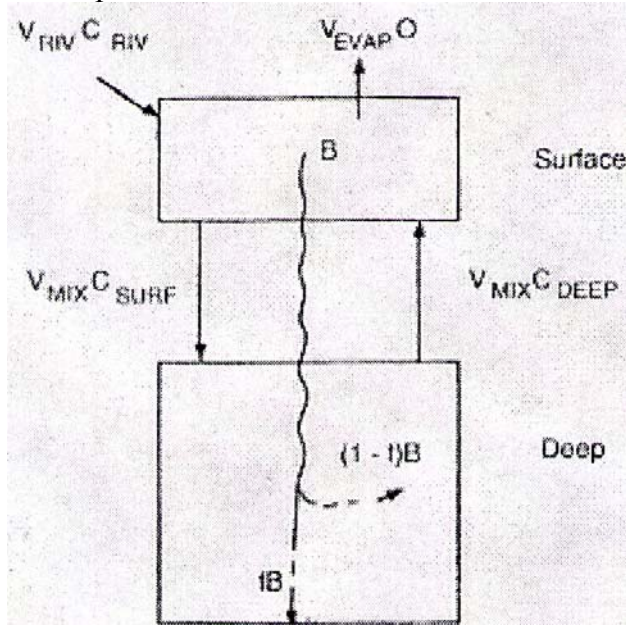
Group III (e.g. nutrients (Si, P, C, N) and trace metals)

The main balance is input by rivers and removal as biological debris to sediments. The sediment removal is in the form of a fraction of the biologically produced particulate material that escapes remineralization.

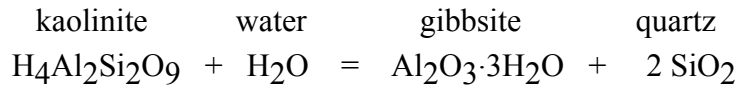
$$V_r C_r = f B$$

where f is the fraction of biogenic flux (B) buried.

The internal cycling in the ocean can be described by a simple two-box model (see below) that we will explore in class next week.



2. A proponent of "reverse weathering" has proposed that the minerals gibbsite, kaolinite and quartz exist together in equilibrium in the ocean according to the following reaction.



The activity of water is defined in such a way that pure water has an activity of 1.0. If water has an activity of 0.90 that means that there is 90% water and 10% salt.

a) Calculate the activity of water would be if these three solid phases were in equilibrium as described by this reaction. Below are the standard Gibbs Free Energies of formation for these phases. Remember that $\Delta G_r^\circ = -2.3 RT \log K = -5.708 \log K$ (for G in kJ)

<u>Phase</u>	<u>ΔG_f° (kJ mol⁻¹)</u>
Gibbsite	-2310.0
Kaolinite	-3799.0
Quartz	-856.7
water	-237.2

b) Could this reaction be in equilibrium in seawater? Explain your answer.

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Appendix: Classification of the Igneous Rocks. Igneous rocks with the same composition can be volcanic (cool rapidly at the earth's surface) or plutonic (cool slowly inside the earth). The normative mineralogical compositions are shown by the curves. The corresponding rock names are given across the top.

