Lecture 12 - What Controls the Composition of River Water and Seawater

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 river water and seawater?** The approach is to understand the source and fate of the major seawater constituents.

Questions: What are the main sources of the chemical constituents of the ocean?
                Does the chemistry of the sea look like the sources?
                What is the meaning of residence time?
                What are the marine sinks of the major ions?

In past lectures 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.

Sources: Rivers   Sinks: Sediment Burial
             Hydrothermal   Hydrothermal
             Wind/Rain   Volatilization/Sea-spray
             Pore water flux

$$d[C]_{sw} / dt = F_{atm} + F_{riv.} + F_{pf} - F_{sed} - F_{vol} \pm F_{hydro}$$

In the early days of chemical oceanography it was thought that, because of the long residence times involved, the major ion composition of seawater had been approximately constant over geological time and that chemical equilibrium might explain that composition. With the growth of the field 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 for describing the ocean over geological time scales.

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 the table below and shown in the schematic figure. Some characteristic ratios are also compared. To a first approximation, seawater is mainly a Na^+ and Cl^- solution while river water is a Ca^{2+} and HCO_3^- solution. It is pretty clear that we cannot make seawater simply by evaporation of river water. Other factors must be involved and significant chemical reactions and modifications must take place.
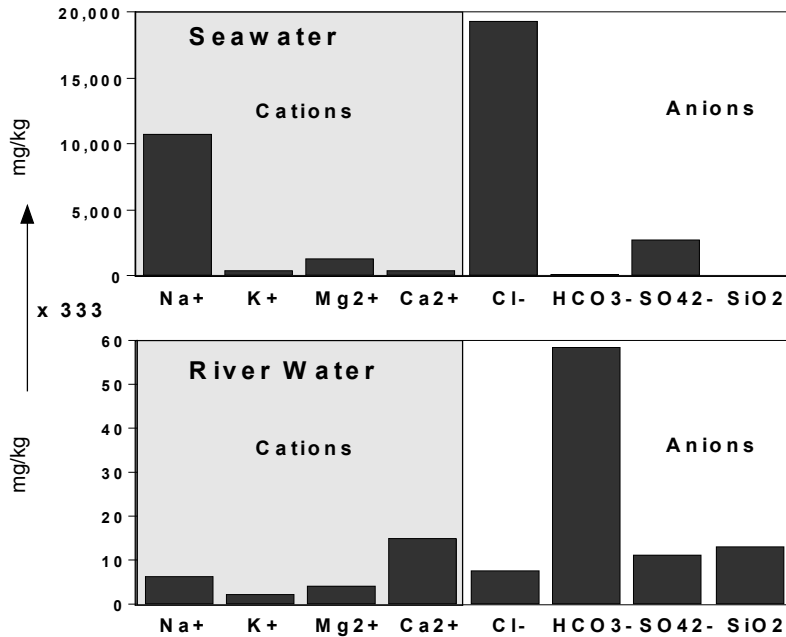
The composition of average seawater and river water in mmol kg^{-1}.

Element	Seawater (mmol kg^{-1})	River water (mmol kg^{-1})
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$_3^-$

	Na/K	Mg/Ca	Na/Ca	(Ca+Mg)/HCO3
Oceans	45.6	5.22	45.9	26.64
Rivers	6.0	0.42	0.8	0.59

Note that some of the dissolved constituents in river water do not come from weathering of continental rocks but rather are recycled from the ocean via aerosols and rainfall. These are called "cyclic salts" and if one assumes that all the chlorine in river water is cyclic (Cl in crustal rocks is ~0.01%) one can correct for the "cyclic salt" contribution of all other major elements by applying the constancy of composition of seawater.

There is significant variability in the chemical composition of rivers between continents and in different rivers within each continent depending on the weathered rocks in the drainage area (Holland, 1978; Livingston, 1963).

Following is a review the names and chemical formulas for some of the important rock forming minerals. The silicate part is mainly from Drever (1982).

1. Igneous rocks – The ultimate source of most cations and silicate dissolved in rivers and the ocean is igneous rocks, which are made of minerals like feldspar, mica and quartz.

Potassium Feldspar	$KAl_2Si_2O_5(OH)_4$
Sodium Feldspar	$NaAlSi_3O_8$
Biotite Mica	$KMg_3AlSi_3O_{10}(OH)_2$
Quartz	SiO_2

2. Clay minerals – Clay minerals are formed when igneous rocks weather. It's the main constituent of fine-grained ($< 63\mu$) particles in mud. They are less rich in cations compare to the source material.

Kaolinite	$Al_2Si_2O_5(OH)_4$
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}$

3. Authigenic Minerals – Minerals that precipitate from solution at the Earth surface temperature and pressure. These are the evaporite minerals that form in places like the Dead Sea and the Great Salt lake; minerals that form in anoxic sediments; and minerals that make up shells of plants and animals that live in the ocean and fresh waters.

Halite	$NaCl$
Gypsum and Anhydrite	$CaSO_4(H_2O)_n$, $CaSO_4$
Pyrite	FeS_2
Calcite and Aragonite	$CaCO_3$
Opal	SiO_2

In general, the weathering reaction on continents can be written as **congruent** or **incongruent** reactions. 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.

General weathering reactions that create the chemistry observed in rivers involve CO_2 reaction in soils with sedimentary and igneous rocks or O_2 reaction with reduced compounds. There are primarily three categories of weathering reactions
   (a) Those between CO_2 and $CaCO_3$ and
   (b) Those between CO_2 and aluminosilicate rocks
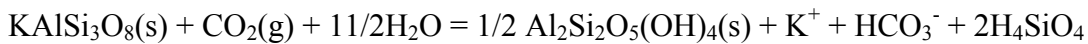   (c) Oxidation of reduced compounds like organic matter or pyrite.

Weathering of $CaCO_3$ is considered a congruent reaction. CO_2 in soils reacts with water to form H^+ that dissolves $CaCO_3$:
$$CaCO_3(s) + CO_2(g) + H_2O = Ca^{2+} + 2HCO_3^-$$
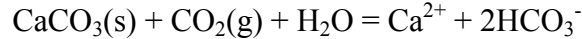
Weathering of aluminosilicate minerals to clay minerals are examples of incongruent reactions. CO_2 in soils reacts with aluminosilicate rocks to form clay minerals:

Silicate minerals + $CO_2(g)$ + H_2O = clay minerals + HCO_3^- + $2H_4SiO_4$ + cation

For example, the weathering of the potassium feldspar mineral called orthoclase $(KAlSi_3O_8(s))$ to the clay mineral called kaolinite $(Al_2Si_2O_5(OH)_4(s))$ is an important reaction in soils from humid climates.

$$KAlSi_3O_8(s) + CO_2(g) + 11/2 H_2O = 1/2\ Al_2Si_2O_5(OH)_4(s) + K^+ + HCO_3^- + 2H_4SiO_4$$

Similarly weathering of: Biotite mica => kaolinite

Biotite   Kaolinite
$$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + 15H_2O => Al_2Si_2O_5(OH)_4 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 4H_4SiO_4$$

There is a myriad of aluminosilicate reactions involving all the major cations. 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, $CO_2(g)$ is consumed and HCO_3^- is produced. The bicarbonate concentration released is equivalent to the cations released according to the stoichiometry of the reaction. Notice that both the carbonate and silicate reactions consume CO_2 and produce bicarbonate, HCO_3^-, and cations in solution.

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 as follows: among the mafic minerals (those with Mg and Fe), olivine weathers much faster than pyroxene followed by amphibole and the most resistant is 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.

Weathering of carbonate minerals consumes one CO_2 from the atmosphere and produces two HCO_3^-, (one C is from CO_2 and one from the carbonate mineral) thus there should be about twice as much HCO_3^- as Ca^{2+} (charge balance). If we plot of HCO_3^- versus Ca^{2+} for river waters we see most of the world's major rivers fall close to the line $HCO_3^- = 2Ca^{2+}$, which is consistent with weathering of carbonate minerals being a major control. Most rivers that don't fall on such a line have more HCO_3^- than expected from carbonate rock weathering; those that lay above the line are consistent with a silicate weathering source for some of the HCO^{3-}. The Rio Grande is the only major river with relatively more Ca^{2+} (below the line) because gypsum can be a major source of Ca^{2+}.

Most of the variability in river water composition between different continents is due to Ca^{2+} and HCO_3^- concentrations. 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.

In addition to weathering of carbonate and silicate rocks, weathering of salt deposits, which contain halite (NaCl) and gypsum ($CaSO_4$), 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 HCO_3^- which comes from atmospheric $CO_2(g)$. Significant fluxes of Cl^- and SO_4^{2-} 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.

The other important source elements to seawater are hydrothermal vent solutions. The composition of end-member hydrothermal vent solutions at 350°C like rivers is also very different from seawater. These solutions affect the concentrations of some of the major seawater ions Mg, Ca, SO_4 and Alkalinity as well as many trace elements.

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.

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., H_2O, HCl, CO_2) 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) === seawater (1L) + sediments (0.6kg) + air (3L)

Lars Gunnar Sillén a Swedish inorganic chemist who specialized in solution chemistry in 1959 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 (1961) argued that Goldschmidt's reaction could go both directions. The reverse reaction would be called "reverse weathering" and it happens in the ocean.

Sillen's ocean model was composed of nine components: HCl, H_2O and CO_2, which represent acid volatiles from inside the earth, and KOH, CaO, SiO_2, 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, then the chemistry of seawater and atmosphere (including seawater pH and atmospheric P_{CO2}) would be fixed by knowing the value for two

independent variables. He argued that these were temperature and Cl^-. The value of temperature 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 ($CaCO_3$)
4. Quartz (SiO_2)
5. Kaolinite ($Al_2Si_2O_5(OH)_4$
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 ($Mg_3(OH)_6Mg_3Si_4O_{10}(OH)_{10}$
8. Montmorillonite ($Na_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$
9. Phillipsite (zeolite) $M_3Al_3Si_4O_{16}(H_2O)_6$ 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 as suggested by Sillen's model or have originated in land and delivered as detrital material.

The Chemical Mass Balance for Seawater
Mackenzie and Garrels, (1966) took another approach they wanted to explain how river water and its chemical load can turn into seawater. They compared the amount of material supplied to the ocean by rivers with the amount in the ocean and concluded 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. They constructed a model based on a river balance. They first calculated the mass of ions added to the ocean by rivers over 10^8 years. This time period was chosen because geological evidence suggests that the chemical composition of major salts in seawater has remained relatively constant over that period, and this is also the time scale of building mountain ranges. They assumed river input is balanced only by sediment removal; in this balance, SO_4^{2-} is removed by $CaSO_4$ and FeS_2 in proportion to their abundance in the sedimentary record (50/50). Ca is removed as $CaCO_3$ with enough Mg to correspond to the natural proportions. Chloride is removed as NaCl; enough H_4SiO_4 is removed to make the correct amount of opal sediments. Some Na^+ is taken up and Ca^{2+} released during ion exchange reactions in estuaries. At this point (after accounting for all observed minerals in the sedimentary record) they still had to account for removal of 15% of the initial Na, 90% of the Mg, 100% of the K, 90% of the SiO^2 and 43% of the HCO_3^-.
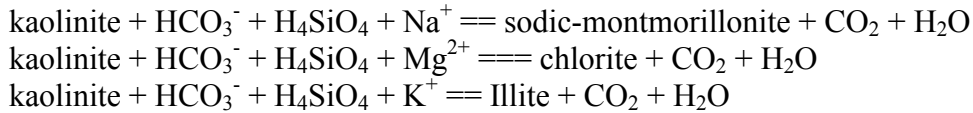
Problems with this calculation:
- They assumed steady state and it is unlikely river flow has been constant for 10^8 years.
- If the calculation is generally correct, what are the missing removal mechanisms?

Mackenzie and Garrels proposed that reverse weathering reactions in ocean sediments were the sinks for the remaining ions (HCO_3, SiO_2, Mg, K, Na). These reverse reactions can be written in the general form of:

clay mineral $+ HCO_3^- + H_4SiO_4 +$ cation $===$ Cation rich silicate $+ CO_2 + H_2O$

The specific reactions proposed to remove the excess ions were:

$$kaolinite + HCO_3^- + H_4SiO_4 + Na^+ == sodic\text{-}montmorillonite + CO_2 + H_2O$$
$$kaolinite + HCO_3^- + H_4SiO_4 + Mg^{2+} === chlorite + CO_2 + H_2O$$
$$kaolinite + HCO_3^- + H_4SiO_4 + K^+ == Illite + CO_2 + H_2O$$

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. Most clay minerals in marine sediments are of detrital origin (Drever, 1971; Kastner, 1974). A recent study has shown that authigenic minerals do form under certain circumstances (Michalopoulos and Aller, 1995) and can account for a fraction of the needed sinks (~10%).

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.

Kinetic Model of Seawater
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. The main input and removal fluxes for major seawater ions is shown below in the table. 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}).

An input-output balance for major seawater ions and alkalinity.

Component In Seawater	Concentration (mmol/kg)	Ocean Inventory (10^{15} mol)	River Input (10^{12}mol/y)	Atmospheric Cycling (10^{12} mol/y)	Ion Exchange (10^{12}mol/y)	Hydrothermal Activity (10^{12} mol/y)	Carbonate Deposition (10^{12}mol/y)
Cl	545	710	10.0	-10.0		?	
Na	468	608	11.8	-9.3	-1.9	?	
Mg	53	69	8.0	-0.5	-1.2	-7.8	
SO$_4$	28	37	3.7	-0.5		-3.8	
K	10	13	3.2	-0.1	-0.4	+1.3 (-4.0)	
Ca	10	133	17.1	-0.1	-2.6	+3.1 (+2.0)	-24.7
Alk	2.4	3.1	47.8		-0.5	-0.4	-49.4
ΣCO$_2$	2.3	3.0	43.7			+0.5	-49.4

Numbers in parentheses under hydrothermal activity refer to low temperature basalt weathering.

The elements in the table above can be grouped according to their major removal pathways.

Group Ia: (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 that become evaporite basins. 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 tens of millions of years. Seawater cycling through aerosols is also an important sink for Cl.

Group Ib: (Mg, SO₄, K) For these elements, the main input is from rivers and the main sink is by hydrothermal circulation through ocean crust.

Thus:

$V_r C_r = V_{hydro} (C_{sw} - C_{exit\ fluid})$
for Mg^{2+}, $C_{exit\ fluid} = 0$
thus: $C_{sw} = (V_r / V_{hydro}) C_r = 300\ C_r$

The dominant control is the hydrothermal circulation rate (V_{hydro}), which is driven by tectonic activity. We can do the calculation backwards by assuming that the composition of seawater and river water is known. 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 (Ca, Na) (e.g. the remaining cations with long residence times)
Consider the charge balance for seawater
$2[Ca^{2+}] + [Na^+] + 2[Mg^{2+}] + [K^+] = [HCO_3^-] + [Cl^-] + 2[SO_4^{2-}]$
or rearranged:
$2[Ca^{2+}] + [Na^+] - [HCO_3^-] = [Cl^-] + 2[SO_4^{2-}] - 2[Mg^{2+}] - [K^+]$
$\phantom{2[Ca^{2+}] + [Na^+] - [HCO_3^-] = }$ This side is controlled by tectonics (see above)
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 (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.
$V_r C_r = f\ P$ where f is the fraction of biogenic flux (P) buried.

Seawater and the Global Biogeochemical Cycle

The ocean formed from condensation of the volatiles, which out-gassed from the solid earth, and some gases dissolved in the water to form the early seawater. HCl and CO_2 probably introduced Cl⁻ and HCO_3^- to seawater. Oxygen was absent, S was mostly in the

form of insoluble sulfides and Fe and Mn were in their reduced soluble form and thus quite abundant in solution. Na and K were probably in a similar state as today.

In the Precambrian, pCO_2 is estimated to be one hundred times more than today (needed because of the early faint sun paradox), so oceanic pH would have been lower, allowing more dissolved Ca and Mg and HCO_3^- as well as Sr, and Ba.

By 3.8 By we have evidence for abundant sedimentary rocks, such as evaporites, carbonates, and shale, which are much like today in their mineralogy and composition, indicating that weathering processes and sedimentation were similar to the present. In the late Precambrian, photosynthesis produced oxygen and consumed CO_2; the pO_2 increased, and dissolved Fe was oxidized, forming banded iron formations. Also, reduced S species were converted to sulfate and became more abundant in solution. The decrease in atmospheric pCO_2 would result in higher oceanic pH, and Ca and Mg would precipitate to form the extensive dolomite beds of the later Precambrian. The composition of the ocean shifted towards the general proportions that we see today.

How similar to present day seawater was the chemical composition of past oceans?

Could we set the fluctuation boundaries for elemental composition of seawater throughout the geological history? One-way of doing this is by examination of the sequence of minerals precipitated in evaporites. As water evaporates, minerals will precipitate in a certain order, depending on their solubility. If we evaporate a beaker of seawater, carbonates will precipitate first (calcite and dolomite). Gypsum and anhydrite ($CaSO_4$) will precipitate when seawater is reduced to about 0.25 of its volume. Halite ($NaCl$) will precipitate when it is down to 10% and after that other minerals such as KCl and $MgSO_4$ will precipitate. The same sequence is seen in old evaporites – the question is, how much can we vary the concentrations of the major elements in seawater and still get this sequence of precipitation?

If we triple the sulfate or Ca concentrations, carbonate and gypsum will precipitate simultaneously; but such association is not observed. If Ca is much greater than SO_4, Ca will remain after all of the sulfate is removed from solution and $CaCl_2$ will occur; this is not seen. If we had a lot less Ca, then NaCl would precipitate before gypsum; also not observed. Also, HCO_3^- must be < 2 x Ca, as Ca is always left after all the carbonate precipitated from solution as calcite and dolomite to form $CaSO_4$ minerals. The fact that we do not see pure $MgCO_3$ sets a limit on the upper Mg concentrations; but since dolomite does precipitate, the Mg/Ca ratio should be large enough to permit this. These types of arguments led to the conclusion that in general all major elements in seawater should have been within about a factor of two of their present day concentrations.

In the last few years (Hardie et al., 2000) scientists looked more carefully at the evaporite record and noticed that the sequence is slightly different at different geological periods. There are some geological periods where KCl (sylvite) is dominant, while at other times $MgSO_4$ is dominant. These periods correspond to oscillations in the dominant type of carbonate mineral precipitated (calcite with less Mg and aragonite with high Mg). This

record has been interpreted as representing changes in ocean chemistry (more or less Mg) that are induced by changes in the rate of hydrothermal activity. This is supported by fluid inclusion composition (Timofeeff, et al., 2001). This should have consequences to atmospheric pCO_2, global sea level and climate.
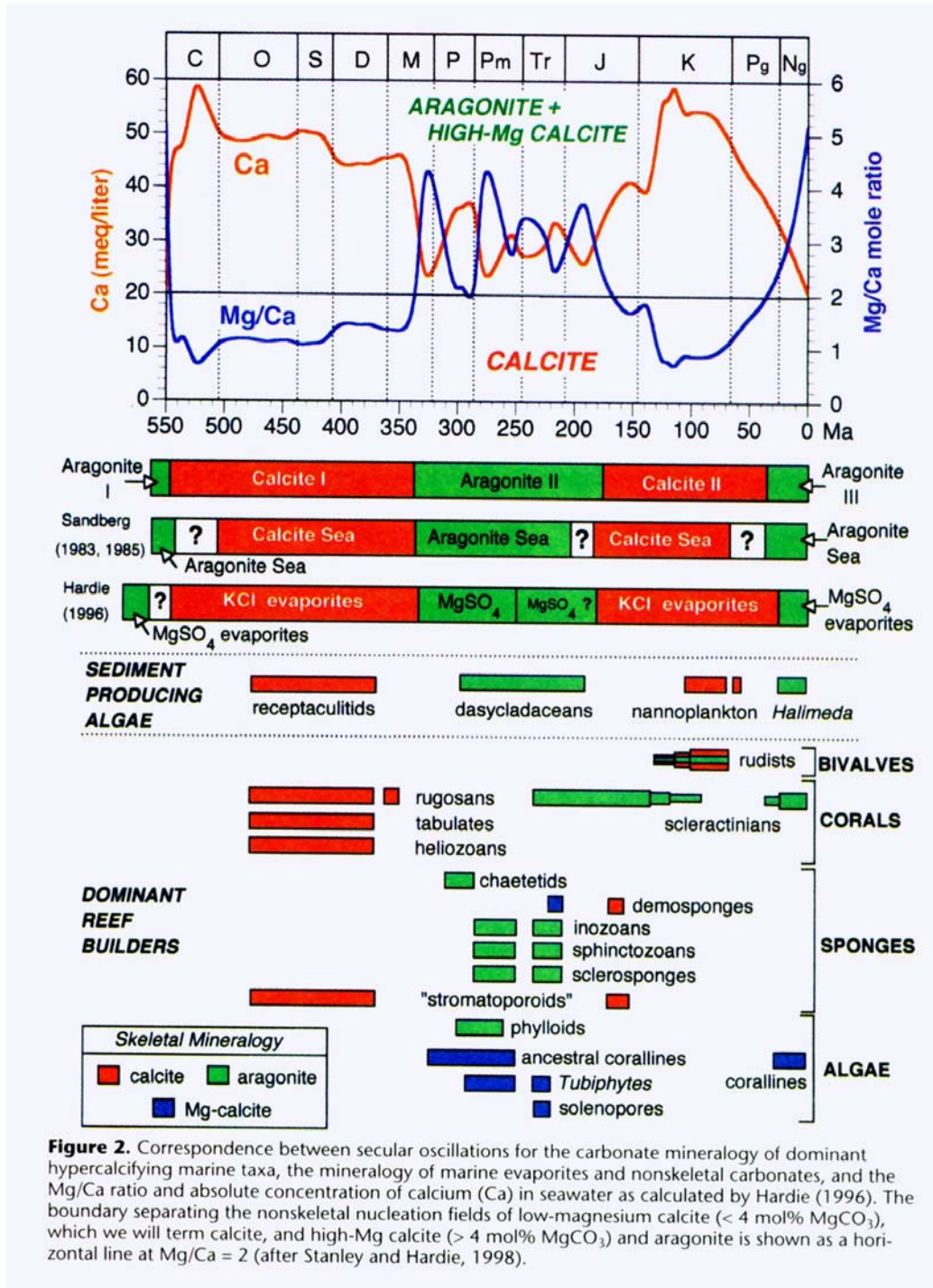

Figure 2. Correspondence between secular oscillations for the carbonate mineralogy of dominant hypercalcifying marine taxa, the mineralogy of marine evaporites and nonskeletal carbonates, and the Mg/Ca ratio and absolute concentration of calcium (Ca) in seawater as calculated by Hardie (1996). The boundary separating the nonskeletal nucleation fields of low-magnesium calcite (< 4 mol% MgCO₃), which we will term calcite, and high-Mg calcite (> 4 mol% MgCO₃) and aragonite is shown as a horizontal line at Mg/Ca = 2 (after Stanley and Hardie, 1998).

**How can changes in spreading rate affect sea level?**
As the seafloor moves away from the ridge and gets older, it cools, contracts, and subsides resulting in an increase in the ocean depth (depth increases with square root of age). If the hydrothermal activity is extensive and spreading rates are high, the oceanic crust is younger, thus contracts less, and occupies more volume of the deep basins displacing seawater and resulting in high sea level stands (transgressions).
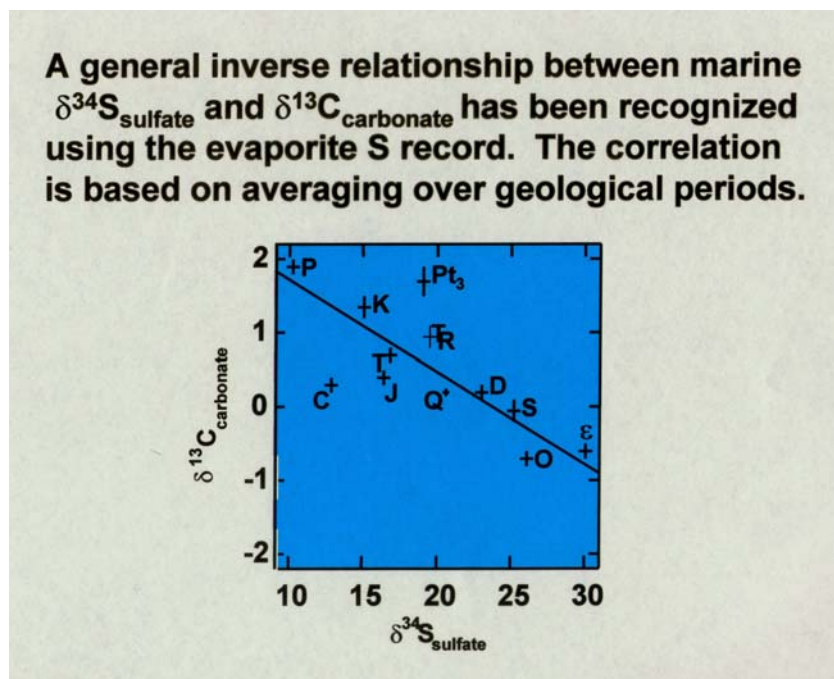
Feedbacks in the Global Biogeochemical Cycle
In order to maintain the relatively constant major elements composition over time, some mechanism have to operate to restore the system after perturbations occur. Many "feedback loops" are involved in the global biogeochemical cycle two important examples are described.

The Oceanic Redox Balance and Atmospheric Oxygen
Geological evidence (life) suggests that the mass of atmospheric oxygen has not changed by more than approximately a factor of 2 or 3 from the present atmospheric level ($\sim 38 \times 10^{18}$ moles) since the onset of the Cambrian. On geologic time scales, the burial of organic matter and pyrite in sediments and their oxidation during weathering are considered the dominant controls on the mass of atmospheric oxygen through the following reactions of organic carbon and pyritic sulfur burial (oxygen release) and weathering (oxygen consumption).

$$CO_2 + H_2O = CH_2O + O_2$$

$$2Fe_2O_3 + 16Ca^{2+} + 16HCO_3^- + 8SO_4^{2-} = 4FeS_2 + 15O_2 + 16CaCO_3 + 8H_2O$$
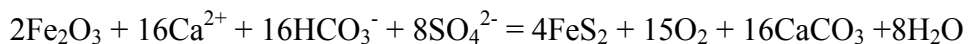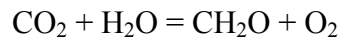
To maintain relatively constant atmospheric oxygen partial pressures, it has been suggested that a negative relation between pyrite and organic C burial would operate. Such a relation implies an inverse correlation between the isotope records of S and C. Indeed, averaged over geological time scales the $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$ records seem to exhibit a negative correlation.

A general inverse relationship between marine $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$ has been recognized using the evaporite S record. The correlation is based on averaging over geological periods.

Climate Carbon and Weathering

Garrels and Mackenzie have suggested a feedback loop that operates to control atmospheric pCO2 and thus Earth's surficial temperatures. In this scenario, during periods of extensive volcanism and tectonic activity when more CO_2 is out gassed, this "excess" CO_2 in the atmosphere results in increased temperatures through the greenhouse effect. High temperatures promote more weathering, which consumes the CO_2 and restores the balance. Similarly "connections" have between suggested between high CO_2 leading to increased weathering resulting in increased supply of nutrients to the ocean which triggers productivity, further reducing atmospheric CO_2, as well as a relationship between the atmospheric CO_2 content and a direct dependence of land plants productivity which results in sequestration of the "excess" CO_2.

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