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# Chemical Reactions and the Composition of Sea Water

The ocean is an enormous and extremely complex aqueous solution. There are more than a billion cubic kilometers of water in the ocean, 3.5% of which, by weight, is dissolved solids (*1*). Along with a vast array of organic and inorganic compounds and complexes, all of the elements in the periodic table probably occur in seawater.

In spite of its size and complexity the composition of the ocean, particularly the inorganic constituents, is remarkably uniform the world over. This homogeneity is due to the rapid circulation and mixing of the ocean, which takes place, at most, in a few thousand years. The winds mix the ocean at the surface. Density changes, due to cooling, evaporation, and the freezing of sea ice, mix the ocean depths.

Greater than 99% of the dissolved constituents of the sea are composed of the seven ions listed in Table 1 (*1*).

The concentration of these ions varies about 10% over the entire ocean. The ratios between ion concentrations varies far less than 10% and approaches analytical reliability. Thus the principal causes of variation are addition or removal of water by precipitation and evaporation, freezing and thawing of sea ice, and river influx.

Table 1. Composition of Average Seawater

| | *g/kg* |
|---|---|
| Cl | 19.35 |
| Na | 10.76 |
| $SO_4$ | 2.71 |
| Mg | 1.29 |
| Ca | .41 |
| K | .39 |
| $HCO_3$ | .14 |

Table 2. Composition of Dissolved Solids in Average Seawater and River Water

| | Per cent of solids | |
|---|---|---|
| | Seawater | River water |
| Cl | 55.1 | 6.5 |
| Na | 30.4 | 5.3 |
| $SO_4$ | 7.7 | 9.4 |
| Mg | 3.8 | 3.4 |
| Ca | 1.2 | 12.5 |
| K | 1.1 | 1.9 |
| $HCO_3$ | 0.4 | 48.7 |
| $SiO_2$ | 0.02 | 10.9 |

Table 3. Residence Times of Ions in Seawater

| | R.T. (million years) |
|---|---|
| Cl | 100 |
| Na | 70 |
| $SO_4$ | 10 |
| Mg | 10 |
| Ca | 1 |
| K | 7 |
| $HCO_3$ | 0.100 |
| $SiO_2$ | 0.020 |

Major chemical reactions must be taking place in the sea. If we compare the composition of seawater with that of river water, the source of the dissolved substances in the sea, we see that they are quite different—Table 2 (*1, 2*).

Seawater is essentially a NaCl solution; river water is a $Ca(HCO_3)_2$ solution, rich in silica. Different chemical reactions proceed at different rates in the sea. The ratio of the total amount of an ion in the sea to the amount added yearly to the sea by rivers is the residence time of that element in the sea—Table 3. This calculation is valid because geological evidence indicates that the composition of seawater has remained nearly constant for hundreds of millions of years.

These residence times are not corrected for "cyclical salts;" that is salts removed from the sea surface as spray, incorporated into rain, and returned to the sea by rivers. This correction would increase some of the residence times significantly. Nonetheless, all of the residence times are much less than the age of the ocean —3000 million years or more. Thus, all elements being added to the sea are constantly being removed.

Removal of an element from seawater requires that it be formed into a solid and incorporated into the sediments on the sea floor. Two mechanisms of removal appear possible: (1) simple precipitation, and (2) reaction with an existing solid.

## Precipitation

Examination of the ion products, or the best estimates of the ion activity products, in seawater indicates that the only combinations of common ions which approach saturation in the sea are those of the calcium and the magnesium carbonates.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (1)$$

$$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \rightarrow CaMg(CO_3)_2 \qquad (2)$$

Surface seawaters are two to four times supersaturated with respect to eqn. (1), and two to three orders of magnitude supersaturated with respect to eqn. (2). Deeper waters are less supersaturated, and are undersaturated with respect to at least eqn. (1), due to increased total pressure, $CO_2$ pressure, and decreased temperature.

## Reactions with Solids

Rivers bring to the ocean about 20 billion tons of sediment each year (*3*). The coarser fractions of this load, the relatively unreactive sands and gravels, are deposited near the river mouths. The finer materials, which make up the greater part of the river load, are carried into the open ocean. These fines are to a large extent aluminosilicate compounds, produced by weathering of crustal rocks. The aluminosilicates can react with seawater to remove dissolved elements from the water (*4*).

$$3.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + Na^+ + 2.6\ SiO_2 + HCO_3 \rightarrow 3\ Na_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + CO_2 + 4.5\ H_2O \quad (3)$$

A kaolinite-like material reacts to form a Na-montmorillonite.

$$Al_2Si_{2.4}O_{5.8}(OH)_4 + 5\ Mg^{2+} + 0.6\ SiO_2 + 10\ HCO_3^- \rightarrow Mg_5Al_2Si_3O_{10}(OH)_8 + 10\ CO_2 + 3\ H_2O \quad (4)$$

A kaolinite-like material reacts to form chlorite.

$$2.5\ Al_2Si_{2.4}O_{5.8}(OH)_4 + K^+ + SiO_2 + HCO_3^- \rightarrow 2\ K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + CO_2 + 3.5\ H_2O \quad (5)$$

A kaolinite-like material reacts to form illite.

Of the two types of reactions—simple precipitation and reaction with mud—it should certainly be expected that the first, precipitation, would be easy, chemically, to follow in the ocean, while the second, reactions with mud, would be rather messy chemically. Just the opposite appears to be the case. The aluminosilicate-seawater system approaches equilibrium, while the carbonate-seawater system does not.

## Aluminosilicates

In 1959, Lars Gunnar Sillèn (*5*) suggested, on the basis of theory, that reactions between silicates and seawater regulated the concentration of the major dissolved constituents, as well as bicarbonate and *p*H. His idea was not well received at first because clay mineralogists had been putting clays in seawater for years and observing minor changes at best. It was "well known" that clays were unreactive.

A few years later Fred Mackenzie and Robert Garrels (*6*) performed experiments which strongly suggested that Sillèn was right, and that the reactions involved were relatively rapid. Figure 1 illustrates the results of the first of these experiments.

Bermuda surface seawater contains essentially no dissolved $SiO_2$ due to the fact that planktonic plants—diatoms—continuously remove dissolved $SiO_2$ from the water to form their skeletons. When well-crystallized clays were added to this water, within a few hundred hours, $SiO_2$ was lost to the water and the $SiO_2$ concentration of average seawater (4–9 ppm) was approached.

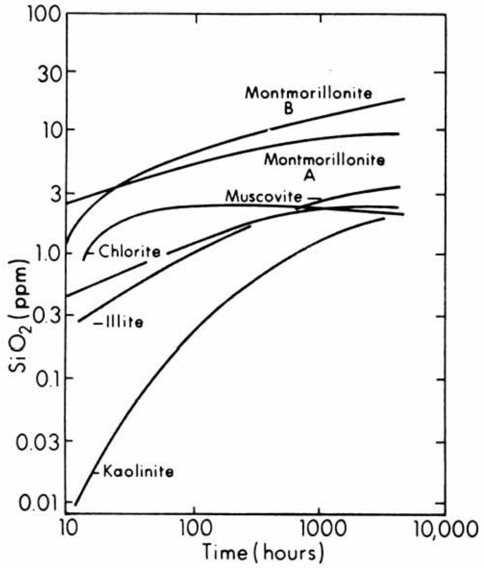

Figure 1. Release of $SiO_2$ to silica-free seawater from various clay minerals. After (*6*).

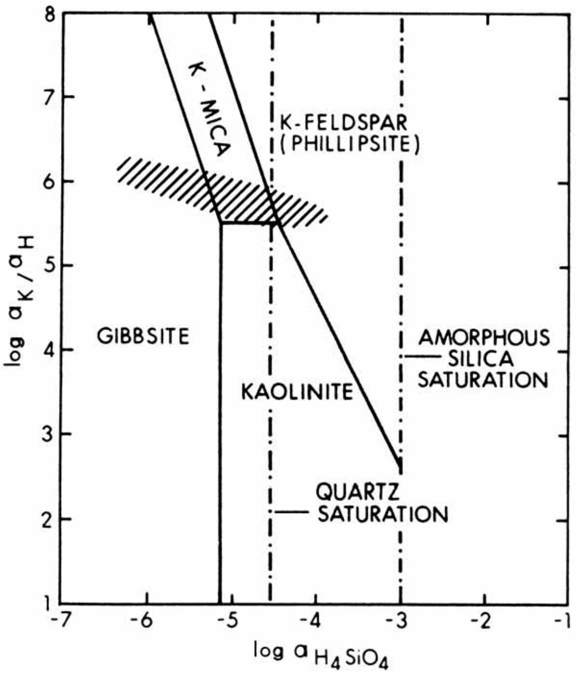

Figure 2. Activity diagram of the system aK, aH, $aH_4SiO_4$ at 0°C. Shaded area is range of seawater. After (*16*).

Further, Garrels and Mackenzie (*4*, *7*, *8*) and Helgeson, *et al.* (*16*) produced activity diagrams, such as Figure 2, by extrapolation from higher temperature experiments, showing the stability fields of common aluminosilicates.

Figure 2 indicates that average seawater at 0°C (the bulk of seawater is colder than 5°C), is in equilibrium with common aluminosilicates found on the sea floor—kaolinite, illite, and phillipsite, in the case of the potassium system. Similar diagrams and interpretations were made in the sodium and magnesium systems.

Thus, Garrels and Mackenzie support Sillèn's model and present experimental evidence that reactions are relatively rapid and approach true equilibrium. We cannot, at present, demonstrate where in the oceans these reactions occur. Hopefully, the end of the story will eventually be found.

## Carbonates

The carbonate-seawater system is generally out of equilibrium. Near-surface seawaters are supersaturated with respect to all stable calcium and magnesium carbonate phases, yet there is no evidence that chemical precipitation occurs in the ocean to any significant extent. Deep waters below several thousand meters are undersaturated with respect to all $CaCO_3$ phases, yet the average $CaCO_3$ content of sediment sampled from deeper than 5000 m is 11% by weight (*9*).

Nearly all of the $CaCO_3$ precipitated in the oceans is formed biologically by marine plants and animals building their skeletons. Even the organisms do it the hard way, commonly depositing phases that either are stable at high pressures (aragonite), or at high temperatures (calcites with up to 20 or so per cent magnesium in solid solution). Only a few groups of organisms deposit the stable mineral phase, calcite (*10*).

A few years ago Robert Schmalz and I (*11*) were conducting experiments to determine the solubility of this assortment of biologically-secreted carbonates in seawater. The experiments were simple: the sea shell was ground up, added to seawater, stirred on a magnetic mixer, and the *p*H of the slurry was monitored until equilibrium or constant *p*H. The equilibrium *p*H is easily related to the solubility. Equilibrium in our experiments was usually reached within an hour! How unlike the sea outside our laboratory.

In an attempt to understand the reason for disagreement between the lab and field observations, I set out to study the fine carbonate in suspension in all seawater (*12*). I reasoned that this material should be the most reactive in the ocean because of its high surface to volume ratio, and the high water to solid ratio. I was wrong! Not only was carbonate present, in a wide array of mineral phases, in both supersaturated and undersaturated seawaters, but the suspended carbonates were resistant to HCl to a *p*H of 6.0.

Finally, upon microscopic examination, I found the explanation—all the carbonate particles in suspension in the sea were encapsulated in an amorphous organic coating. Thus they were protected from reaction with the seawater.

Having discovered carbonate-organic interactions, other experiments followed to determine how these coatings were formed and how they affected other carbonate processes in the sea.

Erwin Suess and I performed an apparently ridiculous experiment, the results of which are illustrated in Figure 3 (*15*). We added amounts of ground calcite ranging from 13 to 1300 mg to 100 ml portions of filtered coastal New Jersey seawater. There was no reaction (change in *p*H) with 13–300 mg, some reaction with 500–700 mg, and equilibrium within 30–40 min with 1000–1300 mg.

Next the 300 mg sample of calcite was rinsed in distilled water and reacted with 50 ml of seawater—a ratio of 600 to 100. Again nothing happened (line A). The same 300 mg sample was then washed with hot $H_2O_2$, rinsed and reacted with another 50 ml sample, producing a proper 600:100 reaction (line B).

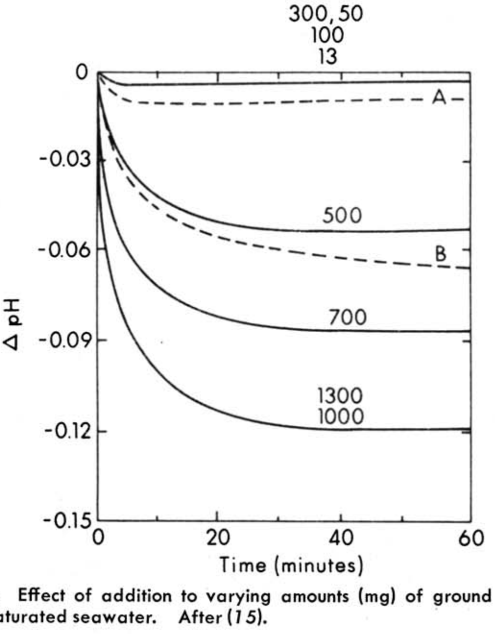

**Figure 3.** Effect of addition to varying amounts (mg) of ground $CaCO_3$ to supersaturated seawater. After (*15*).

Our interpretation of this series of experiments was that the surface area of up to 300 mg of calcite was rapidly coated with dissolved organic molecules in 100 ml of seawater, preventing precipitation of carbonate on the nuclei. There were not enough organics to coat larger amounts of calcite, so the inorganic reaction did occur. It is notable that the adsorption of organics is faster than the precipitation of carbonate.

These, and other experiments, seemed to explain the lack of reaction between carbonates and seawater. However, we still wondered if dissolved organics also might regulate nucleation from supersaturated seawater. Pytkowicz (*14*) had previously demonstrated that magnesium in solution inhibited carbonate nucleation in seawater.

To investigate this, natural seawaters containing varying amounts of natural dissolved organics, were further supersaturated with respect to $CaCO_3$, by addition of $Na_2CO_3$, to a *p*H of 9.5 (*13*). The samples were stirred and the *p*H monitored. After a period of time—minutes to hours—the *p*H dropped rapidly, and the water became white with precipitated carbonate. Three such experiments are illustrated in Figure 4.

The range of 1.2–3.0 mg C/l strongly affected the nucleation rate. The mechanism of inhibition of carbonate nucleation by dissolved organics is not entirely clear. Certainly there are insufficient moles of organics for a simple molar interaction.

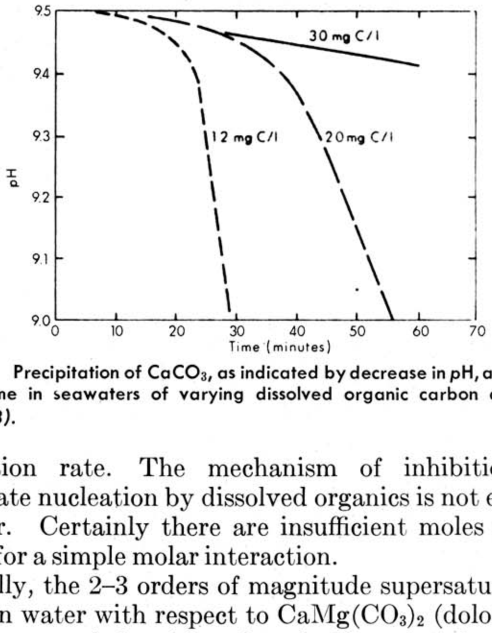

**Figure 4.** Precipitation of $CaCO_3$, as indicated by decrease in *p*H, as a function of time in seawaters of varying dissolved organic carbon contents. After (*13*).

Finally, the 2–3 orders of magnitude supersaturation of ocean water with respect to $CaMg(CO_3)_2$ (dolomite), a common rock-forming mineral, has never been explained adequately.

Thus the regulation of calcium concentration in seawater is clearly a disequilibrium process, or at best a kinetically very slow equilibrium one.

In summary

1) In spite of the ocean's enormous size the composition of seawater is nearly constant because the ocean is rapidly mixed.

2) Calculations of the residence times of elements in the ocean indicate a continuous removal of all elements as solids.

3) Two probable mechanisms for removal of dissolved materials are precipitation and reaction with an existing solid.

4) Reaction with a solid—mud brought to the sea by rivers—appears to be an equilibrium reaction, controlling the concentration of $K^+$, $Na^+$, an $Mg^{2+}$ in seawater.

5) Precipitation, involving only Ca and Mg carbonates, does not occur chemically. The regulation of the $Ca^{2+}$ concentration

of seawater is a complex of biological and organic chemical processes.

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