The geochemical control of seawater (Sillen revisited)

The current view of how seawater composition is regulated emphasizes the balance between inputs and outputs

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Sillen's 1961 discussion of the physical chemistry of seawater (and its subsequent elaboration in 1967) is a seminal publication in the field of chemical oceanography. Yet one is pressed to find more than a handful of present-day chemical oceanographers who actually subscribe to Sillen's thermodynamic view of ocean chemistry. Current models for seawater composition emphasize the dominance of balances between the various inputs and outputs; balance sheets have become more important than solubility relationships in explaining oceanic chemistry. The difference between these divergent views is not just a matter of mathematical and chemical formalism. In one case, one would expect a very constant composition of the ocean and its sediments over geological time; in the other, historical variations in rates of exogenic processes should have caused changes in ocean composition and may be reflected in the sedimentary record.

A principal aim of Sillen's classic paper was to provide an explanation for the low alkalinity of the ocean compared to its ionic content; as Sillen noted, the acids and bases of the oceans are almost balanced: "We are about 0.5% from the equivalence point."

In the historical view of Goldschmidt, the major ion composition of the oceans is the result of a one-way reaction:

\[
\begin{align*}
600 \text{ g Igneous rock} + 1 \text{ kg Volatiles} & \rightarrow \\
600 \text{ g Sediments} + 1 \text{ kg Seawater}
\end{align*}
\]

The almost perfect balance of acids and bases during this process is an unlikely situation. (Comparison of material fluxes to the oceans over geological time with estimates for the masses of dissolved and sedimentary material provides, of course, an even more compelling reason to doubt that a one-way process is responsible for the present-day ocean composition.)

In the modern view of a steady-state balance between inputs and outputs for major ions, the low oceanic alkalinity seems just as precarious: Relatively small changes in anionic fluxes compared to cationic fluxes could result in large historical excursions in seawater alkalinity. Unless some rather tight feedback mechanisms are provided, the remarkable acid–base balance of the oceans still appears as an unlikely coincidence. Sillen provided a chemically satisfying solution to this problem by proposing a heterogeneous equilibrium (over geological time, not necessarily locally or over observable intervals), for example involving reactions such as:

\[
\begin{align*}
1.5 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s}) + \text{K}^+ &\rightarrow \\
\text{KAl}_3\text{Si}_3\text{O}_10(\text{OH})_2(\text{s}) + 1.5 \text{H}_2\text{O} + \text{H}^+
\end{align*}
\]

Calcite

\[
\text{CO}_2(\text{g}) + \text{Ca}^{2+} + \text{H}_2\text{O}
\]

There is but one problem with this elegant model: The existence of necessary authigenic silicate phases in sufficient quantities has yet to be demonstrated in oceanic sediments. The problem before us is to reconcile the Sillenian concept of a heterogeneous chemical control of seawater alkalinity with the modern ideas of the processes actually controlling the major ion concentrations in the oceans.

Let us first consider the question of input and output balances for the major seawater ions whose concentrations and inventories are summarized in Table 1, columns 1 and 2. A variety of processes are involved in transfers of material in and out of the oceans (Figure 1). Our objective here is to identify the dominant sources and sinks in the oceanic balance sheet.

Ins and outs

The fluvial inputs of materials (Table 1, column 3) are calculated from the mean river concentrations estimated by Livingstone (1963) and the average of the annual discharge estimates of Ltvitchev (1973) and Kozen (1974), \(4.55 \times 10^{16} \text{ L/y} \). The principal uncertainties are associated with the concentration estimates; effort needs to be devoted to a thorough revision of Livingstone's summary. Residence times, in millions of years, are readily calculated by dividing column 2 by column 3.

For chloride, two sinks are of importance: atmospherically recycled sea salt and deposited evaporites. Seafloor hydrothermal activity may also be significant (Edmond et al., 1979a). The deposition of evaporites is related to tectonic activity and as such is difficult to quantify. Certainly, no important deposits are forming today. Conversely, the residence time is so large (\(~ 100 \text{ My}) that an imbalance between input and output rates has little influence on oceanic concentrations over periods less than tens of millions of years. Finally, about half of the chloride at the earth's surface is stored in the sea (Garrels and Mackenzie, 1971), placing well-defined limits on its concentration excursions. For these reasons, we will assume that the chloride cycle is closed, recognizing that for the contemporary ocean this is almost certainly not the case.

Other elements cycle with chloride. This component is usually represented...
as atmospherically cycled sea salt (Garrels and Mackenzie, 1971). Some workers have recently suggested, however, that evaporitic contributions are of substantial importance (Hol-

land, 1978; Stallard, 1980). While sea salt cycling through aerosols is in sea-

water proportions, evaporitic cycling is not; CaSO4 and NaCl are prefer-

entially enriched in evaporite deposits. To estimate fluxes, we assume a 1:2.5 mixture of these respective pathways (Holland, 1978). Sea salt proportions are assumed for the aerosol component (normalized to chlorine), and Na/Cl = 1 and Ca/Na = .021 (the seawater value) for the evaporitic component. The use of the seawater Ca/Na value may underestimate CaSO4 cycling. The resulting fluxes are summarized in Table 1, column 4. The detrital load of rivers has a substantial cation-exchange capacity (∼ 4 × 10^{12} eq/y; Russell, 1970; Sayles and Mangelsdorf, 1977). Upon entering the sea, exchange reactions with this material can alter the primary fluxes of the various cations. Sayles and Mangelsdorf (1977, 1979) have investigated the exchange char-

TABLE 1
Input–output balance for major seawater ions and alkalinity

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mmol/kg)</th>
<th>Ocean Inventory (10^{16} mol)</th>
<th>River Input</th>
<th>Atmospheric/ evaporite cycling</th>
<th>Ion exchange</th>
<th>Hydrothermal activity (10^{12} mol/y)</th>
<th>Low-temperature basalt weathering</th>
<th>Carbonate deposition</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>545</td>
<td>710</td>
<td>10.0</td>
<td>(-10.0)</td>
<td>?</td>
<td></td>
<td></td>
<td></td>
<td>.0</td>
</tr>
<tr>
<td>Na</td>
<td>468</td>
<td>608</td>
<td>11.8</td>
<td>-9.3</td>
<td>-1.9</td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
</tr>
<tr>
<td>Mg</td>
<td>53</td>
<td>69</td>
<td>8.0</td>
<td>-0.5</td>
<td>-1.2</td>
<td>-7.8</td>
<td></td>
<td></td>
<td>-1.5</td>
</tr>
<tr>
<td>SO4</td>
<td>28</td>
<td>37</td>
<td>3.7</td>
<td>-0.5</td>
<td>-3.8</td>
<td></td>
<td></td>
<td></td>
<td>-0.6</td>
</tr>
<tr>
<td>K</td>
<td>10</td>
<td>13</td>
<td>3.2</td>
<td>-0.1</td>
<td>-0.4</td>
<td>+1.3</td>
<td></td>
<td></td>
<td>.0</td>
</tr>
<tr>
<td>Ca</td>
<td>10</td>
<td>13</td>
<td>17.1</td>
<td>-0.1</td>
<td>+2.6</td>
<td>+3.1</td>
<td>+2.0</td>
<td>-24.7</td>
<td>.0</td>
</tr>
<tr>
<td>Alk</td>
<td>2.4</td>
<td>3.1</td>
<td>47.8</td>
<td>0.5</td>
<td>-0.4</td>
<td></td>
<td></td>
<td>-49.4</td>
<td>-1.5</td>
</tr>
<tr>
<td>ΣC</td>
<td>2.3</td>
<td>3.0</td>
<td>43.7</td>
<td>0.5</td>
<td>+0.5</td>
<td></td>
<td></td>
<td>-49.4</td>
<td>-5.2</td>
</tr>
</tbody>
</table>

characteristics of detrital material. Based on their exchange coefficients, fluxes can be estimated (Table 1, column 5). The important effect is in the sodium balance, its cycle being approximately balanced.

In the past decade, ridgecrest hydrothermal metamorphism has been recognized as playing an important role in several geochemical cycles. Two vent systems have been sampled to date, one on the Galapagos Rift at 86° W and the other on the East Pacific Rise at 21° N. The chemistry of the exiting fluids at these locations reflects dilution of a high-temperature end member (generated by reaction of circulating seawater with newly formed basalt) with seawater entrained during ascent of the hot fluid. The high-temperature end member is remarkably uniform: ∼ 350 °C, free of magnesium and sulfate, alkalinity depleted, potassium and calcium enriched, and variably enriched or depleted in sodium and chloride. Because the mixing is conservative, the elemental fluxes are in well-defined proportions; hence, knowing the global flux of one allows estimates of the global fluxes of all. Helium provides this opportunity. In the exiting fluids, the ³He/⁴He ratio is about 7.8 times the atmospheric (and thus "normal" oceanic) ratio. Injection of these fluids into the ocean results in a prominent mid-depth anomaly in the ³He/⁴He ratio. Maintaining this anomaly requires a global flux of ³He of 1000 mol/y (Craig et al., 1975). Elemental fluxes can thus be estimated from their ratio to ³He in the vent waters (Edmond et al., 1979a). This reasoning was originally applied to estimating the flux of heat from such systems (Jenkins et al., 1978). The vent analyses give a heat/³He transfer of 5 × 10^{13} kcal/mol, implying a heat flux of 5 × 10^{16} kcal/y, in good agreement with independent geophysical estimates (4–6.4 × 10^{16} kcal/y). The elemental fluxes summarized in Table 1, column 6 provide a strikingly good balance for the magnesium and sulfate cycles. Potassium and calcium are added to the sea. The chloride and sodium mass/³He ratios exhibit too much variability to define their fluxes. However, their mass/³He ratios show a nearly 1:1 correspondence and so the
net hydrothermal fluxes could be accommodated as were atmospheric and evaporitic recycling. It is important to remember also that the fluxes estimated assume that the observations to date are representative. In this regard, the agreement of results from two very different geologic settings is encouraging.

We have yet to consider fluxes for the most commonly accepted sinks of K, Na, and Mg: reconstitution of degraded clays and authigenesis of aluminosilicates. Attempts to identify the occurrence of these processes have had little success. Holland (1978) has reviewed the various studies and concludes that the fluxes are small at best. Sayles (1979) amplifies this point; the K and Mg contents of marine sediments simply aren’t large enough to accommodate the dissolved river flux.

Where then does potassium go? Although few firm data are available, uptake during low-temperature alteration of basalt is a plausible sink. Seafloor basalts subjected to low-temperature alteration show potassium enrichment, particularly in the secondary minerals (Thompson, 1973; Seyfried et al., 1978; Hart and Staudigel, 1978). The extent of uptake is difficult to assess, however, as both the amount of basalt altered and the average uptake are not well known. We assume quantitative removal to close the cycle. What balances the charge? Laboratory studies of basalt alteration at low temperatures (Seyfried and Bischoff, 1979) and interstitial water studies of deep drill cores (McDuff, 1980) suggest that the charge balance is maintained principally by the release of calcium. Magnesium and sodium may be involved in minor ways, however even the signs of their fluxes are not clear. The resulting fluxes are given in Table 1, column 7.

The only significant, documented, oceanic alkalinity sink is calcium carbonate deposition:

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}
\]

This process balances the final three components (including the CO\(_2\) flux to the atmosphere; Table 1, column 8). Surface productivity transfers material in excess of the river flux to the deep sea. Dissolution is sufficiently rapid below the calcite saturation horizon to create a situation near equilibrium.

The most striking aspect of the cycle portrayed here is the exchange of sodium, magnesium (less sulfate), and potassium for calcium (Figure 2). The importance of this kind of exchange has been noted previously in the context of ridgecrest hydrothermal metamorphism (Edmond et al., 1979b); on the basis of this analysis, we suggest it is common to other removal processes. After all—and to make engineers happy—alkalinity is calcium carbonate, ultimately.

**Steady state**

In our discussion so far, we have concentrated on obtaining a reasonable balance for the fluxes of major ions and alkalinity in the oceans, but we have not explicitly accounted for their actual (steady-state) concentrations. In particular, we are able to account for an alkalinity loss by calcium carbonate precipitation to balance the alkalinity input from rivers, but we have yet to explain why the alkalinity of the ocean is what it is.

Consider the charge balance condition for the major seawater ions:

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

(Other ions, including HCO\(_3^-\), are initially neglected.) On the basis of the previous discussion, the concentrations of all the ions on the right side of this equation are determined by the relative rates of chemical weathering, physical weathering, and flow-through hydrothermal systems. For example, since magnesium and sulfate are completely stripped from seawater by reaction during hydrothermal circulation, their steady-state seawater concentrations are simply proportional to the ratio of the rates of chemical weathering and hydrothermal flow.

For potassium, the situation is not quite as simple. However, if the dominant removal process is scavenging by basalts during low-temperature circulation on the ridge flanks, then K\(^+\) must be controlled by the same geochemical processes as Mg\(^{2+}\) and SO\(_4^{2-}\) (i.e., the ratio of weathering rate to hydrothermal flow rate) although the functionality may be more complicated.

A similar steady-state analysis for sodium and chloride shows that the concentrations are controlled by the relative rates of chemical weathering, physical weathering (rate of formation of detrital clays), and rate of evaporite formation. Although the steady-state analysis may be particularly bad for these two elements, it is worth recalling that their high seawater concentrations preclude any large historical variations.

Finally, the calcium concentration is obtained from the charge balance, making it a complicated function of the various geochemical processes (equivalent to considering the various input and output processes individually):

\[
[\text{Ca}^{2+}] = f(\text{chemical weathering rate, physical weathering rate, hydrothermal flow rate, rate of evaporite formation})
\]

So far the oceanic chemistry model that we have presented is strictly non-Sillenian: Concentrations are controlled by input and output balances and ultimately by geological processes, not by chemical properties. The chemistry (and the buffering) are introduced in our oceanic model simply by considering the heterogeneous carbonate equilibria. Following Sillen, we take the ocean to be in equilibrium both with atmospheric CO\(_2\) and with sedimentary CaCO\(_3\) over geological time:

\[
[\text{Ca}^{2+}][\text{HCO}_3^-] \cdot \frac{K_s}{K_{a2}} = \left(10^{2.3}\right)
\]

\[
[\text{HCO}_3^-][\text{H}^+] = \frac{K_{al}K_{SP}}{P_{CO_2}} \left(10^{-7.4}P_{CO_2}\right)
\]

The constants are selected for an "average" ocean. Making the assumption that the CO\(_2\) content of the atmosphere is controlled at a P\(_{CO_2}\) of 10\(^{-3.5}\) atm by other processes (as discussed later), we now have a complete model for the alkalinity of the ocean. Solving the above equations leads to:

\[
\text{pH} = 5.35 - 0.5 \log P_{CO_2} - 0.5 \log [\text{Ca}^{2+}]
\]

\[
\text{Alk} = [\text{HCO}_3^-] = 10^{-2.05} \frac{P_{CO_2}}{[\text{Ca}^{2+}]^{0.5}}
\]

(A more complete derivation appears in the accompanying box.)

**An expanded model**

More complete expressions for pH and alkalinity can be derived including HCO\(_3^-\) in the charge balance. Let \([\text{Ca}^{2+}] = \lambda + [\text{HCO}_3^-]^{0.5}\), where \(\lambda\) is the sum of the other terms of the balance. \([\text{H}^+]\) is found by solving the cubic equation:

\[
[\text{H}^+]^2 - 10^{-10.7}P_{CO_2} (\lambda + 10^{-7.8}P_{CO_2}/[\text{H}^+]) = 0
\]

Since \(\lambda \gg 10^{-7.8}P_{CO_2}/[\text{H}^+]\), the approximate expression for pH is:

\[
\text{pH} = 5.35 - 0.5 \log P_{CO_2} - 0.5 \log ([\text{Ca}^{2+}] - [\text{HCO}_3^-])
\]

The error introduced by neglecting the bicarbonate term is less than 0.02 pH units. Inclusion of carbonate in the alkalinity expression leads to:

\[
\text{Alk} = 10^{-2.05}P_{CO_2}\frac{[\text{Ca}^{2+}]^{0.5}}{[\text{Ca}^{2+}]^{0.5} + 10^{-6.7}/[\text{Ca}^{2+}]}
\]
In this model, the alkalinity of the oceans is low simply because CaCO₃(s) is reasonably insoluble. Note that the actual value of seawater alkalinity is rather insensitive (exponents of 0.5) to the externally controlled partial pressure of CO₂ and calcium concentration. However, the concentration of calcium itself is probably quite sensitive to individual variations in weathering rate or flow rate through hydrothermal systems. The interdependence among the principal geochemical processes may well have to be invoked to explain the apparent historical constancy in ocean chemistry. For example, the continental weathering rate and the hydrothermal flow rate are both ultimately dependent upon tectonic activity and are therefore likely to be covariant (Holland, 1978).

In order to be viable, our model has to satisfy steady-state conditions for all geochemical compartments, not just the oceans. The major difficulties that we have created so far concern carbon. If CaCO₃ is the only alkalinity sink in seawater, the return flux of CO₂ to the atmosphere is insufficient to balance the atmospheric budget (Table 2). For example, the alkalinity, contributed by the weathering of sodium and potassium silicate phases and eliminated after cation exchange by CaCO₃ precipitation, must result ultimately in an atmospheric carbon drain. Therefore carbon recycling mechanisms must exist in order to buffer the carbon dioxide content of the atmosphere.

The most obvious mechanisms for recycling and buffering of CO₂ in the atmosphere are metamorphic reactions of carbonate rocks into silicate rocks as proposed by Urey (1956), e.g.:

\[
\text{CaCO}_3(s) + \text{SiO}_2(s) = \text{CaSiO}_3(s) + \text{CO}_2(g)
\]

In other words, a direct corollary to our simplistic alkalinity model is that all major reverse weathering reactions (outside of CaCO₃ precipitation) and concomitant CO₂ regeneration take place as metamorphic, not sedimentary, processes.

(An examination of thermodynamic data shows that carbonates and silicates of magnesium, rather than those of calcium, may provide the most suitable buffering mechanism. Magnesium carbonates are, after all, more soluble than calcium carbonates and hence provide a better source of CO₂. See Holland, 1978.)

Many authors consider that atmospheric CO₂ is controlled by biological rather than geochemical processes. The reason is apparent if we consider Table 3. It seems intuitive that pro-

![FIGURE 2](image)

**FIGURE 2**

Exchange of various solutes for calcium

![TABLE 2](image)

**TABLE 2**

Oceanic fluxes of carbon

<table>
<thead>
<tr>
<th>Flux</th>
<th>Atmospheric demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>River input</td>
<td>43.7</td>
</tr>
<tr>
<td>Derived from atmosphere</td>
<td>35.0</td>
</tr>
<tr>
<td>Derived from carbonates</td>
<td>8.7</td>
</tr>
<tr>
<td>Hydrothermal input</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbonate deposition</td>
<td>49.4</td>
</tr>
<tr>
<td>Deposited as carbonates</td>
<td>24.7</td>
</tr>
<tr>
<td>Lost to atmosphere</td>
<td>24.7</td>
</tr>
<tr>
<td>Net atmospheric demand</td>
<td>-12.4</td>
</tr>
</tbody>
</table>

Units: 10⁻¹² mol/y

![FIGURE 3](image)

**FIGURE 3**

The role of carbon

![TABLE 3](image)

**FIGURE 3**

The role of carbon

The left side of the figure shows the effect of carbon fixation on carbonate solubility. Pco₂ and pH. Calcium and alkalinity are fixed at [Ca²⁺] = 10 mM and Alk = 0.0025 eq/L. Uptake of CO₂ from solution leads to carbonate precipitation until Pco₂ decreases to ~ 10⁻⁹ atm and pH increases to ~ 11. The right side of the figure illustrates the important pathways for regeneration of atmospheric CO₂.
The geological storage of organic carbon is worth considering further in order to understand the CO₂ buffering mechanisms. The original carbon dioxide in the atmosphere has to be carbonates since other reservoirs are simply too small (Table 3). However, it is impossible that carbon was transferred to the oceans by simple dissolution of the carbonate. Before CaCO₃ dissolution could have replenished the atmospheric CO₂ consumed by excess photosynthesis, the partial pressure of CO₂ would have had to plummet to nanoatmosphere levels and the oceanic pH would have had to exceed 10.5. As noted by many authors, the present-day increase in P_CO₂ should ultimately be reflected in dissolution of carbonates. Vice versa, a hypothetical decrease in P_CO₂ could only result in an increase in carbonate deposition or a decrease in carbonate weathering. Carbon would then be further lost from the atmosphere and the hydrosphere rather than being regenerated. The carbon dioxide in the atmosphere, continuously depleted by the weathering of silicates, the deposition of carbonates, and (marginally) the synthesis and storage of refractory organic carbon, must then be replenished by metamorphic processes as symbolized by the Urey reaction. Thus, while seawater alkalinity is directly controlled by the formation of calcium carbonate as its major sedimentary sink, it is also controlled indirectly by carbonate metamorphism which buffers the CO₂ content of the atmosphere.

There is little that is very novel in this discussion of the geochemical control of seawater alkalinity. Modern data on elemental fluxes in the ocean have been coupled to the most classical of equilibria carbonate chemistry. The picture which emerges is one of an ocean composition dominated by geo-physical rather than geochemical processes. The acid–base chemistry reflects, however, a fundamental control by heterogeneous chemical processes. That thought, more than the detailed chemistry, is in fact the major message of Sillen.

References

Craig, H.; Clarke, W. B.; Beg, M. A. Earth Planet. Sci. Lett. 1975, 26, 125-32.

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Table 3

<table>
<thead>
<tr>
<th>Reservoirs</th>
<th>Carbon reservoirs and fluxes</th>
<th>10₁² mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td></td>
<td>0.054</td>
</tr>
<tr>
<td>Biosphere</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Ocean</td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>Sediments</td>
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<td>6100</td>
</tr>
<tr>
<td>CaCO₃</td>
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<td>4200</td>
</tr>
<tr>
<td>MgCO₃</td>
<td></td>
<td>900</td>
</tr>
<tr>
<td>CH₂O</td>
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</tr>
<tr>
<td>Net organic storage</td>
<td></td>
<td>0.5</td>
</tr>
</tbody>
</table>

* Calculated from (reservoir mass/2 billion years).

Sources: Table 1, Garrel and Perry (1974), and Garrels et al. (1973)