CLIMATE

Seawater Chemistry and Climate

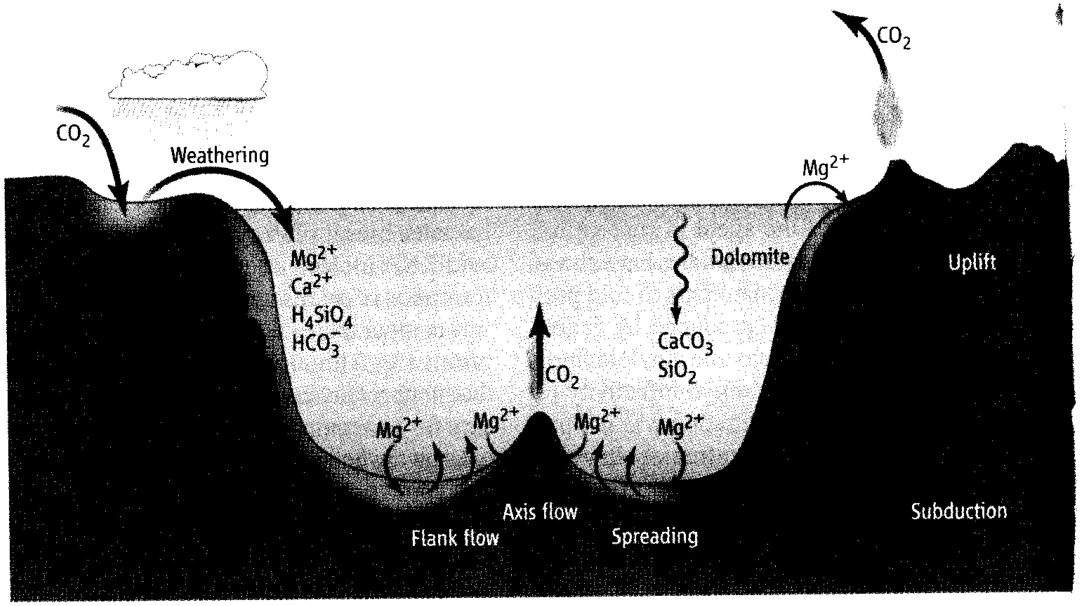
Reconstructions of past seawater chemistry provide insights into the driving forces behind long-term climate change.

Harry Elderfield

The chemical composition of the ocean is determined by rivers, submarine hot springs, and ocean sediments that add or remove elements to seawater. Throughout the oceans, the more abundant elements have near constant ratios to salinity (a measure of total dissolved salts). Thus, records of their past concentrations in seawater should tell us how active these sources and sinks were over long time scales. However, reliable archives of past seawater chemistry have been difficult to find (*1*). On page 1114 of this issue, Coggon *et al.* address this problem by measuring magnesium/calcium and strontium/calcium ratios in calcium carbonate (calcite) veins recovered from ocean crust buried under sediments (*2*). Their Mg/Ca record for the past 180 million years agrees with previous work (*1*), but the Sr/Ca record does not (*3*). The results have implications not only for seawater chemistry but also for climate change.

Earth's climate changes on several time scales. Over tens to hundreds of thousands of years, variations in Earth's orbit around the Sun alter the amount and distribution of external heating. The resulting changes in climate occur within the framework of tectonic processes that take place over millions of years. Driven by Earth's internal heat, tectonics shapes climate by recycling carbon between Earth's interior and surface. Tectonic forcing of climate is crucial for a habitable planet. Our closest planetary neighbors, Mars and Venus, have carbon dioxide in their atmospheres but were unable to escape runaway "icebox" (Mars) and "greenhouse" (Venus) conditions. For Earth to avoid such a fate, a negative feedback must keep runaway warming or cooling in check. Over million-year time scales, it is commonly thought that atmospheric CO_2 reflects a balance between input from volcanic activity and removal by silicate rock weathering feedback (see the figure). This balance, and how it may have changed, is reflected in the chemical composition of the oceans.

The calcite veins studied by Coggon *et al.* were formed by seawater flowing through the upper oceanic crust on the flanks of mid-ocean ridges. The authors dated the veins based on their $^{87}Sr/^{86}Sr$



Long-term climate change and ocean chemistry. On million-year time scales, climate is driven by the input of CO_2 to the atmosphere by plate tectonics. The atmospheric CO_2 reservoir is small and would raise global temperatures unchecked without a chemical weathering carbon feedback. Coggon *et al.* (*2*) have improved understanding of the global Mg cycle, which shares some similarities with the carbon cycle.

Earth Sciences Department, Cambridge University, Cambridge CB2 3EQ, UK. E-mail: he101@cam.ac.uk

ratios and then converted the calcite Mg/Ca and Sr/Ca ratios to seawater values (*2*). The resulting Mg/Ca ratios were ~1 mmol/mol from 180 to 60 million years ago and then rose to today's value of 5.4 mmol/mol. This pattern agrees with other studies using different approaches (*1*).

Coggon *et al.* explain this pattern based on two classic models (*4*, *5*), in which seawater gains Mg from river input and loses Mg during hydrothermal circulation through ocean ridges (see the figure). Hydrothermal processes dominate Mg removal today, but Wilkinson and Algeo (*4*) have argued that removal as dolomite (a sedimentary carbonate rich in Mg) dominated the Mg budget over long periods in the past. Only ~10% of today's sedimentary sink is as dolomite (*6*).

How do the Sr/Ca data fit into this picture? Coggon *et al.*'s seawater Sr/Ca values are ~3 μmol/mol from 180 to 20 million years ago and then tripled to modern values. In contrast, earlier studies found higher values in the past than today (*3*). Coggon *et al.* attribute this discrepancy to uncertainty over Sr partitioning into biogenic carbonates. Literature data show that hydrothermal vent fluids have lower Sr/Ca than does seawater (*7*), and Coggon *et al.* attribute the increasing seawater Sr/Ca (as for Mg/Ca) to a decreasing influence of hydrothermal activity over time. However, Sr and Ca concentrations in hydrothermal fluids vary and may be both higher and lower than seawater values (*7*). When normalized to chloride to account for phase separation, Sr concentrations are, in fact, about two times higher than modern seawater; the Sr/Ca ratios are only lower than in modern seawater because Ca is on average five times higher. Therefore, the situation is more complex. For example, if Ca added from vents is removed as carbonate sediments, then the impact of hydrothermal activity will be to increase Sr/Ca, not lower it.

A key feature of the models (*4*, *5*) is the rate at which Mg is stripped from seawater during hydrothermal alteration in the ocean crust (see the figure). However, estimates of this rate differ widely, with implications for understanding seawater chemistry and long-term climate change.

Many studies have used estimates based on seafloor spreading rates and seafloor generation histories (*8*) that show a decrease of 50% or more in ridge production (and hence Mg removal at ridge crests) in the past 100 million years. This makes sense: Mg removal at ridge crests decreases, and seawater Mg/Ca increases. Lower ridge production also implies a decrease in CO_2 production. This lowers atmospheric CO_2, which leads to a decrease in chemical weathering, less CO_2 removal, and thus a negative feedback on climate. One geochemical model that has taken this approach is the influential BLAG model (*9*), in which the atmospheric CO_2 cycle is driven by the rate of seafloor generation.

However, in 2002, Rowley (*10*) showed that the present distribution of seafloor ages is consistent with an almost constant rate of oceanic crustal area of 3.4 km^2 per year for the past 180 million years. He concluded that "a constant rate of ridge production has important implications for models of sea level and pco_2"—to which we can add, the history of seawater chemistry. How can the Mg/Ca ratio of seawater decrease through time if its major sink has remained constant?

Coggon *et al.* do not use Rowley's result but instead refer to Müller *et al.* (*11*), who argued that Rowley's approach is invalid. Rowley (*12*) has criticized the assumptions made by Müller *et al.* in extrapolating the spreading history or age distribution of oceanic lithosphere. Errors in estimates of the crustal production of seafloor that has been subducted are likely to be very large.

If Rowley is correct, then how could constant global ridge production lead to changing hydrothermal seawater Mg/Ca? One idea is that fast- and slow-spreading ridges may behave differently. Another, pointed out by Coggon *et al.*, is that oceanic crust is altered on ridge flanks. Flanks buried by sediments may remain warm enough long enough to promote Mg removal (*13*).

At present, geophysical constraints on crustal production rate seem to be weaker than geochemical ones, yet they are crucial for the long-term climate balance of CO_2. Taken together with our knowledge of seawater chemistry, they offer the promise to understand the interactions between solid earth processes and the biogeochemical cycles of the major ions in the oceans.

References and Notes

1. H. D. Holland, in *The Oceans and Marine Geochemistry, Vol. 6*, H. Elderfield, Ed. (Elsevier, Oxford, 2003), pp. 583–625.
2. R. M. Coggon *et al.*, *Science* **327**, 1114 (2010); published online 4 February 2010 (10.1126/science.1182252).
3. C. H. Lear *et al.*, *Science* **287**, 269 (2000).
4. B. H. Wilkinson, T. J. Algeo, *Am. J. Sci.* **289**, 1158 (1989).
5. R. J. Spencer, L. A. Hardie, in *Fluid-Mineral Interactions*, Spec. Pub. 2, R. J. Spencer, I.-M. Chou, Eds. (Geochemical Society, St. Louis, MO, 1990), pp. 409–419.
6. E. T. Tipper *et al.*, *Earth Planet. Sci. Lett.* **250**, 241 (2006).
7. M. R. Palmer, *Earth Planet. Sci. Lett.* **109**, 37 (1992).
8. S. E. McCauley, D. J. DePaolo, in *Tectonic Uplift and Climate Change*, W. F. Ruddiman, Ed. (Plenum, New York, 1997), pp. 427–467.
9. R. A. Berner, *Am. J. Sci.* **291**, 39 (1991).
10. D. B. Rowley, *Geol. Soc. Am. Bull.* **114**, 927 (2002).
11. R. D. Müller *et al.*, *Science* **319**, 1357 (2008).
12. D. B. Rowley, *J. Geol.* **116**, 587 (2008).
13. H. Elderfield *et al.*, *Earth Planet. Sci. Lett.* **172**, 151 (1999).
14. I thank J. Maclennan, S. Turchyn, and M. Bickle for helpful discussions.

10.1126/science.1186769