Editorial

Directions in the study of ocean chemistry over the Phanerozoic and its links to geologic processes

To study the changes over geologic time in the salts of seawater is to study not just marine chemistry, but the intertwined tales of geologic processes: tectonics, climate, biomineralization, biological evolution, weathering, and sedimentation. For example, hidden in the history of the concentration and isotopic composition of these salts is information about rates of deep sea hydrothermal venting and the weathering of continental rocks (Berner et al., 1983). There are clues concerning the extent to which the equilibrium temperature of the CO_2-regulating silicate weathering cycle can be lowered by the tectonic uplift of mountain belts (Raymo et al., 1988). And, among many other things, there are answers about the impact of evolutionary innovations, such as planktonic lifestyles and biomineralization, on biogeochemical cycles and vice versa (Wilkinson, 1979; Maliva et al., 1989; Stanley and Hardie, 1998; Holland, 2003).

It has long been realized that concentrations of elements in seawater and their isotopic compositions reflect a balance between inputs and outputs of those salts to the sea. Inputs largely come from weathering. Rivers and groundwater deliver dissolved materials like Mg^{2+}, Ca^{2+}, Sr^{2+}, $SO_4^=$, and $Si(OH)_4$ weathered from continental rocks. The weathering of oceanic crust by the circulation of hydrothermal fluids also adds many salts to seawater, but in a different ratio to which they were added from the continents, and, as well, serves as a sink for Mg^{2+} and a few other elements (Elderfield and Schultz, 1996). Output of salts from the ocean more generally occurs in the form of sediments like calcite, aragonite, and opal. In the Phanerozoic these materials have overwhelmingly been produced through biomineralization rather than abiotically as a result of ocean supersaturation.

It is of great interest to accurately reconstruct the chemical composition of the ocean over geologic time and from this unravel the shifting balances between continental weathering, hydrothermal venting, biological productivity, and sedimentation in the sea. While all of these things are interesting enough to understand on their own, there is the additional motivation that all of these processes play a role in setting atmospheric concentrations of CO_2 and, from this, global climate. The weathering of silicate minerals that fuels river inputs of ions to the sea, for example, converts CO_2 into alkalinity (Berner et al., 1983) and is likely to be the regulator responsible for the persistence of generally moderate climate conditions over billions of years of Earth history. Rates of hydrothermal venting, on the other hand, may be proportional to the global rate of CO_2 emission from the mantle (Berner et al., 1983). Calcareous and organic sediments are long-term repositories for carbon and, through subduction, represent a return path for this carbon back to the mantle.

One approach to writing the history of sea salt concentrations has been to model them based on rates of continental weathering, hydrothermal venting, and sediment formation estimated from the geologic record (e.g. MacKenzie and Garrels, 1966; Berner et al., 1983; Wilkinson and Algeo, 1989; Hardie, 1991). Such efforts have long suggested that changes in the

rates of these somewhat interlinked processes are variable enough to drive fluctuations in the composition of seawater and the atmosphere (Sandberg, 1983; Berner et al., 1983; Wilkinson and Algeo, 1989; Hardie, 1996; Wallmann, 2001). In addition, these models recognize the impact of other processes, such as dolomite formation and microbially mediated sulfate reduction, on the major ion composition of seawater and the gas composition of the atmosphere (e.g. Berner et al., 1983; Wilkinson and Algeo, 1989; Petsch and Berner, 1998).

Another approach to the reconstruction of ocean chemistry has been to turn to marine sediments themselves for compelling evidence of fluctuations. The concentrations and relative abundances of salts like Mg^{2+}, Sr^{2+}, and Ca^{2+} are important to the trace element composition and mineralogy of marine carbonates, features which are known to vary over geologic time (Sandberg, 1983; Dickson, 2002; Steuber and Veizer, 2002; Lear et al., 2003). The mineralogy of evaporites (Hardie, 1991) and the composition of fluid inclusions in evaporite minerals (Lowenstein et al., 2001; Horita et al., 2002) of different ages are also thought to be due to shifts in the concentration and relative abundance of the major ions of seawater. Marked shifts in the abundance, distribution, and character of cherts and siliceous microfossils present in the sedimentary record also indicate massive decline in the concentration of silicic acid in seawater over the Phanerozoic (Maliva et al., 1989).

A third approach to the reconstruction of ocean chemistry and its place in global cycles of climate and tectonics has been the analysis of the isotopic composition of marine sediments. There are many different isotope systems in use for this and they operate in different ways to give information about ocean chemistry. To give what is certainly not an exhaustive list, isotopes of elements such as C, Sr, S, and Ca serve to pinpoint times when there was a notable shift in the input or output of these elements from the sea (Richter et al., 1992; Paytan et al., 1998; De La Rocha and DePaolo, 2000; Zachos et al., 2001; Schmitt et al., 2003). O isotopes, by virtue of indicating the waxing and waning of continental ice sheets, indicate whole ocean shifts in salinity (Zachos et al., 2001). B isotopes, by being sensitive to the pH-dependent speciation of dissolved B, potentially yield information about the pH of past ocean waters (Spivack et al., 1993), and give yet another means of estimating the past CO_2 content to the atmosphere (Pearson and Palmer, 2000).

Papers in this special issue on Ocean Chemistry Over the Phanerozoic and its Links to Geologic Processes provide a small sampling of the variety of work on ocean paleochemistry going on at the present day. The most exciting thing about these papers is the way that most of them are broadly integrative, using reconstructions of several factors concurrently and often in association with modelling to look at the nestling between ocean chemistry, productivity, climate, ocean circulation, and tectonics. The papers in the first part of this issue add to our knowledge of the composition of ocean waters over time through new twists on traditional approaches (Miller et al., 2005; Steuber and Rauch, 2005; Thomas and Bralower, 2005). Another set of papers focuses on improving proxies of marine biogeochemical cycling (De La Rocha and Bickle, 2005; Hall et al., 2005). The bulk of the papers in this issue touch on issues of productivity, the dissolved CO_2 and dissolved O_2 content of ocean waters, global climate, and the sedimentary carbon isotope record (Bowman and Bralower, 2005; Katz et al., 2005; Ridgwell, 2005; Winguth and Maier-Reimer, 2005).

In their paper, Steuber and Rauch (2005) present estimates of the Mg/Ca ratio of seawater in the Cretaceous based on the trace element composition of sedimentary calcite. These estimates are part of an exciting new direction in this work (e.g. Steuber, 1999; Dickson, 2002) whereby the samples analyzed are of the shells or tests of organisms, like echinoids or rudist bivalves, that much more closely, and with much less interference from temperature, record seawater Mg/Ca than foraminifera (Dickson, 2002). These new works are also distinguished by their painstaking attention to diagenetic alteration and their rejection of all samples but those with a high likelihood of having retained their original elemental composition.

Miller et al. (2005) couple the O isotopic composition of seawater, as extrapolated from foraminifera, and combine it with estimates of sea-level change in the Late Cretaceous to early Eocene to suggest the existence of transient ice sheets on

Antarctica during this warm interval. The separation of the temperature from the ice volume components of the O-isotope signal has long been a fundamental problem that needs solving and this is not the first time that records of sea level have been applied to sorting it out (Miller et al., 1987). The new feature of this latest work is the application of inverse modelling (backstripping) to remove the signals of subsidence and uplift, and sediment loading from a local record of sea level to bring to light the global glacioeustatic signal.

Thomas and Bralower (2005) have turned the search for ocean chemistry variations somewhat on its ear, searching not for global changes in seawater chemistry but local changes that could be ascribed to a hydrothermal vent plume. Lacking this signal in their sediments, they have concluded that North Atlantic Igneous Province volcanism lacked a significant submarine component.

The middle set of papers in this issue work towards the improvement of isotopic proxies from which changes in ocean chemistry can be reconstructed. The paper by Hall et al. (2005) presents a brief study of Li isotopes in foraminifera, a promising new tracer of silicate weathering and hydrothermal venting (Tomascak, 2004). Herein is presented an estimate of Li isotopic fractionation by one species of planktonic foraminifera based on sediment core samples spanning the last 36 kyr. The paper by De La Rocha and Bickle (2005), through simple box modelling, explores the potential for the silicon isotopic composition of sedimentary opal to track shifts in the balance between silicon inputs and outputs to the ocean on time scales ranging from that of tens of thousands to millions of years.

The concluding set of papers in this special issue tackles questions associated with productivity and changes in the oxygen content of deep waters or the carbon isotopic composition of marine sediments (Bowman and Bralower, 2005; Katz et al., 2005; Ridgwell, 2005; Winguth and Maier-Reimer, 2005). All of these works do so by combining decades worth of measurements and modelling results from the literature with new modelling work and through this produce novel and sophisticated views of ocean paleochemistry and how it fits into the overall framework of climate, tectonics, and biological evolution over the Phanerozoic.

The work presented by Winguth and Maier-Reimer (2005) attempts to recreate marine conditions at the Permo-Triassic boundary in order to test various hypotheses relating to the mass extinction that occurs at this point (Erwin, 1994). Their results indicate that the deep sea was well ventilated at this time and that the occurrence of anoxic sedimentary deposits at this boundary requires a reorganization of the carbon cycle and a strengthening of the biological pump.

Bowman and Bralower (2005) tackle the Cenomanian–Turonian boundary in their contribution to this volume. Associated with this boundary is an ocean anoxic event (OAE) and an excursion in the carbon isotopic composition of marine carbonates and also possibly of sedimentary organic matter. By comparing the records of total organic carbon in the sediments with the records of carbon isotopes, Bowman and Bralower (2005) attempt to identify the cause in the OAE: an increase in the burial of organic matter, an increase in volcanism, or massive methane hydrate dissociation.

Katz et al. (2005) present a very notable interpretation of the carbon isotopic composition of bulk carbonates and sedimentary organic carbon over the last 205 million years. Their records indicate the existence of an increasing trend in the carbon isotopic composition of marine dissolved inorganic carbon from the Jurassic to the middle Miocene. They ascribe the long-term trend to a steady increase in the fraction of carbon being removed from the system as organic carbon versus carbonate carbon, an increase which is tied to the increase in continental margins that followed the break-up of Pangea. This increase in organic carbon burial would then drive a drop in atmospheric CO_2 over the Cenozoic, itself a long interval of global cooling.

Ridgwell (2005) also tackles big questions about the long-term carbon cycle. He uses estimates of sea level, atmospheric CO_2, Ca^{2+} concentrations, and other parameters from a body of works to model changes in the pH and saturation state of seawater with respect to calcium carbonate over the Phanerozoic. This is done for two different modes of deposition of calcium carbonate: one, prior to the emergence of planktonic Ca biomineralizing organisms, where deposition overwhelmingly occurs on shallow shelves and seas, and the other where the

locus of deposition is the deep sea. The saturation state of the surface ocean appears to be much more tightly regulated in a world where the bulk of the $CaCO_3$ accumulation occurs in the deep sea.

References

Berner, R.A., Lasaga, A.C., Garrels, R.M., 1983. The carbonate–silicate geochemical cycle and its effect on atmospheric carbon dioxide. Am. J. Sci. 283, 641–683.

Bowman, A.R., Bralower, T.J., 2005. Paleoceanographic significance of high resolution carbon isotope records across the CenomanianTuronian boundary in the Western Interior and New Jersey Coastal Plain, USA. Mar. Geol. 217, 305–321 (this issue).

De La Rocha, C.L., Bickle, M.J., 2005. Sensitivity of silicon isotopes to whole-ocean changes in the silica cycle. Mar. Geol. 217, 267–282 (this issue).

De La Rocha, C.L., DePaolo, D.J., 2000. Isotopic evidence for variations in the marine calcium cycle over the Cenozoic. Science 289, 1176–1178.

Dickson, J.A.D., 2002. Fossil echinoderms as monitor of the Mg/Ca ratio of Phanerozoic oceans. Science 298, 1222–1224.

Elderfield, H., Schultz, A., 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. Annu. Rev. Earth Planet. Sci. 24, 191–224.

Erwin, D.H., 1994. The Permo-Triassic extinction. Nature 367, 231–236.

Hall, J.M., Chan, L.-H., McDonough, W.F., Turekian, K.K., 2005. Determination of the lithium isotopic composition of planktonic foraminifera and its application as a paleo-seawater proxy. Mar. Geol. 217, 255–265 (this issue).

Hardie, L.A., 1991. On the significance of evaporites. Annu. Rev. Earth Planet. Sci. 19, 131–168.

Hardie, L.A., 1996. Secular variation in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y. Geology 24, 279–283.

Holland, H.D., 2003. The geologic history of seawater. In: Holland, H.D., Turekian, K.K., Elderfield, H. (Eds.), Treatise on Geochemistry, vol. 6. Elsevier, Amsterdam, pp. 583–625.

Horita, J., Zimmerman, H., Holland, H.D., 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporites. Geochim. Cosmochim. Acta 66, 3733–3756.

Katz, M.E., Wright, J.D., Miller, K.G., Cramer, B.S., Fennel, K., Falkowski, P.G., 2005. Biological overprint of the geological calcium cycle. Mar. Geol. 217, 323–338 (this issue).

Lear, C.H., Elderfield, H., Wilson, P.A., 2003. A Cenozoic seawater Sr/Ca record from benthic foraminiferal calcite and its application in determining global weathering fluxes. Earth Planet. Sci. Lett. 208, 69–84.

Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A., Demicco, R.V., 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions in salt deposits. Science 294, 1086–1088.

MacKenzie, F.T., Garrels, R.M., 1966. Chemical mass balance between rivers and oceans. Am. J. Sci. 264, 507–525.

Maliva, R.G., Knoll, A.A., Siever, R., 1989. Secular change in chert distribution: a reflection of evolving biological participation in the silica cycle. Palaios 4, 519–532.

Miller, K.G., Fairbanks, R.G., Mountain, G.S., 1987. Tertiary oxygen isotope synthesis, sea level history, and continental margin erosion. Paleoceanography 2, 1–19.

Miller, K.G., Wright, J.D., Browning, J.V., 2005. Visions of ice sheets in a greenhouse world. Mar. Geol. 217, 215–231 (this issue).

Paytan, A., Kastner, M., Campbell, D., Thiemens, M.H., 1998. Sulfur isotopic composition of Cenozoic seawater sulfate. Science 282, 1459–1462.

Pearson, P.N., Palmer, M.R., 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. Nature 406, 695–699.

Petsch, S.T., Berner, B.A., 1998. Coupling the geochemical cycles of C, P, Fe, and S: the effect on atmospheric O_2 and the isotopic records of carbon and sulfur. Am. J. Sci. 298, 246–262.

Raymo, M.E., Ruddiman, W.F., Froelich, P.N., 1988. Influence of late Cenozoic mountain building on ocean geochemical cycles. Geology 16, 649–653.

Richter, F.M., Rowley, D.B., DePaolo, D.J., 1992. Sr isotope evolution of seawater: the role of tectonics. Earth Planet. Sci. Lett. 109, 11–23.

Ridgwell, A., 2005. A mid Mesozoic revolution in the regulation of ocean chemistry. Mar. Geol. 217, 339–357 (this issue).

Sandberg, P.A., 1983. An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy. Nature 305, 19–22.

Schmitt, A.-D., Stille, P., Vennemann, T., 2003. Variations of the $^{44}Ca/^{40}Ca$ ratio in seawater during the past 24 million years: evidence from $\delta^{44}Ca$ and $\delta^{18}O$ values of Miocene phosphates. Geochim. Cosmochim. Acta 67, 2607–2614.

Spivack, A.J., You, C.-F., Smith, H.J., 1993. Foraminifera boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. Nature 363, 149–151.

Stanley, S.M., Hardie, L.A., 1998. Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. Palaeogeogr. Palaeoclimatol. Palaeoecol. 144, 3–19.

Steuber, T., 1999. Isotopic and chemical intra-shell variations in low-Mg calcite of rudist bivalves (Mollusca: Hippuritacea)—disequilibrium fractionations and Late Cretaceous seasonality. Int. J. Earth Sci. 88, 551–570.

Steuber, T., Rauch, M., 2005. Evolution of the Mg/Ca ratio of Cretaceous seawater: implications from the composition of biological low-Mg calcite. Mar. Geol. 217, 199–213 (this issue).

Steuber, T., Veizer, J., 2002. Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation. Geology 30, 1123–1126.

Thomas, D.J., Bralower, T.J., 2005. Sedimentary trace element constraints on the role of North Atlantic igneous province

volcanism in late Paleoceneearly Eocene environmental change. Mar. Geol. 217, 233–254 (this issue).

Tomascak, P.B., 2004. Developments in the understanding and application of lithium isotopes in the earth and planetary sciences. Rev. Mineral. Geochem. 55, 153–195.

Wallmann, K., 2001. Controls on the Cretaceous and Cenozoic evolution of seawater composition, atmospheric CO_2, and climate. Geochim. Cosmochim. Acta 65, 3005–3025.

Wilkinson, B.H., 1979. Biomineralization, paleoceanography, and the evolution of calcareous marine organisms. Geology 7, 524–527.

Wilkinson, B.H., Algeo, T.J., 1989. Sedimentary carbonate record of calcium–magnesium cycling. Am. J. Sci. 289, 1158–1194.

Winguth, A.E.M., Maier-Reimer, E., 2005. Causes of the marine productivity and oxygen changes associated with the Permian-Triassic boundary: a reevaluation with ocean general circulation models. Mar. Geol. 217, 283–304 (this issue).

Zachos, J., Pagani, M., Sloan, L., Thomas, E., Billups, K., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. Science 292, 686–693.

Christina L. De La Rocha
Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK
E-mail addresses: christina00@esc.cam.ac.uk; crocha@awi-bremerhaven.de.
Corresponding author. Current address: Alfred-Wegner-Institut für Polar und Meeresforschung, Columbusstrasse, 257568 Bremerhaven, Germany. Tel.: +49 471 4831 1040; fax: +49 471 4831 1149.

Adina Paytan
Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA
E-mail address: apaytan@pangea.stanford.edu.
Tel.: +1 650 724 4073; fax: +1 650 725 0979.