Commentary

Biological skeletal carbonate records changes in major-ion chemistry of paleo-oceans

Isabel P. Montañez*

Department of Geology, University of California, Davis, CA 95616

The history of the chemical evolution of seawater is of first-order importance given its fundamental role in a broad spectrum of geologic, geochemical, and paleontologic phenomena. A growing body of evidence for a more dynamic evolution of seawater chemistry than previously considered has been building over the past two decades. Central to this body of evidence are oscillating global trends, on a 100- to 200-million-year time scale, in the mineralogy of marine carbonate cements (1), late-stage salts in marine evaporites (2), and calcifying organisms that are interpreted to record secular change in seawater chemistry (3, 4). The degree to which the basic seawater signal has varied over the past 550 million years is, however, an issue that has been strongly debated in the literature (e.g., refs. 5–9). This primarily reflects the arguably equivocal nature of the evidence used to infer secular changes in seawater chemistry and the mechanisms for driving that change. Reconstructions of seawater chemical composition based on marine inorganic precipitate and fossil proxy records may be compromised by the influence of various environmental factors, and by the geochemical insults of diagenesis on their mineralogy and chemical composition (5, 10, 11). Complimentary modeling efforts that focus on constraining the mechanism(s) for driving substantial chemical change in seawater are challenged by the uncertainties associated with defining model input parameters (2, 5, 9).

In a recent issue of PNAS, Stanley *et al.* (12) provide compelling, experimentally derived evidence that the skeletal carbonate of biologically simple marine organisms, analogous to inorganic marine carbonate, has the potential to record faithfully changes in the major-ion chemistry of paleo-oceans. Their results, in concert with recently published fluid in-

clusion evidence for secular change in the major-ion chemistry of seawater over the last 550 million years (13), argue strongly for the concurrent trends in nonskeletal and skeletal chemical precipitates as a testament of the magnitude to which the basic seawater signal can be changed. These results also have far-reaching implications for the role of seawater chemistry in influencing the biological composition of reefs and the evolutionary changes in biomineralization through time.

During the Phanerozoic, there have been two periods of aragonite-inhibiting episodes (referred to as "calcite seas") alternating with three aragonite-facilitating episodes ("aragonite seas") (Fig. 1). The resulting mineral trend is synchronous with long-term sea-floor spreading rates, eustasy, plutonic emplacement, and volcanism (1), as well as climate cycles (14), leading to the long-held consensus that secular changes in marine nonskeletal carbonate mineralogy are mechanistically linked to these processes, and thus ultimately a function of plate tectonics (refs. 9, 15, and 16, and references within). It has been suggested that the specific link is the Mg/Ca molar ratio of seawater (2, 17, 18). This strongly debated hypothesis is, in part, founded in the experimental evidence for the significant influence of the solution Mg/Ca molar ratio on carbonate–mineral precipitation (8, †). In aqueous Cl^- solutions typical of modern tropical seawater, low-Mg calcite (<4 mol % $MgCO_3$) precipitates at Mg/Ca ratios of ≤1, whereas high-Mg calcite (>4 mol % $MgCO_3$) precipitates at ratios above 1 and up to the present-day value of 5.2. Aragonite, an orthorhombic polymorph of $CaCO_3$, precipitates along with high-Mg calcite at solution Mg/Ca ratios above 1.5 to 2. The mole % $MgCO_3$ incorporated in high-Mg calcite increases linearly with both ambient Mg/Ca molar ratio and temperature (8, 19, †).

A secular trend in marine potash evaporites (salt deposits characterized by potassium chloride and/or potassium sulfate minerals) that is in-phase with that of Phanerozoic nonskeletal carbonates (Fig. 1) may provide further support for the role of seawater Mg/Ca ratio as the primary influence on the mineralogy and composition of these marine chemical precipitates (2). This reflects that changes in other environmental parameters that can control the carbonate mineralogy, which precipitates from seawater, such as pCO_2, $[CO_3^{2-}]$, and temperature (8, 20, 21), should have little or no effect on the mineralogy of marine evaporites. Variations in the rate of seawater cycling through midocean ridges in response to changes in the production of oceanic crust have been proposed as a viable mechanism for driving secular variation in the seawater Mg/Ca ratio (2, 22). In this model, it is suggested that even small variations (<25%) in the hydrothermal brine flux at midocean ridges may have a profound effect on the composition of seawater. Modeled changes in the seawater Mg/Ca ratio (Fig. 1) are within the range of experimentally derived molar ratios (1 to 5.5) shown to influence carbonate mineralogy, and are synchronous with periods of aragonite and calcite seas.

The hypothesis that seawater Mg/Ca ratio has been the primary influence on the mineralogy of marine chemical precipitates is, however, controversial given that it requires substantial change in the Mg/Ca ratio of paleo-oceans, for which there is no direct evidence. It has been argued that the effect of change in sea-floor spreading rate on the major-ion chemistry of seawater, based on reconstructions of these rates from the geologic record, may be of significantly lower magnitude than necessary to impart changes in the mineralogy of the scale observed in the Phanerozoic (5, 7). Moreover, mineral
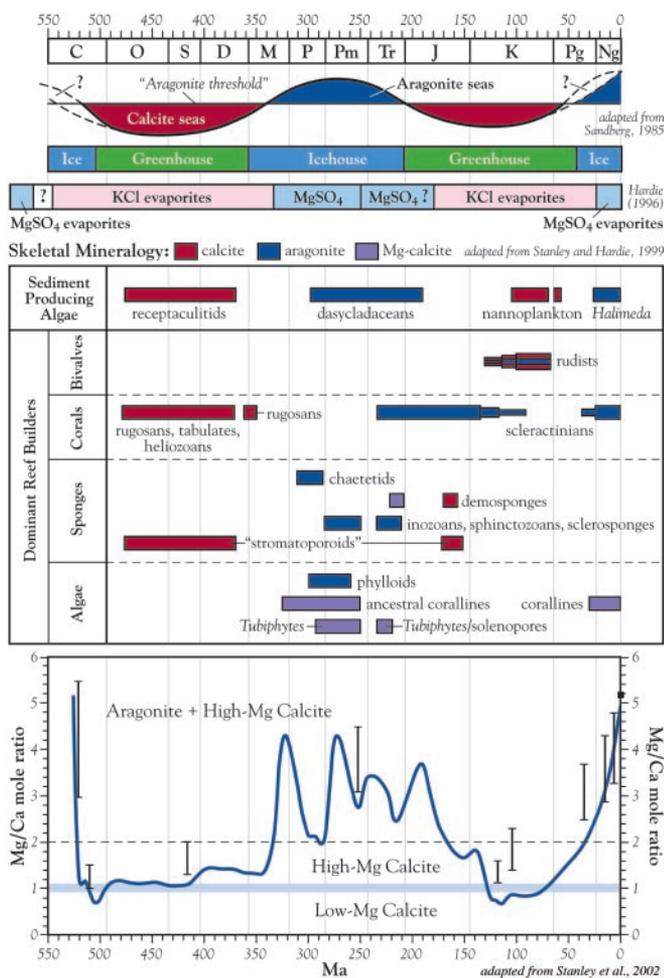

Fig. 1. Temporal relationship between secular fluctuations in nonskeletal carbonate (aragonite and calcite seas) (1), climate cycles (14), late-stage marine potash evaporites (2), and the skeletal mineralogy of major sediment producers and reef builders (3, 4) throughout the Phanerozoic. Also shown is predicted secular variation in seawater Mg/Ca molar ratios based on changes in the hydrothermal brine flux at midocean ridges (blue line) (2). Measured and estimated Mg/Ca mole ratios of paleo-seawater derived from fluid-inclusions in marine halites (vertical bars) are superimposed on the predicted seawater Mg/Ca trend (13). Note that minor adjustments were made to account for differences in time-scales used between references.

organisms as an environmental dipstick of seawater Mg/Ca ratios.

Recently, Lowenstein *et al.* (13) documented systematic changes in the chemistry of evaporated seawater occluded within primary fluid inclusions of Phanerozoic marine halites (i.e., late-stage evaporites), thus providing the most definitive evidence to date for substantial change in the major-ion chemistry of seawater over the past 550 million years. In particular, the empirically measured and modeled Mg/Ca ratios overlap the range in ratios that is predicted by models of change in hydrothermal brine flux driven by changes in ocean crust production (Fig. 1). Moreover, these results indicate that the seawater Mg/Ca ratio likely fluctuated throughout the late Precambrian and Phanerozoic within the range (1 to >4) necessary to impose secular variations in the mineralogy of marine chemical precipitates. This finding appears to be corroborated by the in-phase relationship between their reported seawater Mg/Ca ratios (and Na^+ contents) and the observed fluctuations in the primary mineralogy of marine inorganic chemical precipitates and skeletal carbonates (Fig. 1).

Stanley *et al.* (12) build on this evidence to test whether the fingerprint of systematic fluctuation in paleo-seawater Mg/Ca ratios is recorded in the skeletal mineralogy and Mg content of calcifying marine organisms. They document through the growth of extant coralline algae in synthetic seawater, over a range of Mg/Ca molar ratios, that the ambient Mg/Ca ratio influences the skeletal mineralogy of some simple organisms, thus mimicking the pattern for nonskeletal precipitation. Significantly, their results indicate that the genus *Amphiroa*, which in today's aragonitic oceans produces a high-Mg calcite skeleton, will precipitate low-Mg calcite when grown in ambient seawater with a Late Cretaceous Mg/Ca ratio of 1 to 2.3. A Mg/Ca ratio of 1 has been shown experimentally to induce precipitation of low-Mg calcite over other carbonate polymorphs (8, †).

Three species of algae were grown in artificial seawater differing only in their Mg/Ca molar ratios (from 1 to 5.8). All three species incorporated Mg contents in proportion to the ambient Mg/Ca ratio, thus indicating that their calcification was induced from seawater simply through their photosynthetic consumption of CO_2. Intriguingly, algae that were initially grown in a solution with a modern seawater Mg/Ca ratio or greater (5.8), and subsequently introduced to a solution with an ambient Mg/Ca molar ratio of 2.5, incorporated progressively less Mg within several days until stabilizing at percentages close to those produced by nonskeletal precipitation. The lack of aragonite

proxies of inferred major changes in seawater Mg/Ca ratios may record the modification of seawater by basinal- to global-scale processes, such as the dolomitization of large expansive carbonate platforms during periods of high sea level, rather than secular variation in the basic seawater signal (23).

In the late 1990s, Stanley and Hardie (3, 4) recognized secular fluctuations in the skeletal mineralogy of anatomically simple organisms such as algae, sponges and corals. Their observations indicate that in calcite seas, reefs were dominated by calcitic corals and stromatoporoids, whereas aragonitic sponges, corals and algae, as well as high-Mg calcitic red algae, were the major reef builders in aragonite seas (Fig. 1). Aragonitic scleractinian corals and high-Mg calcitic coralline algae dominate in today's aragonite sea. The concurrence

in this skeletal carbonate trend with that defined by nonskeletal carbonates (and evaporites) led them to propose that the influence of seawater Mg/Ca ratio on carbonate-mineral precipitation could be extended to the skeletal mineralogy of dominant reef-builders and sediment producers through time. If this hypothesis proves to be correct, then it has significant paleoecologic and paleobiologic implications. Previous workers, however, have attributed secular change in the skeletal mineralogy of microfossils and other anatomically simple taxa to the complex interplay of several physicochemical factors, as well as to possible vital or kinetic effects (refs. 15 and 16, and references within). This finding implies that there could be significant uncertainty associated with using the skeletal mineralogy and composition of fossil biologically simple

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precipitation argues for an organic template specificity for calcite (see ref. 24).

Thus, it seems likely that the influence of seawater chemistry on the skeletal secretion of biologically simple organisms such as algae, sponges, corals, and bryozoans is a first-order influence on the observed Phanerozoic trends in biomineralization, marine carbonate sedimentation, and reef composition (3, 4) (Fig. 1). The skeletons of morphologically simple taxa that consist of high-Mg calcite today, probably formed as low-Mg calcite in calcite seas. Stanley *et al.* (12) suggest that the Mg-content of skeletal calcite of even anatomically more complex taxa, such as echinoderms and calcitic bryozoa, may have been lower than present-day equivalents because of the influence of Mg/Ca ratio on carbonate mineral precipitation. It now seems likely that the driving force for evolutionary changes in the biomineralization of cheilostome bryozoans and calcareous sponges was secular change in seawater Mg/Ca ratios (3, 4, 25). The enigmatic evolutionary trend in progressive reduction of calcification (i.e., less robust morphologies or progressively less shell volume) of calcareous nannoplankton over the past 50 million years (26) appears to be a consequence of the rapidly increasing Mg/Ca ratios during the Cenozoic.

The degree of ecologic stability of reef building organisms and, thus, the biologic composition of reefs through time may be a fickle function of the Mg/Ca ratio of paleo-seawater through its influence on skeletal mineralogy (3, 4). Biologically simple taxa have dominated reefs throughout Phanerozoic time, given that their adaptive growth modes have provided them with a competitive edge in the reef ecosystem. However, the inability of major reef builders in the Phanerozoic to remodel their skeletons through resorption during their ontogeny may have made them susceptible to the whims of fluctuating seawater chemistry. Changes in their rates of calcification (i.e., hypercalcification during periods of favorable Mg/Ca ratio and reduced skeletal productivity during unfavorable periods), and, thus, the rise and demise of Phanerozoic reef builders was guided, at least in part, by secular changes in the major-ion content of the paleo-oceans. This model may provide an explanation for two coupled but puzzling phenomena (4, 27, 28). The first is the decline in aragonitic corals as reef builders in Late Cretaceous calcite seas coincident with the rise of predominantly low-Mg calcitic rudists. The second is the failure of early Cenozoic aragonitic corals to have reestablished themselves as builders of massive reefs with the disappearance of rudists from the reef ecologic niche despite considerable diversity in scleractinian corals at that time.

The influence of fluctuating seawater Mg/Ca ratios on the carbonate productivity of major sediment producers (e.g., calcareous nannoplankton for deep-water chalks) and the biologic composition of shallow-water reef builders has major implications for global C cycling and atmospheric pCO$_2$ levels. This reflects the potential of seawater Mg/Ca ratios to impart significant changes in the partitioning of skeletal carbonate of varying mineralogy into shallow- and deep-water reservoirs. Lastly, the change in seawater chemistry over geologic time implied by the recent results of the studies of Stanley *et al.* (12) and Lowenstein *et al.* (13) is substantially greater than previously contended. This necessitates a reconsideration of our current working view of the geochemical cycles of Ca and Mg. There is little doubt that the debate over the nature of the chemical evolution of seawater will continue but these studies develop an argument of unprecedented strength for a chemically dynamic ocean over the past half billion years of Earth history.

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