COMMENTARY

Organic interfaces enhance strontium content of marine barite

Adam F. Wallace^{a,1}

The history of life and environmental change on Earth is told largely by physical and chemical indicators hosted within the sedimentary rock record. Barite (BaSO_4) is one of the few minerals that is known to crystallize from seawater, and due to its relatively high chemical resiliency in nature, its trace element and isotope contents are frequently taken to reflect the composition of its parental fluid. Consequently, barite is often utilized to place constraints on the compositions of ancient waters in a variety of settings (e.g., bulk seawater, hydrothermal brines, sedimentary pore waters, and cold-water seeps) (1). The low barium concentrations that are prevalent in modern seas generally preclude BaSO_4 mineralization (2); however, barite is known to form in association with suspended organic matter in open waters (3) and is a nearly ubiquitous, albeit minor, component of deep-water marine sediments, particularly underlying regions characterized by high biological activity (4). By dint of this correlation, the abundance of barite in sedimentary cores likely reflects the extent of biological productivity in ancient environments (5). The mechanisms by which organic matter promotes barite formation are not fully appreciated; however, it is clear that the presence of living organisms and/or decaying organic matter can establish a locally favorable environment for barite nucleation and growth. This local environment may also be necessary to explain the formation of strontium-enriched marine barites, which are expected to be less stable than more barium-rich compositions in seawater (2). In PNAS, Deng et al. (6) advance the understanding of marine barite formation by investigating the competitive adsorption of strontium and barium on organic interfaces and the influence of surface-directed nucleation on the strontium content of synthetic barite.

Strontium isotopes are not significantly affected by biological cycling (7); therefore, measured isotope ratios (i.e., $^{87}\text{Sr}/^{86}\text{Sr}$) tend to reflect the isotopic composition of the original geologic source. As a radiogenic isotope, the abundance of ^{87}Sr depends upon the decomposition of ^{87}Rb , which is relatively depleted in the upper mantle relative to the continental crust (8).

Fig. 1. Adsorption of ions at the organic–water interface. As barium (red) and strontium (green) compete for adsorption sites on the negatively charged organic substrate (Left), the local cation and sulfate (yellow) concentrations exceed the solubility threshold of a strontium-rich barite that is not favored to form from the bulk undersaturated solution (i.e., where the barite saturation index, SI_{Baite} , is <0) (Right).

Consequently, $^{87}\text{Sr}/^{86}\text{Sr}$ may be used to distinguish between terrestrial and mantle-derived sources of strontium (i.e., to monitor the influx of material derived from continental weathering relative to hydrothermal activity on the seafloor). Due to the long residence time of strontium in the ocean (≥ 4 million years) compared with the mixing time ($\sim 10^3$ y), $^{87}\text{Sr}/^{86}\text{Sr}$ values are relatively consistent throughout the whole ocean (9), and strontium isotope ratios obtained from marine barite likely reflect the bulk marine signal at the time of crystallization. Barite is sometimes susceptible to post-depositional processes that can alter its composition in sedimentary environments. However, the barite- and carbonate-derived marine strontium isotope curves remain highly correlated in sediments that date to at least 35 million years B.P. (10), which indicates that strontium isotope ratios in marine barites are not at all influenced by the crystallization process that occurs in nature.

^aDepartment of Earth Sciences, University of Delaware, Newark, DE 19716

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¹Email: afw@udel.edu.

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Deng et al. (6) found that strontium and barium preferentially adsorb to organic substrates (terminated by sulfhydryl and carboxyl moieties) at levels that locally exceed the solubility limit of $(\text{Ba}_x, \text{Sr}_{1-x})\text{SO}_4$, even when the bulk solution is undersaturated with respect to both barite and celestite (SrSO_4) (Fig. 1). The resulting crystallites were also found to incorporate more strontium in their structures than those grown from identical solutions without organics present. Fortunately, such a mechanism, if it is active in nature, should have no effect on the barite paleoproductivity proxy or the value of the strontium isotope ratio. However, Deng et al.'s findings pose a great challenge for efforts to reconstruct absolute strontium concentrations from barite Sr/Ba ratios (11), which may depend more on the nature of the characteristics of the organic substrate than on the composition of the bulk solution.

The compositions of naturally occurring phases in the barite–celestite series tend not to deviate substantially from those of the series end members (12). For instance, the degree of strontium substitution in marine barite is typically on the order of ~1 to 4 mol % (2, 11, 13). Since intermediate compositions are rarely observed, some speculate that the solid solution may not be continuous. Unfortunately, experimental difficulties (2) and contradictory theoretical results (14, 15) have thus far preempted an accurate assessment of miscibility in the barite–celestite series. Consistent with expectations, Deng et al. (6) observed almost no strontium substitution in their homogeneous crystallization experiments. However, the results of their heterogeneous crystallization experiments were quite unexpected: They found that the compositions of the barite grains that formed in association with the organic film were substantially altered, with 20 to 99% of their barium content replaced by strontium. Through a particularly apt usage of a kinetic model of solid-solution nucleation previously developed by Pina and Putnis (16), Deng et al. (6) show that the strontium enrichment they observed in

the heterogeneous precipitates is consistent with a transition from a growth-dominated regime in the bulk fluid to a nucleation-dominated regime at the organic interface.

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It is notable, that the strontium content of the heterogeneous precipitates exceeds that of the homogenous precipitates, even when the interfacial abundance of strontium relative to barium is less than in the bulk solution. Presumably then, strontium plays some as yet unappreciated role in heterogeneous barite nucleation that it does not play in homogeneous solution. In modern seas, sulfate and strontium concentrations can exceed that of barium by as much as ~1,000 times; therefore, the main role of water-suspended organics in marine barite formation is in the initial accumulation of barium. While the nature of the organic materials that drive this process in nature are still poorly constrained, recent literature has begun to implicate bacteria that mediate phytoplankton decay (17, 18).

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