

Foraminiferal lithium as a paleoceanographic proxy

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Lithium in foraminiferal carbonate shows great potential as an indicator of environmental change over both long and short timescales. The dissolved lithium concentration and isotopic composition of seawater is controlled by rates of hydrothermal interaction with oceanic crust and continental weathering/riverine input, assuming the fractionation factor for the removal processes has remained constant. The lithium isotopic composition of planktic foraminifera (*Orbulina universa*, *Globigerinoides sacculifer*, *Globorotalia menardii*, and *Globorotalia truncatulinoides*) resembles seawater, such that the isotopic fractionation from the precipitation of foraminiferal calcite appears to be minimal. Therefore, differences in foraminiferal $\delta^7\text{Li}$ can reflect fluctuations in hydrothermal and continental weathering rates over million year timescales. For example, data from the mid-Cretaceous (122-98 Ma) shows a decrease in foraminiferal $\delta^7\text{Li}$, suggesting that hydrothermal activity across the Aptian-Albian boundary increased and altered seawater chemistry. This interpretation is supported by changes in microfossil assemblages, a $^{87}\text{Sr}/^{86}\text{Sr}$ minimum, and a significant decrease in foraminiferal Mg/Ca.

Foraminiferal Li/Ca ratios across glacial/interglacial cycles have been invoked as a proxy for changes in seawater carbonate ion concentration. Li/Ca offers two advantages over other trace element proxies in this regard: First, lithium is conservative in the ocean in that it does not significantly interact with the biological cycle. Therefore, lithium incorporation is not dominated by changes in nutrients or biological productivity. Further, lithium has a relatively long residence time compared to bioactive elements such as zinc. As such, short-term Li/Ca records are anticipated to change in response to paleoenvironmental conditions rather than ocean lithium concentrations. On longer time scales (over millions of years) foraminiferal Li/Ca can provide a record of secular changes in seawater lithium concentration. Culturing studies are currently underway to isolate the influence of carbonate ion concentration and other growth conditions on foraminiferal Li/Ca incorporation.

New insight into the utility of carbonate-associated sulfate

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Carbonate-associated sulfate (CAS) occurs at ppm levels in many modern and ancient limestones and dolostones. There is a growing body of evidence confirming that coeval seawater sulfate-S isotope relationships are faithfully preserved in CAS. More recently, careful acid extractions have yielded CAS also suitable for oxygen isotope analysis. For example, modern muds in Florida Bay record the oxygen isotope composition of overlying seawater sulfate, even in settings of pronounced diagenetic sulfate reduction and calcium carbonate precipitation. Although we are careful to use buffers to minimize pH-dependent isotopic exchange, we are exploring the full sensitivity of oxygen isotopes to the CAS procedure. Through these oxygen analyses, we hope to uniquely capture the sources of sulfate to the early ocean as continental weathering fluxes and seawater sulfate concentrations increased with increasing biospheric oxygenation. Oxygen in sulfate provides a unique window on the environments of sulfide oxidation and the internal biogeochemical cycling of S once delivered to the ocean.

CAS concentrations vary dramatically in modern and ancient carbonates, but Precambrian samples are consistently depleted relative to Phanerozoic counterparts. Rather than being entirely a product of diagenetic resetting, our results suggest that primary trends, if not absolute values, are preserved in the concentration data. Nevertheless, the coralline Pleistocene Key Largo Limestone reveals concentrations that decrease by almost an order of magnitude with transformation of aragonite to calcite under meteoric conditions, highlighting the caution necessary in any interpretation of CAS concentrations. Not surprisingly, the S isotope data are buffered to near-seawater values across this transition. We are currently exploring the effects of modern dolomitization, although past comparisons of interbedded Proterozoic gypsum and dolomite suggest that S isotope integrity can be preserved at least during early dolomitization. We are also now able to measure low CAS concentrations via ion chromatography following near-complete removal of the interfering chloride matrix. Most recently, our CAS analyses across pronounced C isotope excursions in the Paleozoic are revealing patterns of rapid isotopic variability previously described only from the Proterozoic.