Seawater calcium isotopes from marine barite: A potential record of carbonate deposition in the oceans

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Carbonate deposition and dissolution significantly affect oceanic alkalinity, atmospheric CO_2 and ultimately Earth's climate. Despite over a century's worth of research on various aspects of the carbonate system, we are just beginning to understand the complexity of the system and elucidate the feedbacks among the processes that control it. The biological precipitation of calcium carbonate largely controls the calcium (Ca) isotope ratio in seawater as a result of the discrimination against heavy isotopes associated with this process. This isotopic fractionation causes seawater to be enriched in the heavier isotopes of Ca relative to its input sources to the ocean, primarily terrigenous and hydrothermal. Reconstructing the seawater Ca isotope ratio over time could be used to quantify the fluctuations in the amount of calcium carbonate deposited in the oceans at any given time assuming some knowledge of the isotopic composition of the sources and sinks.

Previously published paleo-seawater Ca isotopic records used bulk marine carbonates, select species of foraminifera, and phosphorites as their source for reconstruction of seawater Ca isotopic composition. However, multiple factors (temperature, precipitation rate, species-specific vital effects and diagenetic alteration) affect the Ca isotope ratio in each of these phases and its preservation of the seawater signal, thus results are complicated to interpret.

We present Ca isotope data from marine barite, a phase extracted from marine sediments. Barite forms inorganically in the water column and is not directly associated with specific organisms. Assuming that marine barite forms in isotopic equilibrium with contemporaneous seawater and that Ca is incorporated into its crystal structure, it should record the fluctuations in the $\delta^{44}Ca$ of seawater. Preliminary results from coretop samples indicate marine barite does form in isotopic equilibrium with contemporaneous seawater with an equilibrium fractionation factor larger than that interpreted from precipitation experiments for inorganic calcite. When used in conjunction with other phases, marine barite may eliminate complications inherent in previously published data and result in a more coherent paleo-seawater curve.

Zinc isotope variations in phytoplankton and seawater

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The distribution of Zn in the ocean is largely controlled by biological uptake and remineralization, being drawn down from several nanomolar concentrations in the deep ocean to picomolar concentrations in the surface ocean. Zn isotopes may record this biological activity based on the preferential uptake of lighter Zn isotopes by phytoplankton. We have investigated the Zn isotope composition of modern seawater and plankton tows (Fig. 1), and studied Zn isotope fractionation by phytoplankton in culture, to gain a better understanding of how Zn isotopes may be used to trace biological processes in both the modern and ancient oceans.

Sample type/location	$\delta^{66}Zn$ (‰)
Seawater	
Northwest Pacific	+.46
Plankton Tows	
Western S. Atlantic	+0.17 to +0.32
Central N. Pacific	+.44
Northwest Pacific	-0.22 to -0.02
Bering Sea	-0.08 to +0.00
Alaskan Shelf	-0.44 to -0.39

Figure 1: The isotopic compositions of natural seawater and plankton tows.

Isotope measurements were made on an IsoProbe multicollector ICP-MS, with analytical precision between 0.02 and 0.04‰. Seawater was collected from the Northwest Pacific and Zn was extracted by co-precipitation with $Mg(OH)_2$. Our measured value is similar to values measured for continental materials. In-situ plankton were collected by trace metal clean plankton tows from both the Atlantic and Pacific Oceans. Our samples show a range of nearly one permil between the heaviest and lightest plankton tows, which we interpret as evidence of fractionation during biological uptake. The diatom *T. pseudonana* grown in culture was also observed to fractionate Zn, preferentially taking up lighter Zn isotopes with an $\varepsilon = +0.2$ to $+0.4$ ‰.

Additional seawater and plankton tow samples are being measured in order to better understand the distribution of Zn isotopes in the oceans. Addition species of marine phytoplankton are being studied to compare the isotope effects associated with biological uptake.