

## $\delta^{44}\text{Ca}$ evolution during water-rock interaction in a carbonate aquifer

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To improve understanding of Ca isotope transport during water-rock interaction on the continents, we measured  $\delta^{44}\text{Ca}$  values along a 236 km flow path in the Madison aquifer, South Dakota, where fluids have chemically evolved according to dolomite and anhydrite dissolution, calcite precipitation, and Ca-for-Na ion-exchange over a timescale spanning ~15 kyr. We use a reactive transport model that employs rate data constrained from major ion mass-balances to evaluate the extent to which calcite precipitation and ion-exchange fractionate Ca isotopes. Elevated  $\delta^{44}\text{Ca}$  values during the initial and final stages of water transport may result from calcite precipitation under supersaturated conditions and Ca-for-Na ion-exchange, respectively. However, for the bulk of the flow path,  $\delta^{44}\text{Ca}$  values evolve by mixing between dolomite and anhydrite dissolution, with no fractionation during calcite precipitation under saturated conditions. We attribute the absence of Ca isotope fractionation to the long timescale of water-rock interaction and the slow rate of calcite precipitation, which have enabled fluids to chemically and isotopically equilibrate with calcite. We therefore conclude that the equilibrium Ca isotope fractionation factor between calcite and water ( $\Delta_{\text{cal-w}}$ ) is very close to zero. We further reason that instances of  $^{44}\text{Ca}$  enrichment attributed to calcite precipitation must stem from kinetic isotope effects. To the extent that the Madison aquifer typifies other groundwater systems, our study suggests that groundwater  $\delta^{44}\text{Ca}$  values can be modelled according to simple mixing theory, without the need to invoke isotope discrimination during calcite precipitation. We suggest that groundwater may play an important role in transmitting the pristine isotopic signature of Ca mineral weathering to the oceans, by way of surface-groundwater interactions in tributary networks of large rivers.

## Diatom $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , and C/N since the Last Glacial maximum in the Southern Ocean: Evidence for regional and ecological influences

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The carbon and nitrogen isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and C/N ratio of diatom-bound organic matter is commonly used to reconstruct oceanographic processes that contribute to variations in atmospheric  $\text{CO}_2$  over glacial-interglacial cycles. This organic material is presumed to be part of the diatom cell wall and the template for biomineralization, entombed upon silicification and protected from diagenesis. However, this material has not been well characterized and there is no strong sense yet for how variable its composition is between species or among members of the same species growing under different conditions. In addition, the studies that have been carried out on isotopic fractionation by diatoms have focused on the "whole cell" isotopic composition and not specifically that of the material occluded within the matrix of the silica. Some investigation of this matters would go a long way towards refinement of these proxies for nutrient utilization and primary production.

Towards this end, measurements of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N on diatom-bound organic matter were made over the Holocene and Last Glacial Maximum (LGM) from 3 piston cores in the Southern Ocean, one from each of the three sectors. The site in the Atlantic sector differs considerably from the other two sites by having markedly lower  $\delta^{13}\text{C}$ , more variable  $\delta^{15}\text{N}$  and C/N ratios, and a sedimentary diatom assemblage that is never dominated by *Fragilariopsis kerguelensis*. The proportion of *F. kerguelensis* in the samples, and to a lesser degree, the carbon content of the organic matter, have a strong influence on  $\delta^{13}\text{C}$ . Extreme values of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N at the Last Glacial Maximum are also related to the abundance of resting spores of *Eucampia antarctica*. These results suggest that methods for the separation of specific diatom species out of opal sediments would considerably aid in the reconstruction of paleoceanographic conditions from diatom stable isotope and elemental records.