

Chemistry of diatoms and coccoliths records carbon acquisition strategies during biomineralization

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Introduction

A strong biological control over trace element or stable isotopic composition of marine biominerals is frequently viewed as a liability in reconstructing past ocean chemistry and temperature, and the significance of reconstructing the biological processes themselves is often overlooked. We propose that the chemistry of opal, produced by diatoms, and calcite, produced by coccolithophorids, predominantly reflects key biological processes for cellular carbon acquisition. Reconstruction of these biological processes in the past will reveal how marine algae responded to changes in atmospheric CO₂, key to both the past and future carbon cycle.

Biomineralization effects on stable isotopes in coccoliths

Coccolithophorids exhibit strong biological effects in carbon and oxygen isotopic composition. Previously we hypothesized that the size-correlated range of vital effects in carbonate liths produced by different coccolithophore species was due to variable significance of carbon concentrating mechanisms in their C acquisition. Our new culture experiments with coccolithophorids reveal strong plasticity in the magnitude of stable carbon isotope vital effects in coccoliths of *Calcidiscus leptoporus* and *Emiliania huxleyi* with variable CO₂. At high CO₂ coccoliths of both species are more isotopically enriched, but the magnitude is greater in *C. leptoporus* leading to reduced interspecific offsets at high CO₂. In the case of *E. huxleyi*, higher CO₂ conditions resulted in significant reduction in the magnitude of DIC accumulation in the intracellular carbon pool, and more positive carbon isotopic values inside the particulate organic matter. A model of carbon acquisition incorporating both photosynthetic and carbonate production is used to assess mechanisms for these relationships. Stable isotope data from size-separated deep-sea sediments dominated by small, intermediate, and large coccoliths show a range of vital effects which is distinct during several major Cenozoic proxy-inferred climate-CO₂ transitions. Furthermore, where vital effects are significant their magnitude scales with coccolith size in the same sense as modern cultures.

Biomineralization effects on diatom B content

From two species of diatoms, *Thalassiosira weissflogii* and *T. pseudonana*, cultured at a range of pCO₂ from 200 to 2000 ppmv, B content of cleaned diatom opal was measured by Laser Ablation-ICP-MS and Secondary Ion Mass Spectrometry. Determination of growth rate, type of carbon acquired, and silicon and carbon quotas during diatom growth provides data on biomineralization process. B content in *T. pseudonana* is correlated with bicarbonate uptake rate and with normalized Si quotas. For *T. weissflogii*, which is a bicarbonate-restricted user at the pH studied, B content seems to be regulated primarily by the borate/bicarbonate seawater ratio, at pCO₂ < 1000 ppmv. We present a simple cellular model of B and Si uptake by diatoms to quantitatively explore the mechanisms for variable B content and its potential as a proxy.

Oceanic Material recycled within the Subpatagonian Lithospheric Mantle (Cerro del Fraile, Argentina)

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A detailed petrological study of mafic and ultramafic xenoliths from the Cerro del Fraile (Southern Patagonia, Argentina) was developed in order to highlight: I) the mineralogical and geochemical composition of the lithospheric mantle beneath the area, II) the nature of the metasomatising agents which infiltrate the mantle wedge above the Antarctic subducting Plate, III) the processes that allow the mantle to be refertilised and IV) the nature of the material dragged down in the subduction zone and recycled within the south patagonian sub-arc mantle.

Major and trace element analyses of clinopyroxene and orthopyroxene in peridotitic and pyroxenitic rocks suggest that a proto-adakite, deriving from the melting of the subducting Antarctic plate, was responsible for both the metasomatic features of the peridotitic rocks and the crystallisation of the pyroxenites. A few composite xenoliths bridge the two processes - peridotite enrichment and pyroxenite crystallization - indicating that the variously depleted mantle reacts with the incoming melt to generate a newly fertile mantle domain. HREE and Al₂O₃ and MgO contents in pyroxenes indicate a partial melting degree varying from 10 to 25 %. The peculiar enrichment in Zr (-Hf), Th and U of the pyroxenes speaks in favour of the melting of oceanic sediments, which are composed of a remarkable amount of manganese nodules and micronodules and, possibly, organic matter. Some geochemical analogies have been found between the calculated metasomatic melts and the Austral Volcanic Zone adakites. In this case, the amount of sediments involved in the genesis of the infiltrating melts is larger than that previously proposed for the genesis of the erupted Patagonian adakites. Chemical-physical conditions favouring the upward percolation through the mantle wedge of these SiO₂-rich and viscous melts are also discussed.