

Mg and Ca isotope fractionation during CaCO₃ biomineralization

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Biomineralization processes leading to CaCO₃ formation are important in relationship to better understanding proxies and environmental change. The specific factors which affect the uptake of metal ions during skeleton formation remain unresolved. Here we report the first combined use of Mg and Ca isotope measurements on coral and foraminifera and offer interpretation of the natural variations in relationship to biomineralization processes.

The Mg and Ca isotopic composition of a suite of Holocene foraminifera, including 11 planktonic and 2 benthic species, and modern coral from worldwide oceans were determined using MC-ICPMS. All samples fall on mass-dependent fractionation lines on three-isotope plots of Mg (²⁴Mg, ²⁵Mg, ²⁶Mg) and Ca (⁴²Ca, ⁴³Ca, ⁴⁴Ca). This indicates that measurements are free from interferences. For Mg isotopes, a distinct difference is observed between coral and foraminifera. Whereas coral samples show indistinguishable $\delta^{26}\text{Mg}_{\text{SRM980}}$ values of ca. +1.7‰, foraminifera show $\delta^{26}\text{Mg}$ varying from -0.78‰ to -3.82‰. Seawater has the heaviest isotopic composition of +2.60‰. In contrast, Ca isotope compositions of all samples show no significant variation within the 2 σ error ($\pm 0.13\text{‰}$), but are depleted in heavy isotopes by 0.60‰ relative to seawater ⁴⁴Ca/⁴²Ca ratio. In addition, our results do not show any evidence of a temperature dependence.

The similarity in Ca isotope composition between corals and foraminifera suggests that common mass fractionation processes have taken place, and that bulk mineralization of CaCO₃ operates as would an inorganic process. In contrast, the significant differences in Mg isotope compositions between coral and foraminifera, and between foraminifera species themselves, show that different processes operate in Mg²⁺ uptake. There appear to be additional (kinetic) routes of Mg uptake in foraminifera, which are related to cell biology.

This study suggests that the calcification of the studied reef coral and foraminifera is not an intracellular process and further shows that the uptake pathways for different elements could be different even in a single biogenic mineral.

Banded iron formations as monitors of Archaean seawater composition

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Banded iron formations provide an important record of Archaean ocean composition and early life (Grassineau et al., 2001). These sequences have had complex geological histories so it is important to determine the extent to which these compositions have been subject to post-depositional modification.

Here we report the results of a series of leaching experiments for Pb, Nd and REE on oxide and sulphide facies ironstones from the Manjeri Formation of the ~2700Ma Ngezi Group in the Belingwe Greenstone Belt, Zimbabwe. The NERC drill core at the National monument (Hunter et al., 1998) provides fresh samples from the two ironstone horizons.

Sm-Nd isotopic analyses on unleached Al-poor ironstones give the depositional age. More Al-rich ironstones trend towards the Sm-Nd isotopic composition of the clastic sediments on an isochron plot. Samples of both oxide and sulphide facies ironstones were leached with HCl, HNO₃, HBr and acetic acids. Pb-isotopic analyses of the residues and leachates give ages that demonstrate fluid interaction with neighbouring rock layers. Oxide facies ironstones at the base of the sequence, which is deposited unconformably on ~3500 Ma gneiss, give older ages. Sulphide-facies ironstones from high in the Manjeri Formation are overlain by a komatiite-basalt volcanic sequence and give Pb-ages younger than their depositional age. REE exhibit a range of patterns with positive Eu anomalies. The patterns are being investigated to determine the relative contributions from reduced ocean-ridge hydrothermal fluids, oxidized seawater and post-depositional metamorphic fluids.

References

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