Temperature dependence of Ca isotope fractionation in marine carbonates

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Data from both culture experiments and natural samples suggest that Ca isotope fractionation during carbonate shell construction by marine organisms is temperature dependent (Nägler et al. 2000; Zhu and Macdougall, 1998) and therefore potentially useful as a paleothermometer. Here we report direct measurement of the temperature dependence of Ca isotopic composition in cultured *Orbulina universa* and inorganically precipitated aragonite, as well as indirect measurements (through comparison with oxygen isotope and Mg/Ca data) on *Globigerina sacculifer* from a western Pacific ODP site.

Multiple samples of *O. universa* cultured at temperatures of 17, 22 and 27°C (courtesy D. Lea, U.C. Santa Barbara) show a small range of total variation in $^{44}Ca/^{40}Ca$, not much outside current analytical uncertainty. Taken at face value, the data imply a temperature dependence that is less than 0.05‰ per °C. This is significantly smaller than the 0.24‰ per °C reported by Nägler et al. (2000) for cultured *Globigerina sacculifer*. Aragonite precipitated in the laboratory at temperatures of 10 to 40°C appears to show an even smaller temperature dependence of approximately 0.01‰ per °C. However, analyses of *Globigerina sacculifer* picked from Ontong Java Plateau sediment cores (ODP Site 806) show $^{44}Ca/^{40}Ca$ variability that mirrors the oxygen isotope variations for the same samples. Differences between core top and last glacial maximum (based on oxygen isotope data) samples correspond to a glacial-interglacial surface seawater temperature difference of 2-2.5°C if the calibration of Nägler et al. (2000) for the same species is used. This is similar to values inferred from Mg/Ca data for Site 806 (Lea et al., 2000) and thus appears to corroborate the data of Nägler et al. (2000) for cultured *Globigerina sacculifer*. If these results are sustained by further work, they suggest that there are large inter-species differences in the magnitude of Ca isotopic fractionation among foraminifera. Work continues on ways to understand these differences.

References

Lea, D.W., Pak, D.K. and Spero, H. (2000) Science 289, 1719-1724.

Nägler, T.F., Eisenhauer, A., Müller, Hemleben, C. and Kramers, J. (2000) Geochem. Geophys. Geosys. 1, 1-9.

Zhu, P. and Macdougall, J.D. (1998) Geochim. Cosmochim. Acta 62, 1691-1698.

The use and abuse of boron isotopes in natural silicate-water systems

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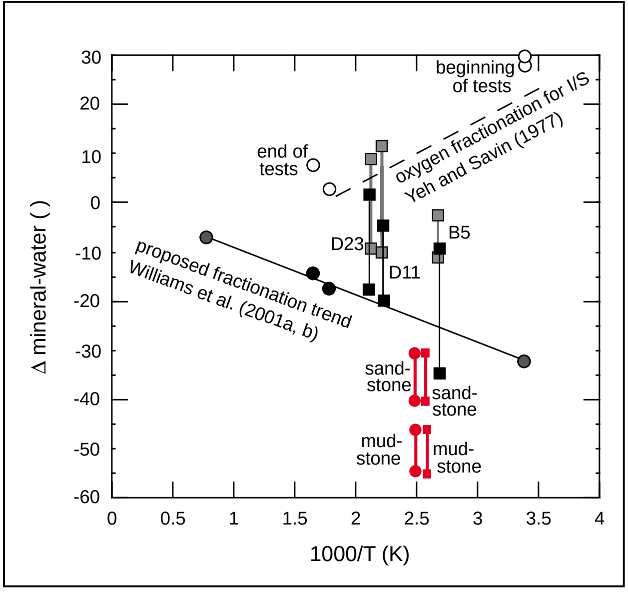
Owing to its wide range of isotope ratios in natural geological settings, boron has been shown to be a suitable proxy to characterize low-temperature geochemical processes and devolatilization reactions. Its fractionation behavior is influenced by factors like pH, mineralogy, and temperature (e.g. Palmer and Swihart, 1996). If compared to waters and carbonates, data for silicate rocks are rather limited because of the demanding laboratory procedures to measure $\delta^{11}B$. In the recent literature, however, fractionation models being based on experimental work between boron and co-existing waters in a closed system proposed a systematic B fractionation in such systems being entirely temperature dependent (Williams et al., 2001a). Based on some additional field data (Fig. 1), the same authors concluded "there is a good agreement between the field results and the experimentally derived B-isotope fractionation curve" and that B isotopes are "a useful geothermometer for low temperatures" (Williams et al., 2001b).



We here report many of our own results as well as data compiled from the literature, which suggests that B fractionation is complex, mineral-specific, and not apparently applicable as a geothermometer.

References

Palmer M.P et al. 1996. *Min. Soc. Am., Rev. Min. Mineralogy* **33**, 709-744.

Williams L.B., et al (2001a) *Geochim. Cosmochim. Acta* **65**, 1769-1782.

Williams L.B., Hervig R.L., Holloway J.R, and Hutcheon I. (2001b) *Geochim. Cosmochim. Acta* **65**, 1783-1794.