Opening the foraminiferal proxy black box a bit further

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Even though our geochemical proxy toolbox is ever increasing and our analytical techniques are getting more sophisticated, our fidelity at reading past ocean climate information has only slightly improved. This is mainly due to the fact that most relationships are still empirical and controlled by more than just the target parameter. The outstanding challenge is to open the black box and develop a mechanistic understanding of proxy incorporation and preservation. We have carried out a whole suite of laboratory experiments to better understand the calcification processes and the pathways of Mg, Sr, Ba, U and B using confocal laser microscopy, TEM, AFM and simultaneous analyses of B/Ca and $\delta^{11}B$ using femtosecond laser ablation and MC-ICP-MS. Together, the results show a high degree of biological control during calcification and proxy incorporation. We have used the benthic foraminifers *Ammonia aomoriensis*, *Amphistegina lessonii*, *Heterostegina depressa* and the planktonic foraminifer *Orbulina universa*. Lessons learned and a tentative model will be presented.

Experimental constraints on Fe isotope fractionation in fluid-melt-oxide-sulfide assemblages

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We report the first experimental data that quantify directly the effect of a fluid phase on stable iron isotope fractionation at magmatic conditions. Our investigation was stimulated by the hypothesis that degassing causes the heavy iron isotope signature measured in degassed rhyolites [1,2], but published experimental studies of iron isotope fractionation lacked a fluid phase.

We used a rhyolite melt, NaCl-bearing aqueous fluid, and magnetite or pyrrhotite. Charges were run at 400, 600, or 800°C, 150 MPa for mineral–fluid, and 800°C and 100 MPa for mineral–melt–fluid; f_{O2} was buffered at ~NNO. Isotopic compositions of starting and quenched phases were obtained by MC-ICP-MS. Time-series runs and the three-isotope method were used to assess equilibrium

Our data indicate that rhyolite melt at 800°C is isotopically lighter than co-existing fluid ($\Delta_{\text{melt-fluid}} \sim -0.20‰ \pm 0.07$ 1SD).Magnetite behaves as predicted ($\Delta_{\text{fluid-magnetite}} \sim +0.75‰ \pm 0.07$ 1SD at 800°C), becoming isotopically heavier relative to both fluid and melt. An andesite-fluid experiment (FMQ+0.5, 1000°C, 150 MPa) yielded an isotopically lighter melt relative to the starting glass, consistent with the coexisting fluid being isotopically heavier than andesite melt. These data suggest that fluid exsolution from silica-rich melts is not the cause for the increased $^{56}Fe/^{54}Fe$ ratio in degassed rhyolites. Interestingly, magmatic and hydrothermal magnetite show distinct iron isotope signatures, suggesting that the iron isotope values of minerals deposited by these processes may serve as geochemical fingerprints of the source reservoir for iron. Additional data from sulfide runs support the observation that individual minerals can fractionate iron differently and that pyrrhotite preferentially incorporates ^{54}Fe into its structure ($\Delta_{\text{melt-pyrrhotite}} \sim -0.75‰ \pm 0.01$ SD at 800°C).

These data corroborate the hypotheses that both fluid exsolution and crystal fractionation could influence the isotopic composition of a melt, but perhaps not as predicted. Owing to the importance of melt degassing as a critical process for the formation of ore deposits, our data may also help resolve debates regarding the origin of deposits that may have formed by either magmatic or hydrothermal processes.

[1] Potraisson and Freydier (2005) Chem. Geol., **222**, 132-147, [2] Heimann *et al.* (2008) GCA, **72**, 4379-4396

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