

Calibrating S isotope fractionation in sulfate reducing bacteria

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The sulfur isotopic composition of sedimentary sulfate and sulfide minerals throughout Earth history is a reflection of the activity of dissimilatory sulfate-reducing bacteria (SRB). The magnitude of the fractionation between sulfur compounds is interpreted as a biochemical consequence of changing environmental conditions. However, quantitatively understanding the isotopic variability within the geological record requires calibrating the physiological controls on dissimilatory sulfate reduction (e.g. sulfate concentrations, relevant electron donor, etc.). We have interrogated these controls with three complementary approaches.

First, through the incorporation of recent biochemical and crystal structure data, we have reexamined the reaction network involved in dissimilatory sulfate reduction. Our revised network adequately describes previous observations, and is experimentally testable.

Second, we measured the production of intermediates in pure cultures of *D. desulfuricans* grown on sulfate/sulfite and lactate/formate. In these experiments we observe the systematic production and consumption of sulfite and thiosulfate. We have tracked the isotopic consequences of each experiment, including the measurement of the site-specific isotopic composition of thiosulfate. These data reinforce our model predictions and provide valuable constraints on the fractionations associated with thiosulfate production and consumption.

Third, we performed community scale experiments in quasi-chemostat microbial reactors to better quantify changes in fractionation in response to sulfate concentrations. Whereas the pure culture work investigates the internal cycling, the reactor work assesses the first-order controls on sulfate uptake.

Through this broad combination of experimental and conceptual approaches, we provide unprecedented insight in the operation of the sulfate reduction pathway: information that can be used to better calibrate and inform our interpretation of sulfur isotopes in the sedimentary record.

Constraining magma-carbonate interaction at Vesuvius, Italy: Insights from stable isotopes and experimental petrology

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At Vesuvius volcano, Italy, abundant high temperature calc-silicate (skarn) xenoliths have been found in many eruptive deposits and, provide evidence for intense interaction between magma and carbonate crust. In order to understand magma-carbonate interaction and to quantify carbonate assimilation processes, we present a combined stable isotope study of natural samples and piston cylinder de-carbonation experiments.

The sample study shows that $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope values of igneous-, skarn- and carbonate rocks indicate that significant crustal contamination of Vesuvius magmas has taken place. Calc-silicate xenoliths define variable degrees of decarbonation and interaction processes between magma and crust, producing progressively more lava-like values [1].

In the experiments, we simulated the processes of carbonate assimilation under magmatic pressure and temperature conditions (0.5GPa and 1200°C) with Vesuvius magma composition and local crust as starting material. We have constructed a high-resolution time-sequence of magma-carbonate interaction in our experimental products with short but increasing dwell run-times (t_d), of 0, 60, 90 and 300 sec [2]. We observe a progressive carbonation of the host melt, and rapid liberation of large quantities of CO_2 coming from the breakdown of the enclosed carbonate. Variable degrees of carbonate assimilation and chemical mixing between carbonate and silicate melts are observed, with diffusion processes playing an important role at melt interfaces.

The combination of petrological evidences and experimental products allows insights into the processes and time-scales of magma-crust interaction and reinforces the hypotheses that carbonate assimilation is an ongoing and significant magmatic process at Mt. Vesuvius.

[1] Turi *et al.* (1976) *Contrib. Mineral. Petrol.* **55**, 1–31.

[2] Deegan *et al.* (2010) *J. Petrol* **5**, 1027–1051.