Si isotope fractionation during precipitation of silica by cyclic freezing and adsorption of monosilicic acid on gibbsite

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Cyclic freezing of aqueous solutions containing silicic acid can be used to precipitate amorphous silica through complex precipitation-dissolution reactions. In such a dynamic system kinetic isotope effects during an unidirectional transfer from silicic acid to a solid may be equalized by cyclic dissolution of the previous precipitated silica and slow isotopic equilibrium between solutions and solids is potentially attained.

We performed several sets of freeze-thawing experiments to decipher the silicon isotope fractionation during precipitation of amorphous silica at pH 4.5 and 7. The initial solutions contain 1.6 mmol L^{-1} of Si and 0.1 or 1 mmol L^{-1} of Al (TEOS and $AlNO_3 \cdot 9H_2O$). The solutions were frozen and thawed within 24 hours by up to 130 cycles and sampled at regular intervals.

Experiments with high initial Al concentration ([Al] = 1mmolL^{-1}) show changing $\delta^{30}Si$ values with time. The $\delta^{30}Si$ solution values increased during the first 20 freeze-thaw cycles to up to 2.4‰ and then showed a decline to almost starting values of 0‰ after 130 days. Experiments with low Al concentrations ([Al] = 0.1mmolL^{-1}) remained at the value of the initial solution throughout.

Supplementary adsorption experiments, with monosilicic acid (0.36 mmol L^{-1} Si) and gibbsite (55 m^2 L^{-1}) were carried out at pH 7. Adsorption of silicic acid results in an increase of $\delta^{30}Si$ values and a quasi isotopic/chemical steady state is reached at ~ 300 h.

We developed a mass balance approach and applied time-dependent fractionation factors consisting of $\alpha 1_{precipitate-solution}$ and $\alpha 2_{precipitate-solution}$ to the freeze-thaw system. Model results predict that during the first 20 freeze-thaw cycles presumably kinetic fractionation was dominant with a 1000ln ($\alpha 1$) = -4.5‰. This value is close to what is observed by adsorption of silicic acid onto gibbsite. Once the system reaches a steady-state the modeled fractionation factor changes to 1000ln ($\alpha 2$) = 0‰. $\alpha 2 = 1$ possibly represents the equilibrium isotope fractionation factor and indicates no discrimination of silicon isotopes between dissolved silicic acid and newly formed amorphous silica or hydroxyalumosilicate.

A profile of multiple Sulfur isotopes for the Oman ophiolite

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The Oman ophiolite is regarded to represent the best example of fast-spreading oceanic lithosphere on land. Here, we present the first multiple sulfur isotope profile through all components of the (ancient) oceanic lithosphere (Fig. 1), together with sulfur abundances and a petrographic study.
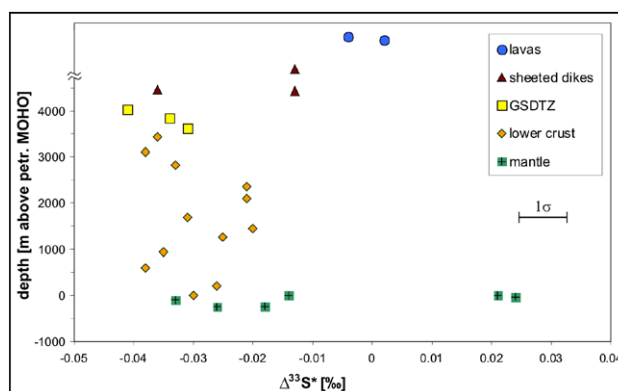
Figure 1: $\Delta^{33}S^*$ values of Cr-reducible sulfur versus depth for a composite section through the Oman ophiolite; $\Delta^{33}S^* = \delta^{33}S - 1000 \times ((1 + \delta^{34}S / 1000)^{0.515} - 1)$ [1]; GSDTZ represents the gabbro/sheeted dike transition zone.

Our results indicate that upper crustal rocks of the Oman ophiolite (lavas and sheeted dikes) exhibit: (i) pervasive alteration due to intense circulation of seawater; and (ii) microbial reduction of seawater sulfate occurring within the lavas during low-temperature alteration. Samples from the gabbro/sheeted dike transition zone and lower crustal rocks are affected by a high-temperature alteration resulting in leaching and redistribution of sulfide-S. $\Delta^{33}S^*$ values of Cr-reducible sulfur (CRS) between -0.020‰ and -0.038‰ clearly differ from those of upper crustal rocks (Fig. 1). This could either suggest that intense sulfur leaching processes operate in those units, or that oceanic lower crust has a primary multiple sulfur isotopic composition that deviates from the postulated mantle value ($\Delta^{33}S^* = 0.0‰$; [1]). Samples from the mantle portion of the Oman ophiolite display the widest ranges in $\delta^{34}S$ and $\Delta^{33}S^*$ reflecting multi-stage serpentinization processes.

[1] Farquhar *et al*. (2002) *Science* **298**, 2369–2372.