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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 δ^{30}Si values with time. The δ^{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 δ^{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 $\alpha 1_{\text{precipitate-solution}}$ and $\alpha 2_{\text{precipitate-solution}}$ to the freeze-thaw system. Model results predict that during the first 20 freeze-thaw cycles presumably kinetic fractionation was dominant with a 1000ln (α1) = -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 (α2) = 0‰. α2 = 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.