

Extreme silicon isotope fractionation between silicic acid and aqueous organosilicon complexes: Implication for silica biomineralization

F. M. STAMM^{1*}, M. MÉHEUT¹, T. ZAMBARDI², J. CHMELEFF¹, J. SCHOTT¹, AND E.H. OELKERS^{1,3}

¹GET, CNRS/URM 5563, Université Paul Sabatier, 14 avenue Edouard Belin, 31400 Toulouse, France
(*correspondence: franziska.stamm@get.omp.eu)

²LEGOS, OMP, 14 avenue Edouard Belin, 31400 Toulouse, France

³Earth Sciences, University College London, Gower Street London WC1E 6BT, UK

Silicon (Si) is one of the most common elements on Earth, present in rock-forming minerals, plants and natural fluids, and playing a key role in the geological and biological cycles at the earth surface. It usually occurs as silicic acid (H₄SiO₄) in aqueous fluids but can also form organosilicic complexes in the presence of organic ligands (e.g. diphenol, polyalcohols). Investigating the impact of such complexes on the Si isotopic fractionation is thus crucial to better understand Si behavior in natural systems.

For this purpose we performed isotope exchange experiments at 25°C and chemical equilibrium between amorphous silica and solutions containing 85-90% 6-fold Si-catechol complexes involving 5-membered rings configurations. Using the ‘three isotope method’^[1], we have quantified equilibrium Si isotope fractionation between Si-catechol complexes and amorphous silica and silicic acid, respectively: $\Delta^{30}\text{Si}_{\text{Si-catechol-SiO}_2(\text{am})} = -19.3\text{‰}$ and $\Delta^{30}\text{Si}_{\text{Si-catechol-H}_4\text{SiO}_4} = -18.8\text{‰}$. These experimental values are in excellent agreement with first-principle calculations of Si isotope fractionation between quartz and silicic acid and quartz and the Si-catechol complex ($\Delta^{30}\text{Si}_{\text{Si-catechol-H}_4\text{SiO}_4} = -18.9\text{‰}$).

Using the same three isotope method, very important enrichments in ²⁸Si of silica-meglumine (Si-N-methylglucamine) solutions containing 4-, 5- and 6-coordinated Si have been also measured.

These results may explain some puzzling isotope compositions recorded in marine silica biomineralizations such as sponge spicules.

[1]: Matsuhisa, Goldsmith & Clayton (1978), *Geochim. Cosmochim. Acta* **42**, 173–182.