

Silicon isotope fractionation implying liquid phases at 300K: importance of configurational disorder

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Silicon isotope fractionation during Si precipitation in surface environments has received great interest in recent literature [1] for its potential to constrain weathering processes. *Ab initio* methods have the potential to provide independent and useful informations to understand the elementary processes responsible for such fractionations involving liquid phases [2]. In this study, we explored liquid/liquid ($\text{H}_4\text{SiO}_4/\text{H}_3\text{SiO}_4^-$) and mineral/liquid (quartz/ H_4SiO_4) fractionation of Si at equilibrium within the harmonic approximation [3]. Two 40ps trajectories of H_4SiO_4 (or H_3SiO_4^-) + 64 water molecules were simulated at 300K with the CPMD code, using BLYP functional. Then, using DFPT on configurations quenched at 0K, zone-center phonon frequencies were calculated to obtain their fractionation properties ($\ln\beta^{30/28}(\text{Liq.})$). In these systems, the effect of configurational disorder on the fractionation properties was studied in details. In parallel, $\ln\beta^{30/28}(\text{Quartz})$ have been computed to study a mineral/liquid equilibrium fractionation.

Based on a set of 10 independent configurations extracted from the trajectories, significant variations have been observed on the values of $\ln\beta^{30/28}(\text{Liq.})$. The calculated dispersion (σ) is large : **0.43‰** for H_4SiO_4 and **0.38‰** for H_3SiO_4^- . Thus, in the case of Si in solution, the configurational disorder should be taken into account for a realistic computing of fractionation properties.

The mean values of $\ln\alpha^{30/28}(\text{Quartz, H}_4\text{SiO}_4) = +2.18 \pm 0.14\text{‰}$ (SE, N=10) and $\ln\alpha^{30/28}(\text{H}_4\text{SiO}_4, \text{H}_3\text{SiO}_4^-) = +1.51 \pm 0.16\text{‰}$ (SE, N=10) at 300K have been calculated including the error due to the liquid disorder. Regarding the calculated fractionation in quartz/liquid systems, the solution is predicted to be lighter than the precipitate, inconsistently with every natural observations. Thus, the precipitation is probably a process out of equilibrium in this system. Most importantly, a significant fractionation related to a single proton exchange ($\text{H}_4\text{SiO}_4/\text{H}_3\text{SiO}_4^-$ equilibrium), is predicted.

Consequences on the explanation of silicon fractionation during precipitation will be discussed.

[1] Opfergelt, C. R. *Geoscience* 344 (2012) 723-738 [2] Kowalski et al., *GCA* 101 (2013) 285-301 [3] Rustad and Bylaska, *JACS* 129 (2007) 2222-2223

Sorption of dissolved organic matter on boom clay

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Dissolved organic matter (DOM) plays a significant role in a geological nuclear waste repository by enhancing or retarding the transport of radionuclides in the environment. It is thus a key aim to understand the equilibriums DOM-rock which govern the DOM mobility. DOM sorption was studied on a large variety of soils and minerals with different DOM sources [1],[2]. However, most of works was carried out after removal of the indigenous DOM, neglecting therefore some key aspects of the sorption. Boom Clay, potential host rock under study in Belgium, is a formation rich in organic matter with 1.7 wt% of TOC. The objective of this work is thus, to study the interactions of the indigenous DOM with the Boom Clay rock in undisturbed conditions. To this end, we propose to use a sequential leaching of the indigenous DOM: from a crushed solid, under a controlled pCO₂ and in a synthetic solution representative of the pore water. This method allows to quantify the fraction of soluble organic matter and the equilibrium DOM in solution/DOM sorbed.

Three different rock samples were considered with, for each, four liquid/solid ratios. No influence of the liquid/solid ratios was noticed on the amount of DOM extracted, which was estimated between 0.037 and 0.104 wt% of the total rock according to the origin of the samples. A linear behaviour in desorption was highlighted with K_ds in good agreement for all the samples. However, the dimensions of the system were observed to strongly influence the K_d values. Indeed, average K_ds of 2.7, 4.3 and 10.3 L.kg⁻¹ were measured for liquid/solid ratios of 4, 6.7 and 16.7 L.kg⁻¹ respectively. The quantification of DOM sorption is thus dependent on the studied system and the notion of K_d should be considered with care. However, the approach used here offers reference values that account for the different sorption mechanisms encountered in situ, including potential competitive effects. Behind a pure quantification of the interactions DOM-rock, our work aims at understanding the mechanisms involved and notably the influence of DOM molecular weight on sorption. Batch sorption experiments are, indeed, on-going with different size fractions of the indigenous DOM. The results and limits of the sequential leaching approach will be discussed together with the influence of molecular size on the measured K_d values.

[1] Kaiser *et al.* (2000), *Organic Geochemistry*, **31**, 711-725.

[2] Kahle *et al.* (2004), *Organic Geochemistry*, **35**, 269-276