



Quantifying lithium isotope fractionation during clay formation at low temperatures

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Lithium isotopes can significantly fractionate during water-rock interactions, resulting in natural waters highly enriched in ^{7}Li while residual solids and sediments display isotope composition often close or lighter than the fresh rock one¹. Recent studies have shown the potential of this isotope tool to bring new constraints on silicate weathering in various contexts². However, modelling $\delta^{7}\text{Li}$ measured in continental and hydrothermal waters requires a good knowledge of (1) the fractionating processes (2) the magnitude of these fractionations (3) the controlling factors and laws. Laboratory experiments can lead to quantitative constraints, usable in weathering models.

Recently, we have shown that the incorporation of Li into octahedral sites of Mg-rich smectite results in significant Li isotope fractionation, which follows a linear law as an inverse function of temperature between 250°C and 90°C. Smectites synthesized at lower temperatures, between 90°C and 25°C, displayed similar isotope fractionation ($\sim -10\text{\textperthousand}$) (relative to the solution), and were characterized by lower crystallinity and weaker number of stacked layers³.

In this study, we focus on low temperature syntheses (25°C to 90°C). The experiment duration was increased (4 weeks / 8 weeks / 16 weeks / 29 weeks), in order to improve smectite crystallinity and quantify its role on Li isotope fractionation. We also perform syntheses of kaolinite and Al-rich smectite at 200°C, for quantifying the role of the type of clays and the chemical composition of the smectite on the incorporation of lithium in clays and on Li isotope fractionation.

First results show that 90°C and 75°C smectite synthesized during 8 weeks display $\Delta^{7}\text{Li}_{\text{clay solution}}$ which are 4‰ and 5‰ lower than for smectite synthesized at similar temperatures but during shorter periods. Also, the isotope signatures of both smectites (synthesized at 75°C and 90°C) are not similar, in contrast with previous findings. On-going investigations at 60°C and 25°C should allow us to better determine the relationship with temperature. However these results already suggest a major role of the smectite age and crystallinity on Li isotope fractionation. On the other hand, kaolinite and Al-rich smectite synthesized at 200°C display similar isotope fractionation as Al-free smectite synthesized at the same temperature (-3.5‰), suggesting negligible influence of the type of clay and chemical composition on the Li isotope fractionation corresponding to its incorporation into octahedral sites.

1. Huh *et al.*, GCA 62, 2039-2051, 1998; 2. Millot *et al.*, GCA, *in press*; 3. Vigier *et al.*, GCA 72, 780-792, 2008.

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