



Quantifying the isotopic fractionation of lithium during clay formation at various temperatures

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Recent studies have shown that the geochemical cycle of lithium isotopes is mainly controlled by isotopic fractionations associated to secondary clays. In particular, it has been inferred that the neoformation of smectites during ocean basalt weathering could explain the Li isotopic signature of the ocean ($\delta^7\text{Li} = 31.2$ per mil, significantly heavier than its sources ($\delta^7\text{Li} = 9$ per mil for hydrothermal flux and 23‰, for dissolved continental flux). Similarly, it has been shown that weathering of continental crust by superficial waters produce ^6Li enriched secondary minerals and high $\delta^7\text{Li}$ waters (Huh et al., 1998). This makes lithium a potential powerful tracer of silicate weathering intensity. It is therefore important to study fractionation factors involved in clay formation.

It has been previously observed that Li-rich clays are generally Mg-rich clays. Also, dissolved lithium correlate mainly with magnesium in silicate draining waters, suggesting similar sources. As a consequence, we first focus on constraining the lithium isotopic fractionation linked to Li-Mg substitution reaction during smectites (hectorites) crystallization. Following a method developed by Decarreau (1980), we have experimentally synthesized hectorites over a large range of temperatures from a solution highly enriched in lithium. These experiments should constrain equilibrium isotopic fractionation factors. Lithium in hectorites is found in two different sites: substituted to Mg^{2+} (within the octahedral sites), and in an exchangeable interlayer site. After synthesis, all the exchangeable lithium has been removed with a NH_4Cl solution, by using a dialysis technique. A CaCl_2 solution has also been used for comparison.

Li isotopic compositions for clays and solutions have been measured using an Elan 6000 ICP-MS. Some of the samples have also been measured by MC-ICP-MS for intercalibration purpose. The analytical procedure for Li elution has been modified from James and Palmer (2000). Results given by Elan 6000 for JB-2 and JG-2 rock reference materials are 4.1 per mil and 0.3 per mil (± 0.9 per mil, 2σ) respectively, which compares well with published values.

First results show that the measured isotopic fractionations between hectorite and solution are significant and decrease with increasing temperature (from 3.5‰ at 200°C to 10 per mil at 90°C). All duplicate experiments yield identical $\delta^7\text{Li}$ within analytical uncertainty. Also, clays saturated either with NH_4Cl or with CaCl_2 lead to similar isotopic compositions. Lithium contents for clays decrease with temperature and in all cases the amount of lithium incorporated by clays is too small to have changed the Li isotopic signature of the parent solution, as predicted. The isotopic composition of the clay is also constant through time (for a given temperature) and yields equilibrium fractionation factors.