

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

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Recent studies have shown that the surface geochemical cycle of lithium isotopes is mainly controlled by isotopic fractionations associated with clay formation. Weathering of continental crust by superficial waters can produce residual phases in soils that are depleted in ⁷Li, and high $\delta^{7}\text{Li}$ river waters. Also, the neoformation of smectite in the ocean could explain the seawater Li isotopic signature ($\delta^{7}\text{Li} = 31.2\text{\textperthousand}$), significantly heavier than its sources ($\delta^{7}\text{Li} = 9\text{\textperthousand}$ for hydrothermal flux and $23\text{\textperthousand}$ for dissolved continental flux), considering a minimum isotope fractionation of $19\text{\textperthousand}$ during Li uptake by clays.

We have constrained the lithium isotopic fractionation linked to Li-Mg substitution during smectites (hectorites) crystallization. For this, we have experimentally synthesized hectorites at various temperatures (from 25°C to 250°C), using solutions highly enriched in lithium. All the exchangeable lithium has then been removed with NH₄Cl before clay isotopic analyses.

Li isotopic compositions ($\delta^{7}\text{Li}$) for reference materials, the synthesized clays and corresponding solutions have been measured using an Elan 6000 ICP-MS. Some of them have also been measured using a Neptune MC-ICP-MS, for intercalibration purpose. Both techniques are consistent within analytical uncertainties (1% and 0.5% respectively at the 2σ level). $\delta^{7}\text{Li}$ obtained for the reference materials are consistent with published values.

The measured isotopic bias ($\Delta^{7}\text{Li}$) between hectorite and solution is significant, and, decreases with increasing temperature (from $-1.6\text{\textperthousand}$ at 250°C to $-11\text{\textperthousand}$ at 25°C). The solution matrix has little effect on the isotopic fractionation but on the relative amount of lithium incorporated into the clay structure. The theoretical isotopic fractionations, as a function of temperature, have been estimated and are consistent with the experimental values, except for the highest temperatures for which some simplification used in the calculation may not be valid. Both, experimental and theoretical results, suggest a maximum Li isotope fractionation of $13\text{\textperthousand}$ at seafloor temperature, significantly lower than the values used for ocean budget. A low isotope fractionation would imply either a ratio of hydrothermal/continental inputs for lithium that is significantly lower than estimated, or another Li sink in the ocean.