

Li and Mg isotope fractionation during clay mineral formation

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The formation of clay minerals is a key process which can remove elements from solution. The properties of the clay which forms, for example its cation exchange capacity, subsequently controls how available those elements are to subsequent leaching and biogeochemical cycling. Recent work on the isotopes of Li and Mg has highlighted the potential of using these systems to assess the balance between secondary clay mineral formation and primary weathering rates in catchments. The majority of this work is based on field data and extracting fractionation factors from this data, required for modelling these systems, is challenging. Synthesising clay minerals with a well-defined composition in the laboratory can provide quantitative information on the fractionation of isotopes during clay formation and their dependence on environmental variables.

In this study we analysed the Li and Mg isotopic composition of two different types of clay mineral: stevensite and smectite. Two series of experiments were conducted, one assessing the effect of pH and the other, the effect of temperature on fractionation. The pH experiments were all conducted at room temperature. For all experiments the bulk solid, a 1M ammonium chloride leach and the residual solid after leaching were analysed, in addition to the initial and final solution compositions.

For both isotope systems, the clay is enriched in the light isotope compared to the starting solution. Apparent fractionation factors decrease with increasing temperature and there were no clear trends with pH, within the range analysed. Further, the bulk composition is a mixture of an exchangeable pool enriched in the heavy isotope and a residual pool enriched in the light isotope.

The direction of Mg isotope fractionation observed here is opposite to that inferred from field data and that observed in high temperature (>80 °C) clay synthesis experiments. It is, however, in agreement with low temperature (<50 °C) experiments. Based on the synthetic clay data we suggest that it is not the incorporation of Mg into the structure of the clay which is responsible for the observed fact that rivers are lighter than the rocks from which they are derived but rather the uptake of Mg into the exchangeable pool, which in the natural environment would include organic molecules.