

MEASURING LI-ISOTOPE FRACTIONATION IN CLAYS BY HIGH RESOLUTION NEUTRON DIFFRACTION: A TEST ABOUT THE PERSISTENCE OF WATER IN MARS.

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Introduction: Geochemistry of Lithium (Li) isotopes provide important information about the weathering of primary silicates in aqueous environments. Li can be found, in the range of ppm, in almost all of the basalt bearing minerals, because of its small ionic radius, similar to Mg. The two stable isotopes of Lithium, ⁷Li and ⁶Li, have a large relative mass difference (~15%) that results in significant fractionation between water and secondary minerals phases, mostly clays, the main weathering product of basalt dissolution. Clay minerals preferentially incorporate the light isotope in their structural lattice, thus leaving the remaining water with a heavier isotopic signature. This behaviour open interesting possibilities for the use of lithium isotopes as a proxy to understand the degree and extent of basalt weathering in aqueous mediums, providing important information about the Earth's Early Ocean and helping to determine the prevailing conditions during the formation of water bodies in the past of Mars. [1], [2], [3], [4].

The substitutions of Li in two crystallographic sites of clay minerals may complicate the interpretations of bulk Li-isotope ratios. It has been suggested that the magnitude of the isotopic fractionation of Li between water and clay may be different at the interlayers than in the octahedral sites of clay minerals. Actually it is unclear whether Li-isotopic fractionation only occur during the process of clay nucleation and growth (i.e., in trioctahedral hectorite), or by Li migration from the interlayer to either an octahedral position or to the ditrigonal cavities (i.e., in dioctahedral montmorillonites and beidellites), depending on the charge of the layer. In this study, we performed high resolution neutron scattering experiments to evaluate whether is possible to discriminate by neutron diffraction the isotopic ratio of lithium isotopes entering in the octahedral framework of clay minerals after contact with solutions containing both Li isotopes. The determination of lithium isotopic signature by this technique is based on the very different Scattering Length Densities (SLD) of both isotopes, that can selectively affect the intensity of various reflections, in the neutron scattering diagrams. To this end, we are analyzing the neutron scattering spectra of various clays before and after lithium adsorption using the Rietveld method by including the different scattering lengths of, ⁶Li and ⁷Li in the calculation of the intensities.

2. Experimental set-up: We are using dioctahedral and trioctahedral smectites. In the dioctahedral case, it is expected that lithium migration from the interlayer occurs to compensate the differences on layer charge. In order to analyze this process, Li-exchanged sample were prepared by using the Gene Kelly procedure (GK) i.e.: washing clays with LiCl and heating overnight at 300 °C. The GK test was used to determine whether Li⁺ ions remain at the interlayers- in smectites with tetrahedral charges- or are attracted to the vacant octahedral sites in dioctahedral smectites. Octahedral charged clays (montmorillonites) become non-expandable after GK test due to the incorporation of Li⁺ to octahedral sites, while regularly interstratified smectites (i.e. montmorillonite-beidellite) have particular distributions of negative layer charges, inducing the incorporation of Li⁺ to both positions and previsibly in different ⁶Li /⁷Li isotope ratios. The experiments were performed in the High Resolution Neutron Powder Diffractometer (E9) of the HZB in Berlin.[4].

3. Structural Analysis and Preliminary results: The Rietveld structure-refinements are being done with the program FULLPROF [5].

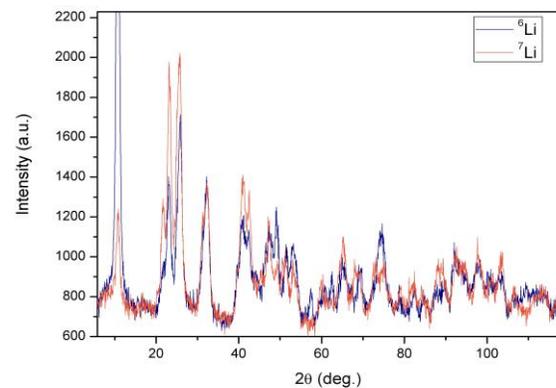


Figure 1. Beidellite spectra calculated for different Li-isotope ratios at the octahedral positions.

In order to track the effect lithium isotopes on the diffraction profile, preliminary spectra were calculated by using the Neutron Scattering Lengths of both lithium isotopes (figure 1). Data were taken from the NIST

database. As is shown in Figure 1, there are appreciable changes on the intensities of various reflections, following the relative occupancies

Consequently, each isotope was considered separately in the structural model. Refinement of the various smectites employed in the experiments, was done according to this procedure. The diffraction profiles were modelled using the (TCH) pseudo-Voigt profile-function. The background was determined using a refinable fifth-order polynomial or a cubic spline of 30 selected points. An example of refinement for the case of beidellite/montmorillonite is shown in figure 2. The upper plot (a) shows the Rietveld refinement of the mineral sample “as received”, i.e.: prior to adsorption of Li^+ by thermal treatment at 300°C .

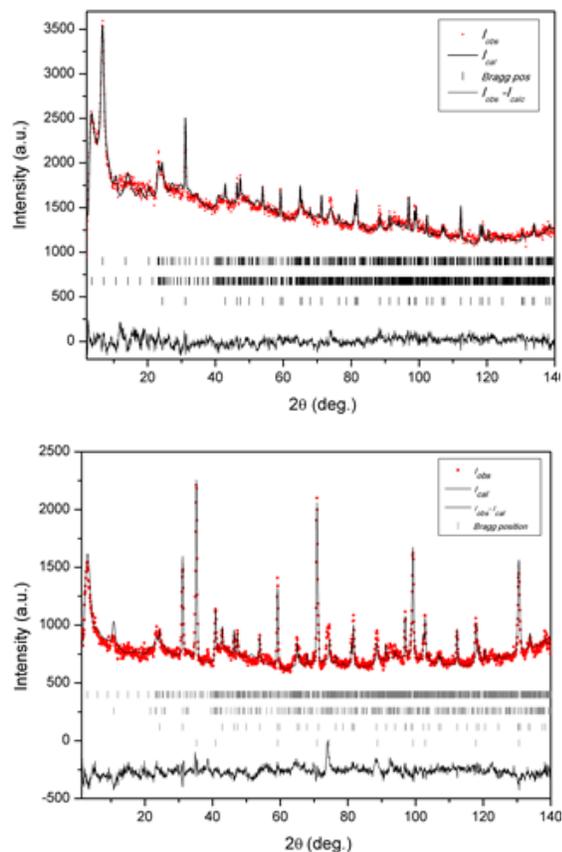


Figure 2. Rietveld plots of (a): mixed-layer beidellite/montmorillonite at 25°C before Li adsorption. (b): after GK treatment with LiCl at 300°C . Refinements were done by including the ratio

The observation of two basal reflections (001) clearly suggest the presence of a regularly interstratified beidellite/montmorillonite structure. In this case the refinement was done by using two similar phases but with different c -parameters. Results of quantitative phase analysis show similar wt% amounts for both mixed phases. In addition, accessory quartz (14%) was included in the refinement. Figure 2(b) corresponds to the same phase after Li adsorption and thermal treatment at 300°C . In spite of lithium incorporation to the octahedral framework, the two (001) swelling reflections are still observed, although the reflection at $\approx 27\text{\AA}$ is weaker. This suggests that the incorporation of Li^+ to the octahedral set was not enough to provide a complete compensation of charges and that some tetrahedral charge is still present in the interstratified structure. The latter is probably due to the substitution of tetrahedral Si by Al in beidellite. Consequently, refinement of atomic positions involving Li^+ was done by including both lithium isotopes at the octahedral position (0,0,1/2) and at interlayer position (0,1/2,0). Relative occupancy at every position of each isotope was refined employing atomic constraints.

Preliminary calculations of $\delta^7\text{Li}$ normalized to L-SVEC were obtained from the Rietveld occupation factors. Resulting fractionation values were $\delta^7\text{Li} \approx -0.63$ for the octahedral position and $\delta^7\text{Li} \approx 0.02$, for the swelling position. These results are consistent with a selective incorporation of the light isotope to the octahedral sites. Comparison of the isotopic signatures determined from experiments based on this technique, with the Li -isotopic ratios in clays obtained from meteorite samples, may provide important insights regarding the weathering processes and the persistence of water on Mars.

References: [1] Losa-Adams et al (2014), *LPS VL*, Abstract #1777. [2] Fairen et al.(2015) *Geochem. Geophys. Geosyst.*, 16(4):1172-1197. [3] Magna, T.B. (2015), *Geochim Cosmochim Acta* 162:46–6. [4] Tomascak P.B. et al. (2015) *Advances in Lithium Isotope Geochemistry* [5] D. M.Többsen et al (2001) *Materials Science Forum* 378-381, 288-293 [6] J. Rodriguez-Carvajal (1993), *Physica B*, 192, 55.