

UNRAVELING THE HISTORY OF WATER ON MARS USING LITHIUM ISOTOPE FRACTIONATION MODELS. E.L. Adams¹, C.G. Lozano¹, L.G. Duport¹, A.F. Davila² and A.G. Fairen³,

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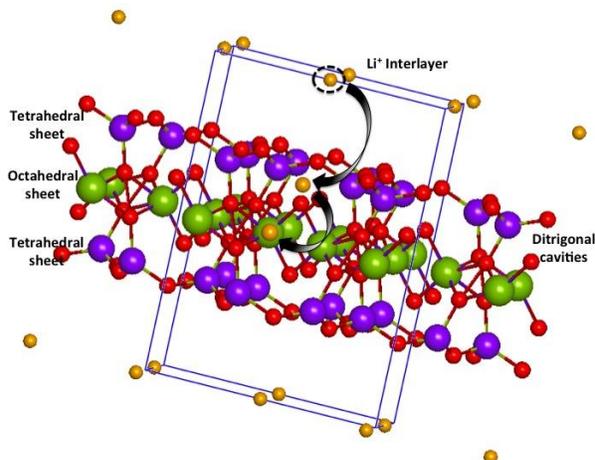
Introduction: Lithium is incorporated as trace element in most of basalt-bearing minerals, namely olivines, clinopyroxenes and plagioclase feldspars, where Li abundance lies in the order of 1-200 ppm depending on their source area. Lithium incorporation into a secondary mineral is a solvent-mediated process that can provide information about the duration, extent and conditions of aqueous interaction between primary minerals and water.

The analysis of Li isotopes could provide additional information that Li abundances alone will not tell. The selective incorporation of the lighter isotope (⁶Li) to secondary minerals, and consequently the evolution through time of the Li isotopic signature, reflects the interaction between chemical and physical weathering processes that are unequally affected by changes on pH and temperature. These processes might be significant in the context of hypothetical early water bodies on Mars, where the precipitation of secondary phases could have been controlled by the balance between evaporation and cooling [1,2] through reverse weathering processes.

Here we present geochemical models intended to help understand the Li isotopic composition of secondary minerals on Mars. We describe different case studies of Li isotope fractionation. We show that our models are relevant to extract lessons about the extent of basalt weathering on Mars, and therefore can be useful to determine the environmental conditions on the planet in the past.

Modeling Li isotope fractionation into secondary mineral lattices: For modeling purposes, we assume an initial value of ⁷Li = 5 %, the average isotopic signature of unweathered basalts. It is also assumed that the dissolution of basalt leads to the release of both isotopes (⁶Li and ⁷Li), without significant isotope fractionation. Secondary minerals incorporate a significant fraction of the dissolved Li. Isotope fractionation is mediated by the preferential incorporation of the lighter isotope (⁶Li) into some of the solid phases which are forming as secondary minerals, especially clays. Significant fractionation also occurs after the formation of oxihydroxides and hydroxides, like ferrihydrite or gibbsite. Although Li isotope fractionation into solid phases always implies a preferential uptake of the lighter isotope (⁶Li), the incorporation of Li into clays and other secondary phases entails a complicated process,

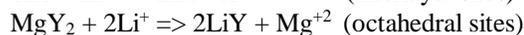
involving either reversible adsorption or irreversible incorporation within the vacant sites of the mineral structural framework. Uptake of lithium by smectites [3] may occur during the process of clay nucleation and growth, or by migration from the interlayer to either an octahedral position or to the ditrigonal cavities, depending on the charge layer (Figure 1). Li isotope fractionation occurs in both positions. This process can



take place at low temperature during the evolution from smectite to illite.

Figure 1. Lattice sites for Li incorporation during isotope fractionation in smectites.

Our geochemical models dealing with the selective uptake of each Li isotope by clays were conducted by implementing in the *Phreeqc* [4] code a specific algorithm that splits the total amount of sorbed Li between ⁶Li and ⁷Li isotopes, under the assumption that fractionation occurs following a Rayleigh distillation process. We have generated a model accounting for the multisite nature of lithium incorporation in smectites, by considering a two-site model. In this case, the sum of the different sorption sites densities was made equal to the published value of the cation exchange capacity [x]. The Li⁺ distribution between solution and smectite is determined by the extent of exchange reactions occurring on the X and Y sites (X= interlayer sites, and Y= octahedral sites) that can be defined, using the Gaines-Thomas convention [5], as follows:



where K is an interlayer cation, and Mg⁺² is an octahedral cation on the smectite framework. A mass

action law equation, with a constant K, can be defined by:

$$K_{K/Li} = \frac{E_{Li^+} [K^+] \beta_{K^+}}{E_{K^+} [Li^+] \beta_{Li^+}}$$

$$K_{Mg/Li} = \frac{E_{Li^+} [Mg^{2+}] \beta_{Mg^{2+}}}{E_{Mg^{2+}} [Li^+]^2 \beta_{Li^+}^2}$$

K, the equilibrium constant, determines the reversibility degree of the equation (K= direct rate/reverse rate).

Results: A particularly differential aspect of basalt weathering on Mars, compared to Earth, might have been the specific role played by simultaneous evaporation and cooling over the amount and type of secondary minerals forming. The present-day value of δ^7Li in terrestrial seawater is in a steady state (31‰), which seems to reflect the interplay between the uptake of Li by secondary minerals (leading to heavy signatures in the riverine input and lowering Li concentration in solution) and the amount of Li directly derived from the dissolution of igneous rocks with lower isotopic signature. On Mars, if evaporation and freezing acted as complementary sources of supersaturation, then the net effect would have been an increase of the precipitation of secondary minerals (i.e. clays), but not an increase of the dissolution of primary minerals (i.e. basalt). In consequence, the amount of Li with low isotopic signature supplied by the primary minerals would have remained constant, therefore improving the efficiency of the Rayleigh process and leading the system towards heavier $\delta^7Li_{[solution]}$ values. In consequence, an steady state of the δ^7Li value was no attained (figure 2).

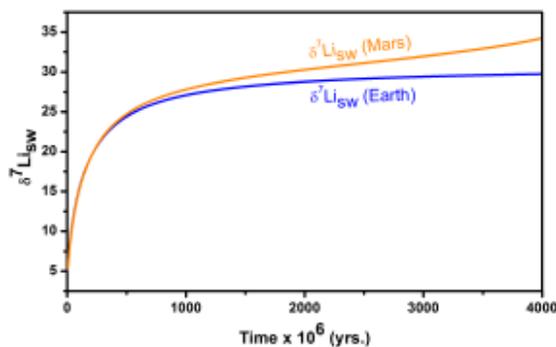


Fig. 2. Comparative evolution of δ^7Li in terrestrial seawater, without evaporation, leading to an steady state, and in Mars, where evaporation induces a increasing trend.

The evolution of Li isotopic signatures is very dependent on pH, because it depends on the balance between the amount of 6Li derived from the dissolution of pri-

mary minerals and the amount of secondary minerals involved in the selective uptake of 6Li . Assuming that dissolved CO_2 was the most relevant factor triggering pH changes in the early Martian environments [6], we have analyzed the influence of a CO_2 atmosphere on the rates of silicate dissolution. We modeled different situations including the effect of simultaneous evaporation and cooling, which are the two additional variables that affect supersaturation. Our results are presented in Figure 3.

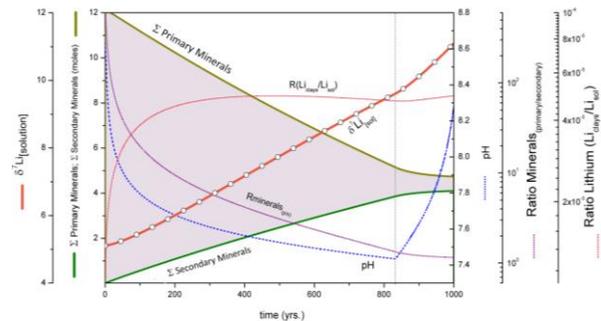


Fig.3. Balance between primary and secondary minerals in dependence of pH under evaporation and the resulting δ^7Li .

Conclusions: Considered together, the results reported here strongly suggest that the analysis of d^7Li trends in the sedimentary record of martian environments could be highly informative of the simultaneous role of evaporation and freezing in modifying the sequence of precipitation of secondary phases, and in the duration and intensity of pH fluctuations induced by episodic volcanic outgassing. In presence of atmospheric gases like CO_2 , the final pH value will depend on the interplay between the alkalinity, driven by the rate of dissolution of primary silicates, and the buffering effect of carbonate species. Hence, comparative analyses between the secondary minerals undergoing fractionation and those retaining the $\delta^7Li_{[water]}$ signature at the moment of crystallization (i.e., Li incorporated to sulfates) may provide important clues about the geochemical evolution of the surface of Mars.

References: [1] Fairén et al. (2009) *Nature*, 459, 401-404. [2] Fairén et al. (2011) *Nature Geosc.* 4, 667-670. [3] Decarreau, et al. (2012) *Geochim. Cosmochim. Acta* 85, 314-325. [4] Parkhurst, D. L., and C. A. J. Appelo (1999) *U.S. Geological Survey, Water-Resources Investigations Report* 99-4259, 312p. [5] Steefel et al. (2003) *J. Cont. Hydrol.* 67, 219-246. [6] Fairén et al. (2004) *Nature* 431, 423-426.