# LITHIUM ISOTOPE FRACTIONATION ANALYSES: AN UNEXPLORED STRATEGY TO TRACK THE WEATHERING OF BASALTS ON MARS.

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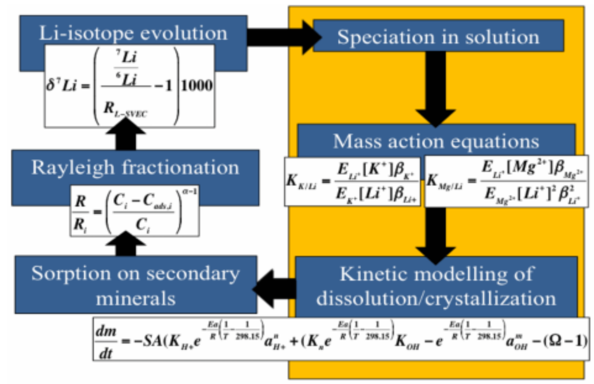
**Introduction:** Lithium (Li), the lightest of the alkali elements, has geochemical properties that include high aqueous solubility (Li is the most fluid mobile element) and high relative abundance in basalt-forming minerals (values ranking between 0.2 and 12 ppm). Li isotopes are particularly subject to fractionation because it is such a light element, and the two stable isotopes of lithium – $^7$Li and $^6$Li – have a relatively large relative mass difference (~15%) that results in significant fractionation between water and solid phases. The extent of Li isotope fractionation during aqueous alteration of basalt depends on the dissolution rate of primary minerals – the source of Li – and on the precipitation kinetics leading to formation of secondary phases. Consequently, a detailed analysis of Li isotopic ratios in solution and secondary mineral lattices could provide clues about past martian weathering conditions, including weathering extent, temperature, pH, supersaturation and evaporation rate of the initial solutions in contact with basalt rocks [1,2].

**Expected information from Li isotopes:** The selective incorporation of the lighter isotope 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 of pH and temperature [3]. In Earth's oceans, the actual steady-state for $\delta^7Li_{sw}$ physically represents the balance between the amount of Li dissolved and amount of Li trapped on the secondary mineral lattices. In the end, such a balance can be related to the ocean evolution towards a stationary pH, being that pH is the main factor influencing the kinetic control between dissolution and precipitation of silicates, according to the overall silicate-carbonate geochemical cycle. On Mars, presumably this evolution has been rather different than on Earth, subject to evaporation, sublimation and freezing, and probably never reaching a steady state for pH conditions.

**Modeling Li isotope fractionation:** In this work we discuss the different ways in which martian aqueous processes could lead to Li isotope fractionation, and their eventual incorporation into secondary minerals. We describe different case studies of Li isotope fractionation, and 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 [4]. A flow diagram of the modelling set-up is shown below:




**Strategies for future *in situ* analyses:** To perform an analysis of Li isotopes on Mars, future surface robotic explorers on Mars must contain an instrument payload capable of supplying all the relevant data, including: (1) an instrument that can perform selective mineralogical analyses, such as an x-ray diffraction (XRD) instrument; (2) an instrument capable of detecting trace amounts of Li in minerals, such as a LIBS instrument; and (3) an instrument that can perform selective isotopic analyses, including Li isotopes. Alternatively, sample collection and return missions being currently developed (such as Mars2020) may focus in the identification and collection of samples containing Li, which would eventually be analyzed in Earth laboratories. The minerals that would preferentially adsorb Li would be the main target for the prospect isotopic analysis.

**Conclusions:** The combination of Li isotope fractionation modeling and Li isotopic data obtained by future exploration of Mars is an unexplored strategy to understand basalt weathering processes and environmental conditions early in the planet's history.

**References:** [1] Vigier, N., et al. (2008), *Geochim. Cosmochim. Acta*, 72, 780-792. [2] Tang et al. (2007), *Int. Geol. Rev.*, 49, 374-388. [3] Ryu, J.-S., et al. (2014), *Geochim. Cosmochim. Acta*, 145, 103-115. [4] Fairén, A. G., et al. (2015), *Geochemistry, Geophysics, Geosystems*, in press.

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