

# Unraveling the History of Water on Mars using Lithium Isotope Fractionation Models

E.L. Adams<sup>1</sup>, C.G. Lozano<sup>1</sup>, L.G. Duport<sup>1</sup>, A.F. Davila<sup>2</sup> and A.G. Fairen<sup>3</sup>.

<sup>1</sup>Universidad de Vigo. 36200 Vigo. Spain, <sup>2</sup>SETI Institute, Mountain View, CA 94043, USA. <sup>3</sup>Department of Astronomy, Cornell University Ithaca, 14853 New York, USA.



Cornell University

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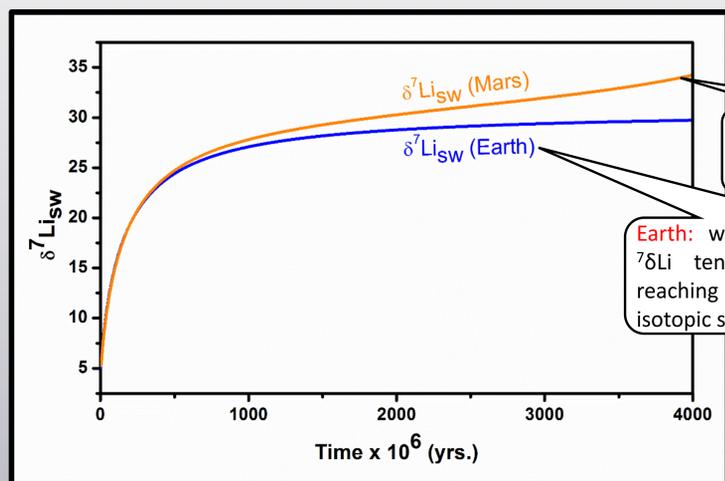


## Introduction

Lithium (Li) is incorporated as trace element in most basalt bearing minerals (1-200 ppm) [1]. Its isotopes are subject to fractionation as result of ion exchange processes between the basalt, water and secondary phases. Dissolution of basalt occurs according to a congruent mechanism that by itself does not cause an appreciable fractionation [2].

The selective incorporation of <sup>6</sup>Li to secondary minerals and the evolution through time of the Li isotopic signature reflect the interaction between chemical and physical weathering processes that are unequally affected by changes in 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 [3, 4] through reverse weathering processes.



**Mars:** with evaporation process. The <sup>7</sup>Li tends to increase over time.

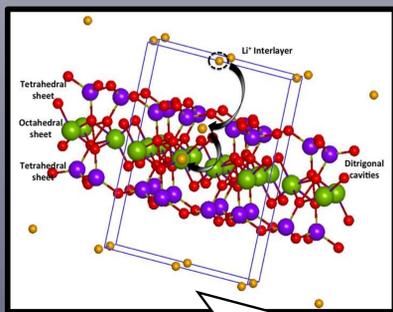
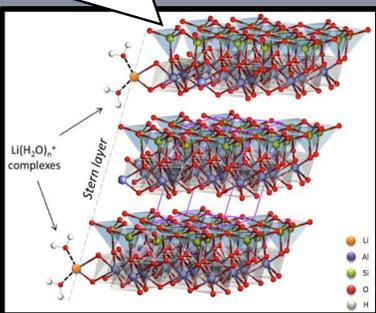
**Earth:** without evaporation process. The <sup>7</sup>Li tends to equilibrium over time, reaching a value near to the current isotopic signature, <sup>7</sup>δLi=+32.4‰.

## Modeling Li isotope fractionation into secondary mineral lattices

We assume an initial value of <sup>7</sup>δLi=5‰ for our models, that corresponds to the average isotopic signature of unweathered MORB basalts [1,5]. The selective incorporation of the <sup>6</sup>Li to secondary minerals follows a complicated behavior, involving either reversible adsorption or irreversible incorporation within vacant sites of the structural framework that can provide information about the duration, extent and conditions of aqueous interaction between primary minerals and water.

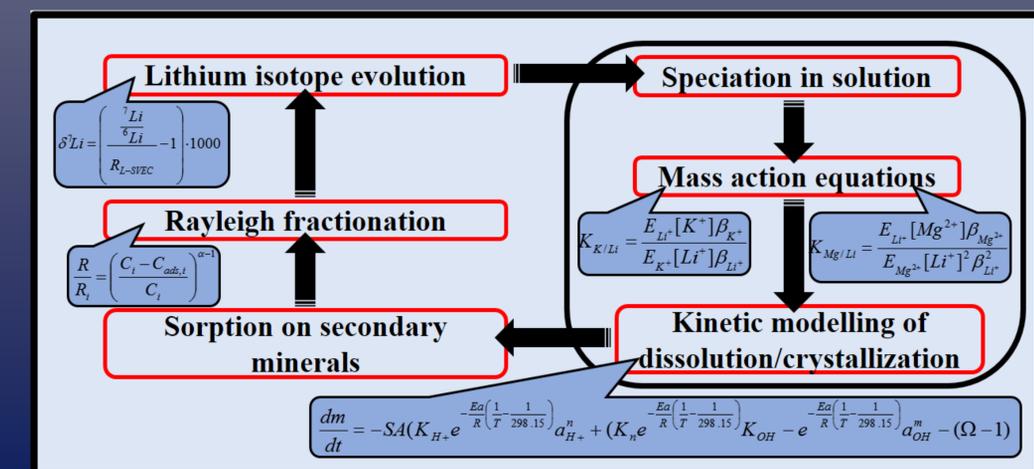
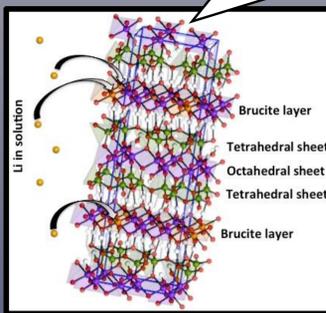
Uptake of Li-isotopes by secondary minerals occur:

**Kaolinite:** attracts external cations only by negative charges of terminal O<sup>2-</sup> ions exposed on the edges of the structural sheets.



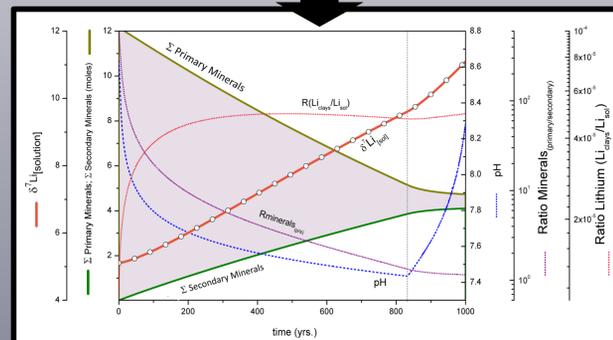
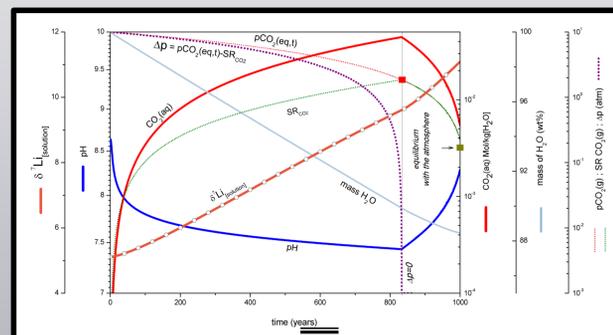
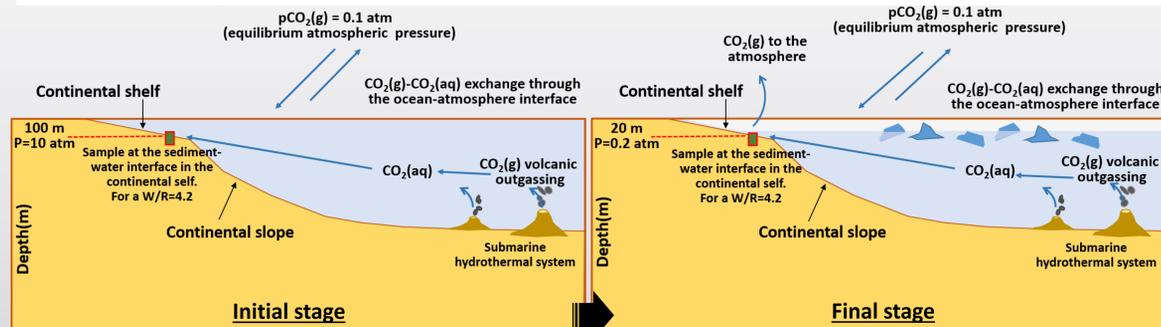
**Smectite:** (1) During the process of clay nucleation and crystal growth. (2) By migration from the interlayer to either octahedral position or to the ditrigonal cavities.

**Chlorites:** Lithium replaces Mg<sup>2+</sup> in the brucite layer.



## Case studies

We analyzed the evolution of <sup>7</sup>δLi in water and clay minerals resulting from basalt weathering under different physico-chemical conditions, including the presence of CO<sub>2</sub> derived from volcanic outgassing simultaneous to water evaporation and/or freezing. This is relevant to simulate the weathering of basalts on Early Mars and therefore can be useful to determine past environmental conditions.



In the absence of CO<sub>2</sub>, the pH is controlled by silica alkalinity through the precipitation of clays. But if CO<sub>2</sub> is present, the pH is controlled by carbonate alkalinity through the interplay between CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>=</sup> species.

### Geochemical scenario:

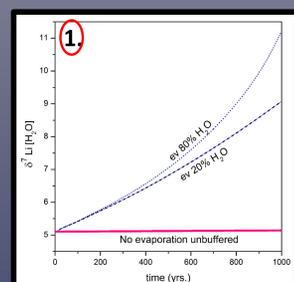
We analyzed the influence of a CO<sub>2</sub> atmosphere on the rates of silicate dissolution because we assume that dissolved CO<sub>2</sub> was the most relevant factor triggering pH changes in the early martian environments [6].

We assumed a continuous supply of CO<sub>2</sub> from volcanic/hydrothermal sources under simultaneous cooling and evaporation conditions, which are the two additional variables that affect supersaturation.

$$v_{CO_2 \text{ scape}}(t) = k (P_{eq}(t) - pCO_2(t))$$

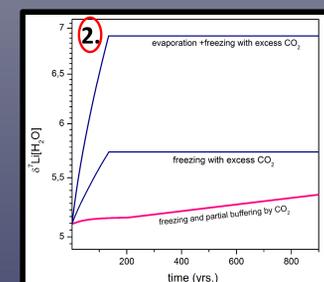
## Discussion

These plots illustrate the evolution of <sup>7</sup>δLi during basalt weathering as a function of the mechanisms that create supersaturation (evaporation and/or cooling) and volatiles that modify the pH (CO<sub>2</sub> or other volatiles). This controls the balance between silicate dissolution and secondary mineral precipitation.



### Lithium isotope fractionation pathways

- Starting from a process at 298 K, when supersaturation is created by evaporation of different amounts of water.
- Evolution in presence of CO<sub>2</sub>, when supersaturation is created either by cooling or simultaneously by cooling and evaporation.



## Conclusions

With our models, we show as different interplays of variables (pH, CO<sub>2</sub>, increase of ionic strength, etc.) influence the balance between primary and secondary phases, the amount of Li in solution or Li uptake by clays resulting in different lithium isotope fractionation pathways.

The application of our models to data obtained by future missions (e.g., lithium isotopic evolution in a sediment column) will contribute to decipher the geologic history and specifically the physico-chemical evolution of water on Mars.

### Acknowledgements

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### References

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