



Subject offered for a contract starting October 2017

## SUBJECT TITLE: **The chemical and isotopic behaviour of Lithium in glasses, melts and magmas**

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Financing: Doctoral contract with or without teaching assignment

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### Project Goal

This PhD project is aimed at exploiting Lithium based-tracers of magma evolution, especially during latest pre-eruptive stages, when strong degassing and extensive crystallization occur. The focus is on lithium isotopic fractionation behaviour between the residual melt-phase and the separated fluid phase feeding volcanic plumes or subsurface hydrothermal systems. The goal of this PhD project is pushing a step forward geochemical interpretation of magmatic degassing by investigating the effects of compositional and intensive variables (e.g.  $X_{H_2O}$  in the vapour, oxygen fugacity, chemical and structural state in the melt/glass phase, etc.) on the degree of lithium isotope fractionation in selected magmatic compositions (e.g., basalt and andesite) and also in corresponding and representative simple systems.

Results on Li isotope fractionation will be used to track and model pre-eruptive magmatic/volcanic processes due to degassing and crystallization on a selection of natural samples from a major volcanic suite.

Outcomes of this projects will also be relevant for Material Sciences and for the wide range of industrial applications based on lithium glass-ceramics (e.g., from the design of mirrors for telescopes in Astronomy, to the production of fire-resistant windows).

### Rationale

In Earth Sciences, lithium is the lightest alkali metal, but also one of the fastest diffusing elements in silicates. Many studies have shown that Li isotopes in the outer layers of Earth (hydrosphere, crust and lithospheric mantle) can be strongly fractionated owing to the large relative mass difference between its two isotopes,  $^6\text{Li}$  and  $^7\text{Li}$ . Indeed, observed Li isotope fractionation in the near-surface environment occurs in excess of 60‰. Lithium isotopic fractionation has been documented in a variety of geological processes, such as weathering, hydrothermal alteration, metamorphic dehydration and diffusion. In contrast, little isotopic fractionation is inferred to occur during high temperature igneous differentiation, be it in basaltic or granitic systems, even though they have not been extensively investigated.

It appears that typical HT processes of fractional crystallization do not appreciably affect the  $\delta^7\text{Li}$  signature inherited from its parent magma. When found, abnormal  $\delta^7\text{Li}$  values preserved in the ancient lithospheric mantle suggest modification via fluids/melts derived from recycled

oceanic crust. Similarly, a combination of prograde metamorphism and arrested kinetic Li isotopic fractionation associated with basaltic intrusions and variable protolith compositions are used to explain the variability observed in lower crust granulite xenoliths. Therefore, at temperatures of melting and crystallisation of mantle-derived magmas, Li isotopes do not show appreciable permil-level mass fractionation. Corroborating evidence of this was found upon examination of bulk rocks and olivine separated from basaltic lavas, which yield constant isotopic values. Therefore, studies of igneous systems have chiefly focused on the potential of Li isotopes as a geochemical tracer fingerprinting the cycling of Li derived from specific (low-temperature) sources through the solid Earth.

Nevertheless, early works on Li isotopes in crustal systems suggested that significant isotopic effects could be seen in evolving granitic suites, and proof was given for mass fractionation at near-solidus temperatures in such systems exists. The evidence that -i) large Li isotopic fractionations (up to 20‰) occur between minerals and hydrothermal fluids (e.g., in aqueous fluid-rich granitic pegmatite systems at relatively low temperatures) and that - ii) lithium is particularly sensitive to vapor transfer, either in shallow magma conduit shortly before eruption or during post-eruptive degassing of thick lava flows makes lithium an interesting tracer for volcanic processes. To assess the strong potential that lithium has to be an important tracer of magmatic degassing, two main issues have to be addressed quantitatively: -i) its solubility behaviour in volcanic gases and hence its gas-melt partitioning behaviour, and -ii) the associated isotopic fractionation between  $^6\text{Li}$  and  $^7\text{Li}$ .

In terms of the second aspect, few and contrasting data exist, depending on the considered phase assemblage. For example, in granite-H<sub>2</sub>O systems, heavy  $^7\text{Li}$  partitions preferentially into the gas/fluid phase, and the extent of such fractionation decreases with increasing temperature. Furthermore,  $^6\text{Li}$  diffuses faster than  $^7\text{Li}$ , thus large isotopic fractionation occurs during diffusion. These two types (equilibrium and kinetic) of isotopic fractionation may occur during magma degassing and provide precious information on late pre-eruptive degassing stages. In order to improve our knowledge on pre-eruptive phenomena, extensive investigation of lithium, particularly its isotopic behaviour, in volcanic and shallow igneous processes is necessary and here proposed.

### Experimental methods and techniques

- **Synthesis of glass chips.** This includes volatile-free and volatile-saturated systems (natural-analogs) and also simple systems, at different conditions (e.g., fO<sub>2</sub> and XH<sub>2</sub>O).
- **Crystal nucleation and growth** of feldspar and spodumene (simple systems)
- **Structural and crystal-chemical investigations.** Raman spectroscopy, Li NMR, XANES at the Li K-edge (CLS facility in Saskatoon Canada), Inelastic X-ray Scattering (IXS)
- **$^7\text{Li}/^6\text{Li}$  determination:** Ion microprobe on the glass+crystal material (in situ), and eventual adoption of TIMS and MC-ICP-MS techniques on bulk samples .