



Subject offered for a contract starting October 2018

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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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, with observed Li isotope fractionation in the near-surface environment 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.

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 hence the gas-melt partitioning, and -ii) its isotope fractionation between ^6Li and ^7Li .

For what concerns the second aspect, heavy ^7Li partitions preferentially into the gas/fluid phase (H_2O -rich) over the silicate rock/melt, and the extent of such fractionation decreases with increasing temperature. Furthermore, ^6Li diffuses faster than ^7Li , thus large isotopic fractionation occurs during diffusion. These two types (equilibrium and kinetic) of isotopic fractionation may occur during magma degassing.

Unlike gas-melt/rock in volcanic and shallow igneous processes, it appears that typical HT processes of fractional crystallization do not affect the appreciable $\delta^7\text{Li}$ signature inherited from the pristine rock system, such that abnormal $\delta^7\text{Li}$ values preserved in the ancient lithospheric mantle, typically showing a quite homogeneous $\delta^7\text{Li}$, suggest modification of fluid/melt derived from recycled oceanic crust. Similarly, combination of prograde metamorphism, arrested kinetic Li isotopic fractionation associated with basaltic intrusions and variable protolith compositions is used to

explain the variability observed in lower crust granulite xenoliths. It appears that at temperatures of melting and crystallizing mantle magmas, Li isotopes do not show permil-level mass fractionation. Corroborating evidences of this arise by examination of bulk rocks and olivine separates from basaltic lavas, which yield consonant isotopic values. Nevertheless, evidence for mass fractionation at near-solidus temperatures in granitic systems exists. Early work on Li isotopes in crustal systems suggested that significant isotopic effects could be seen in an evolving granitic system. Therefore, with the exception of these fractionation pathways, studies of igneous systems chiefly focus 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.

From the point of view of material science, Li is a very important component of glass-ceramics, which largest part found on the market are in fact lithium aluminosilicate glasses. Their success comes from the combination of several properties: transparency, zero or close to zero thermal expansion and the ability to withstand temperatures of the order of 700°C for hundreds of hours without modifications of their properties. This allows them to be the best-choice material for many applications ranging from astronomy (e.g., mirrors of telescope use (Zerodur® glass-ceramics manufactured by Schott) to consumer products such as cooktops and cooking ware or fire-resistant windows.

Lithium is also an important industrial metal and is mainly used as sacrificial anodes in batteries for its high electrochemical equivalent and low electrochemical potential, but it is also used as a reducing agent in organic chemistry and in the synthesis of vitamins.

Objectives of the PhD

We foresee PhD projects and research proposals aimed at –i) studying the role of lithium in glass, melts and glass-ceramics, -ii) assessing the lithium abundance and isotope fractionation in glass, melts and magmatic systems and –iii) using Li isotope fractionation to follow and better understand magmatic/volcanic processes due to crystallization and degassing.

Experimental methods and techniques

- Glasses and material synthesis. This includes both simple and natural-analog systems, as well as volatile-free and volatile-saturated systems, the latter to extract Lithium in the final gas phase.
- Viscosity measurements, crystal nucleation and growth, with emphasis on spodumene (simple systems) and feldspar.
- Raman spectroscopy
- Li NMR
- XANES at the Li K-edge at CLS, Saskatoon Canada
- Inelastic X-ray Scattering (IXS) to obtain lithium K-edge spectra at high temperatures in order to determine change and evolution in the Li environment as a function of temperature
- Ion microprobe to measure $^6\text{Li}/^7\text{Li}$ in the glass+crystal material (in situ)
- Eventual adoption of TIMS and MC-ICP-MS techniques on bulk samples . Because the gas phase of the volatile-saturated systems will not be directly characterized, this would allow establishing Lithium elemental and isotopic fractionation by mass balance with respect to initial contents. It will also allow precise comparison with L-SVEC standard)