

## Alternative Anions: Exploring the negative side of geochemistry

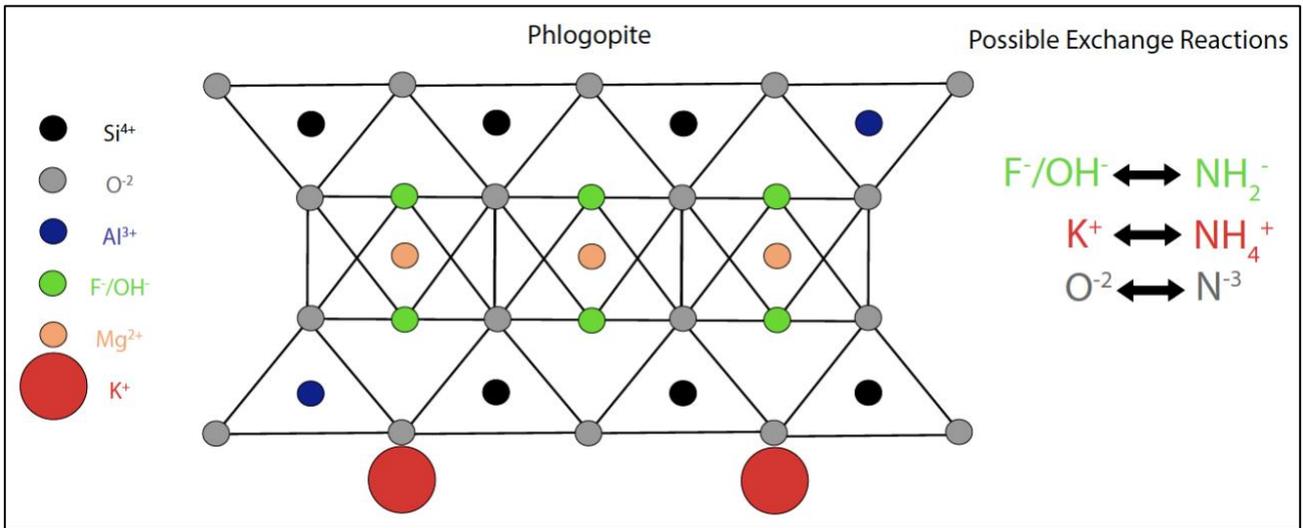
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<b>Key Words</b>	<ol style="list-style-type: none"> <li>1. The Deep Volatile Cycle</li> <li>2. NMR Spectroscopy</li> <li>3. Atmosphere-formation</li> </ol>
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### Broad Overview

One of the ultimate goals in science is to illuminate the processes responsible for the development of habitable conditions on Earth, and this project will provide fundamental constraints on the storage, cycling, and release of important biologically-active elements to Earth's surface environment. Achieving this ambitious goal requires an understanding of the physical-chemical controls on the development of habitability on the planet's surface, sub-surface, and marine environments. In this regard, the chemical nature of biologically-significant elements like fluorine, chlorine, and nitrogen are paramount. Their addition to a planet's surface is the result of both surficial and subsurface processes, including weathering and meteoritic influx, but are primarily added through volcanism. Therefore, how these elements are stored within rock-forming minerals is information essential to understanding how their chemical activity varies through time, and their provenance in Earth's formative years, as life got started.

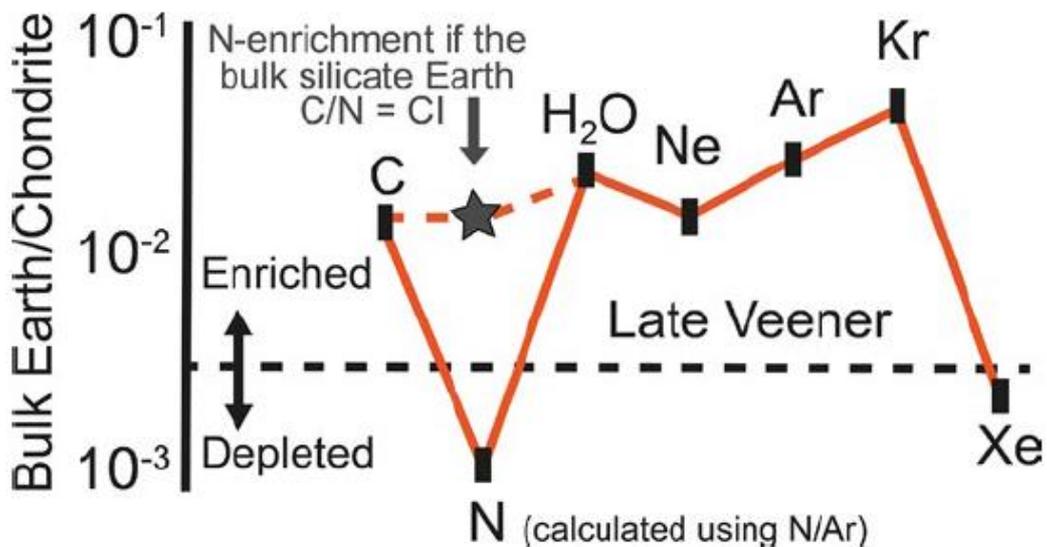
### Introduction

All science is built upon experiments, observations, and assumptions. **One such assumption, in the field of geoscience, is that the negative charge-balance for most rock-forming minerals is provided by oxygen anions.** However, there is a wealth of data from experimental and natural samples which shows that the most abundant minerals on Earth can contain other anions – such as fluorine, chlorine, and nitrogen (see [Joachim et al., 2017](#); [Li et al., 2013](#)). Noteworthy, these anions are not benign – they are important elements involved in the modulation of Earth's climate, and the origin of life itself. The anions in question have similar ionic radii to oxygen, and therefore can fit in the same site within a crystal lattice. However, they are also highly reactive and can, thus, form several compounds which can substitute for other elements within a crystal lattice (see Figure 1, with nitrogen as an example).



**Figure 1. Conceptual model showing the possible exchange reactions (substitutions) for N species within the mineral phlogopite.**

Excitingly, the incorporation mechanisms for these dynamic (redox- and pH-sensitive) elements are largely unknown (see [Joachim et al., 2017](#); [Li et al., 2013](#)). One can creatively apply the laws of thermodynamics to propose a wide-range of possibilities involving a vast array of substitution mechanisms, but this will not provide a solution beyond reasonable doubt. For example, many workers have tried to explain the occurrence of Cl<sup>-</sup> and F<sup>-</sup> in olivine and orthopyroxene (the most abundant minerals on Earth), but this has been to no avail because there are several possible substitutions mechanisms including [F<sub>2</sub>]<sup>2-</sup> → [MgO<sub>2</sub>]<sup>2-</sup> or [F<sub>4</sub>]<sup>4-</sup> → [SiO<sub>4</sub>]<sup>4-</sup> (i.e., [Bernini et al. 2013](#); [Crépeisson et al., 2014](#)). Furthermore, [Dalou et al. \(2012\)](#) and [Beyer et al. \(2012\)](#) explain correlations for Al<sup>3+</sup> vs. F<sup>-</sup>/Cl<sup>-</sup> due to a proposed equilibrium where the substitution of F<sup>-</sup>/Cl<sup>-</sup> exchanging for O<sup>2-</sup> is balanced by Al<sup>3+</sup> exchanging for Si<sup>4+</sup>. In addition, there exists a missing nitrogen conundrum – where some workers consider nitrogen to be the most depleted of the volatile elements (see [Zerkle & Mikhail, 2017](#) – Figure 2). One of the problems here is that nitrogen can (conceptually) partition in a silicate mineral (i.e., phlogopite) in multiple ways: i.e., NH<sub>4</sub><sup>+</sup> → K<sup>+</sup>, NH<sub>2</sub><sup>-</sup> → OH<sup>-</sup>, or N<sup>3-</sup> → O<sup>2-</sup> (Figure 1). Importantly, the substitution mechanisms outlined above are all physically plausible, possible, probable, and quantifiable (at the University of St Andrews).



**Figure 2: The Cl chondrite-normalized estimated abundances of H, C, N, and noble gases in the bulk Earth (from [Zerkle & Mikhail, 2017](#)).**

## Open Questions

- Is the depletion of nitrogen shown in Figure 2 real, or does it imply a hidden reservoir yet to be quantified (i.e., [Zerkle & Mikhail, 2017](#))?
- What proportion of Earth's halogens were accreted to Earth during the late veneer vs. lost during the moon-forming impact (i.e., [Clay et al., 2017](#))?
- What is the total inventory of volatile elements in the bulk silicate Earth, and core (i.e., [Marty, 2012](#))?

These are tangible problems, with multiple plausible solutions, conceptually-speaking. The approach here is to constrain how these elements are bound within mineral phases, and the controls on their incorporation. These data would permit accurate calculations for their partitioning behaviour and storage capacities.

### **The specific scientific objectives for this Ph.D. project are as follows:**

[1] Constrain the incorporation mechanism for nitrogen in phlogopite, phengite, and other K-rich phases (where nitrogen is presumed to be present solely as  $\text{NH}_4^+$  ions).

[2] Constrain the incorporation mechanism for F, and Cl in (experimentally-derived) ferromagnesian phases (i.e., olivine and clinopyroxene), and silicate melts.

## Methodology and Facilities

Dr Mikhail manages the Mineral Synthesis Facility hosted in the School of Earth and Environmental Science. This facility comprises of a [Rockland 250-tonne piston-cylinder press](#) and two [Daltech controlled-atmosphere furnaces](#). This facility is capable of simulating pressure and temperature conditions ranging from 0 to 4.5 GPa and 100 to 1800 °C. This equates to the conditions of the atmosphere to a depth of ca.150 km within planet Earth. Prof Ashbrook manages the University solid-state NMR facility, alongside an active research group. This NMR facility hosts two [Bruker Avance III spectrometers \(600 MHz and a 400 MHz\)](#), equipped with a range of double- and triple-resonance probes capable of spinning rates from 5 kHz to 65 kHz. Prof Ashbrook also has access to a local computing cluster and has contributed significantly to the [University's Kennedy cluster](#). The University of St Andrews also hosts the electron microscopy facility comprising of [FEI Microscopes Titan Themis STEM](#), [Scios Dualbeam FIB](#), [Jeol Microscopes JEM-2011 TEM](#), [JSM 5600 SEM](#), and a [JSM-6700F SEM](#).

## Timeline

**Year 1:** Sample selection and expansion of the ongoing method development. Constraining the petrography, petrology, and geochemistry of the sample suite.

**Year 2:** Begin the quantification for the nature of lattice-bound F, Cl, and N for a suite of characterised materials. Present results at international meeting (Goldschmidt) and a national meeting (Geochemistry Group Research in Progress).

**Year 3:** Continue the quantification for the nature of lattice-bound F, Cl, and N – following the most promising data. Experimentally constrain the physical and chemical controls in the most exciting system (i.e., effect of  $\text{H}_2\text{O}$ ,  $f\text{O}_2$ , Pressure, Temperature). Present results at international meeting (Goldschmidt) and a national meeting (Geochemistry Group Research in Progress).

**Year 3.5:** Finish loose ends and write thesis.

## Student Training and Support

This programme of research and development will provide the St Leonard's College Interdisciplinary Doctoral Student with training in petrology, geochemistry, and solid-state chemistry. The student will be a member of the Mikhail and Ashbrook research groups and will have desk and lab space in in each area to ensure full integration in each subject. The student will also become a member of the St Andrews Centre for Magnetic Resonance, through which they will be able to meet with PhD students from different schools across the University and present their work annually. The student will be trained in spectrometer operation by Dr Dawson, in computation work by Professor Ashbrook. Drs Mikhail and Mare will train the student in the experimental petrology laboratory and in the electron microscopy facility. The student will have the opportunity to improve their transferrable skills in several ways, including but not limited to; the option to attend the university courses run by CAPOD, external research workshops, and presentations at group meetings. The latter meetings, both in Earth Sciences and Chemistry, will enable the student to improve at communication of the interdisciplinary research to a less specialist and more diverse audience. The student

will also be expected to attend national and international meetings in both research fields, presenting posters and, where possible, giving oral contributions.

### **References & Further Reading**

Bernini et al. (2013) Partitioning of halogens between mantle minerals and aqueous fluids: implications for the fluid flow regime in subduction zones. *Contributions to Mineralogy and Petrology*

Beyer et al. (2012) Fluorine in nominally fluorine-free mantle minerals: experimental partitioning between olivine, orthopyroxene and silicate melts with implications for magmatic processes. *Earth and Planetary Science Letters*

Clay et al. (2017) Halogens in chondritic meteorites and terrestrial accretion. *Nature*

Crépeau et al. (2014) Clumped fluoride-hydroxyl defects in forsterite: implications for the upper mantle. *Earth and Planetary Science Letters*

Dalou et al. (2012) Experimental determination of F and Cl partitioning between lherzolite and basaltic melt. *Contributions to Mineralogy and Petrology*

Joachim et al. (2017) Effect of water on the fluorine and chlorine partitioning behaviour between olivine and silicate melt. *Contributions to Mineralogy and Petrology*

Li et al. (2013) Nitrogen solubility in upper mantle minerals. *Earth and Planetary Science Letters*

Marty, B. (2012) The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. *Earth and Planetary Science Letters*

Zerkle & Mikhail. (2017) The geobiological nitrogen cycle: From microbes to the mantle. *Geobiology*

### **Further Information**

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