Volatile element and critical metal cycles beneath the Greenland Craton

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Overview
Critical metals, such as Hf, Nb REE, underpin modern technologies and are mined from mantle-derived igneous rocks. However, the geological processes in the mantle that precede the formation of such deposits remain poorly constrained. This project will develop nitrogen isotopes in alkaline igneous rocks as a novel tracer of processes in the mantle that precede the formation of ore deposits of critical metals using Greenland as an example.

It is well known that isotopic systems in mantle-derived samples can originate from distinct sources. Recent evidence from Greenland has shown Archaean isotope signatures in Hf (Finch et al. 2019) and S (Hutchison et al. 2019) isotopes trapped in mantle melts from the mid-Proterozoic Gardar Province. These data suggest that elements, including critical metals, were subducted into the mantle during the Archean and have become involved in ore formation. In other words, rift-related magmatism in the Gardar Province accessed a mantle source which has previously been enriched (‘fertilised’) by subducted crust (Figure 1). It is likely that such recycling processes from crust to mantle and back up significantly improve the likelihood of forming a critical metal deposit. Besides shedding light on the formation of an important natural resource, this model also implies that analyses of alkaline rocks provides insights into the dynamic cycling of important elements in the deep Earth and the mechanics of their concentration in the sub-continental lithospheric mantle (Mikhail et al., 2019; Hutchison et al., 2019), including the remarkable preservation of primordial isotopic signatures (Hallis et al., 2015).
This project will reconstruct the sub-lithospheric nitrogen cycle, which has a conspicuous potential to fingerprint volatile sources from either subducted sediments, the Earth’s mantle or primordial (plume-related) sources. Nitrogen is important because each source has a distinct isotopic signature; crustal ($\delta^{15}$N values $> 0$‰ since at least 2.5 Ga), mantle ($\delta^{15}$N values $-5\pm3$‰) and primordial ($\delta^{12}$N values $< -20$‰), and we know the SCLM samples all three via the data sourced from mantle diamonds (see Mikhail et al., 2014 for an overview). Nitrogen is rarely employed due to the difficulty in measurements. However, the one study of alkaline igneous rocks from Kola (Dauphas & Marty 1999) provided tantalising results that hinted at recycling of surface nitrogen. Technological advances at St Andrews, including a bespoke gas-line and mass spectrometer set-up, allow us to measure routinely N concentrations and isotope ratios at abundances <10 ppm. The development of instrumentation alongside the development of hypotheses at St Andrews allows nitrogen for the first time to be used to advance our understanding of geological element cycles through space and time.

**Methodology**

This programme of research builds on recently published work by the PhD supervisory team (e.g. Hutchison et al., 2019) and will examine several suits of alkali- and carbon-rich igneous rocks to illuminate the coupling (or lack thereof) between the cycling of critical metals alongside carbon and nitrogen in the deep Earth.

The samples in this study represent a range of mantle-derived melts of different ages sourced across the Greenland craton. Further fieldwork in Greenland will bolster the sample cache. This student will apply major and trace element geochemistry alongside stable and radiogenic isotopic tracers ($^{12}$C/$^{13}$C, $^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O, $^{34}$S/$^{32}$S) to establish the mechanisms responsible for the formation and destruction of cratons, using the Gardar province as a case study. The chapter breakdown is envisaged as described below:
1. Samples. St Andrews has one of the most comprehensive sample archives of rift-related magmatism globally, and it has a particularly comprehensive samples suite for the Greenland craton. Nevertheless, fieldwork in the Nanortalik region of Greenland is envisaged as part of the project to boost sample suites through collection of palaeoproterozoic sediments and granitoids which represent samples of Pre-Gardar subducted material.

2. Petrography, major and trace element geochemistry of the samples alongside stable and radiogenic isotope data \((^{13}\text{C}/^{12}\text{C}, \, ^{15}\text{N}/^{14}\text{N}, \, ^{18}\text{O}/^{16}\text{O}, \, \text{S})\) will be used to ascertain the similarities and differences for the source(s) of alkali and carbonatitic sample suites using state-of-the-art laboratories hosted by the St Andrews Stable Isotope Group (STAiG) with methods described in Mikhail et al. (2014), Hutchison et al. (2019), Stüeken et al. (2015). The application of multiple volatile isotopes will be a novel and illuminating approach to studying alkaline igneous systems.

3. The project will focus initially on the Gardar Province of South Greenland to constrain N isotopes across the duration of rifting and across the rift province. Hf isotopes hint at an evolution of the mantle source during rifting with Archaean sources more prevalent at the onset of rifting. Existing S, Nd and Hf isotope data for the Gardar will complement the new N, C, O datasets. Once this has been fully characterised, we will move on to explore the mantle signatures beneath Greenland as a function of time from 3 Ga (Tupertalik carbonatite) to 0.17 Ga (Qeqertaasaq carbonatite).

4. Collectively, these thesis chapters/papers will allow the student to chart, describe, and model the evolution of carbon, and nitrogen isotope systems in the sub-continental lithospheric mantle under Greenland as a function of geological time. It will provide key insights into global element cycling and role this may have in fertilising the mantle prior to the formation of critical element-rich mantle melts.

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**Timeline**

Year 1: Initial training in isotope ratio mass spectrometry, SEM, and LA-ICP-MS. Sample characterisation and filtering using optical petrography and SEM. Summer of 1st year: Field season to bolster sample suite (Southern Greenland). Samples from the Gardar Province of Greenland.

Year 2: C-N-O-S stable isotope analysis of selected samples (STAiG). Present results at national meeting (Volcanic and Magmatic Studies Group 2021, Manchester, UK). Analysis of material from elsewhere in Greenland.

Year 3: Further stable isotope work on the new selected samples (STAiG). Present results at international meeting (Goldschmidt 2022, Chicago, Illinois, USA).

Year 3.5: Write, submit, and defend Ph.D. thesis.

**Training & Skills**

This IAPETUS2 DTP project will provide training in petrology, stable isotope geochemistry, and geochemical modelling. The focus on petrological characterization of minerals, advanced analytical isotope ratio geochemistry, and the formation of an economically profitable
resource (diamond) will provide the student a skill-set to competitively acquire postdoctoral research positions, or to transition from an academic to industrial/economic career upon completion of their Ph.D. degree.

Examples of analytical skills include scanning electron microscopy, laser-ablation ICP-MS, coding with Python, gas-sourced isotope ratio mass spectrometry (STAiG). Training will be provided on a continual basis throughout the PhD. Skills development will be monitored and delivered by the supervisory team.

References & Further Reading


Mikhail et al. (2014) Constraining the internal variability of carbon and nitrogen isotopes in diamonds. Chemical Geology

Mikhail et al. (2019). A secretive mechanical exchange between mantle and crustal volatiles revealed by helium isotopes in $^{13}$C-depleted diamonds. Geochemical Perspective Letters


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