Constraining the Earth’s Nitrogen Flux through the Subduction Factory

The University of St. Andrews
In partnership with Durham University

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Key Words
1. Subduction Zone Geochemistry;
2. Atmospheric-Evolution;
3. Stable Isotope Geochemistry
4. The Deep Volatile Cycle

Overview

Introduction

All else equal, if Earth’s atmosphere was of a different mass, then the planet might be too hot, or too cold, to stabilise surficial oceans of liquid water [1], and this directly relates to whether Earth would be habitable, or not. There are two dominant phenomena which have the power to systematically influence the mass of a planet’s atmosphere over geological time – life, and plate tectonics (see [2] for a discussion). Importantly, the biosphere is not a significant reservoir of N because the ratio of surficial N (biosphere + sediments + hydrosphere) to atmospheric N is only ~0.0001 [3], but biomass burial and subduction over geologic timescales may constitute a significant flux of N from the Earth’s surface into the mantle. The lower upper mantle – alone – has a nitrogen storage capacity ranging from 20-50 times the mass of N in the atmosphere [4], meaning the upper mantle is a significant reservoir. Importantly, Earth’s nitrogen reservoirs are intimately connected by plate tectonics with an unknown flux. In short, plate tectonics is a dynamic 4-D phenomenon resulting in continually forced chemical disequilibrium between the mantle and surface. Plate tectonics drives the N cycle in two ways: (1) it is responsible for ca.90% of Earth’s volcanism which adds C, H, and N to the surface, and (2) it forces surficial material back into the mantle via subduction zones, which removes C, H, and N from the surface. On a planetary-scale, the ratio of this in-out processes is known as the surface–mantle flux. For nitrogen, this flux is poorly constrained (see Fig.1).

Figure 1: Conceptual model of the evolution of the atmospheric N₂ reservoir. A steady decrease would be supported by low abundances of nitrogen in ancient rocks, a steady increase is indicated by some paleobarometric data. See Zerkle & Mikhail [5] for a discussion.

Nitrogen Cycling

As shown in the cartoon below (Fig.2), Nitrogen has two dominant behavioral styles in the mantle wedge. In short, nitrogen will either behaves like a noble gas (i.e. like Ar, as N₂ or NH₃), or it can behave like a large ion lithophile element (i.e. like K⁺, as NH₄⁺). This means the behavior of nitrogen in arc systems is difficult to predict.
However, nitrogen has 2 stable isotopes — $^{15}$N and $^{14}$N — and the surface reservoirs show a different $^{15}$N/$^{14}$N ratio when compared with the mantle (Fig.3). This means that we can use the $^{15}$N/$^{14}$N ratio of arc gas, magma, and lava to constrain how much crustal nitrogen contributes towards arc volcanism. This is what is required to determine Earth’s tectonic nitrogen flux.

**Figure 2.** Conceptual model showcasing the pathways nitrogen can follow during subduction (from Mikhail et al. [7]).

**Figure 3.** Histogram for the nitrogen isotope values of the mid-ocean ridge basalt vs. sedimentary rocks (oceanic).

**The Lesser Antilles**

This PhD project will use the Lesser Antilles arc system as a case study. The aim will be to assess the degree to which nitrogen isotopes can trace subducted crustal nitrogen through a single arc system. The Lesser Antilles has been targeted because the flux of sediments to the arc volcanism is relatively well-constrained – based on traditional isotopic tracers (i.e. Nd & Pb [6]).

**Primary Objectives (PhD Thesis chapters)**

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

[1] Constrain the nitrogen geochemistry of the material subducted beneath Lesser Antilles arc

[2] Constrain the nitrogen geochemistry of the material erupted from the Lesser Antilles arc

[3] Evaluate the usefulness of nitrogen isotopes and N/K ratios as tracers for subducted material at the Lesser Antilles arc compared with other isotopic systems (i.e. Nd & Pb – from published data [i.e. 6])


**Approach**

**Sample characterization.** Major and minor element abundances will be investigated (where required) using X-Ray florescence spectroscopy, electron microprobe, and laser-ablation ICP-MS (Univ. St Andrews and Durham, respectively). This will target whole rock, specific mineral phases (i.e. K-rich phases) and melt-inclusions (where applicable).

**Isotopic Analysis.** For nitrogen isotope determinations, we will employ the sealed-tube combustion technique [8]. This involves a bespoke gas-line attached to a MAT253 (ThermoFischer) isotope ratio mass spectrometer (Univ. St Andrews).

**Methodology**

The student will utilise several analytical methodologies at the host and partner institutions to extract data from natural samples, listed below:

- Gas-line Geochemistry and Gas-Sourced Mass Spectrometry (St Andrews)
- Laser Ablation ICP-MS (St Andrews & Durham)
- Electron microprobe (St Andrews)
- X-Ray florescence spectroscopy (St Andrews)
- Infrared spectroscopy (St Andrews)

**Timeline**

**Year 1:** Sample selection and expanding on the ongoing method development for the sealed-tube combustion technique applicable to the samples in this project. Constraining the petrography, petrology, and geochemistry of the sample suite.

**Year 2:** Constrain the nitrogen geochemistry of the material subducted beneath Lesser Antilles arc. Present results at international meeting (Goldschmidt) and a national meeting (VMSG).
Year 3: Constrain the petrology and nitrogen geochemistry of the material erupted at Lesser Antilles arc. Calculate the nitrogen flux of the Lesser Antilles arc system (and the associated uncertainties), and evaluate of the usefulness of nitrogen isotopes as tracers for subducted material at the Lesser Antilles arc compared with other isotopic systems (i.e. Nd & Pb – from published data [i.e. 6]). Present results at international meeting (Goldschmidt) and a national meeting (VMSG).

Year 3.5: Complete analyses and write thesis.

Training & Skills
This IAPETUS DTP project will provide training in petrology and stable isotope geochemistry, and the data generated will be focused on explaining the Earth’s total volatile fluxes (biased towards nitrogen).

The student will also attend training workshops on micro-analysis (at Bristol University, UK) and isotope geochemistry (with supervisory team).

The focus on petrological characterization of rock and minerals, advanced isotope geochemistry, and geochemical modelling will provide the student a skill-set to competitively acquire postdoctoral research positions, or to transition from an academic to industrial career in mineral resources, or analytical chemistry.

References & Further Reading

Further Information
For further information please contact Dr. Sami Mikhail (sm342@st-andrews.ac.uk).