Climate-changing volcanic eruptions from magma source to ice core archives: a sulphur isotope perspective

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Key Words
volcanoes, ice cores, geochemistry, climate

Overview
Explosive volcanic eruptions loft prodigious quantities of ash, gas and aerosol into the Earth’s atmosphere and can have severe impacts on human health, the environment and the global economy. A detailed record of past volcanic events is critical for improving societal resilience to future eruptions, and of all the surface archives available to Earth Scientists it is the polar ice cores which preserve the finest time-resolved record of past volcanic events.

The key challenge with the ice core record of volcanism is that most analytical techniques fail to provide detailed information about the eruptive style (plume height) and source location (parameters that are essential for evaluating climate impacts). One new and promising tool for fingerprinting plume height and source location is sulphur isotope analysis of ice core sulphate deposits (Figure 1). These analyses can be used to confirm whether the sulphate was formed in the stratosphere (e.g. Baroni et al., 2007) and provide information on the spatial separation between stratospheric and tropospheric aerosol clouds (which is strongly linked to source location, Burke et al. 2019). However,
though the technique has immense potential there is only a qualitative understanding of the atmospheric chemical processes that generate these unique isotope signals because no previous studies have carefully assessed plume isotope evolution from the eruptive source to the ice sheet deposition (Gautier et al., 2018).

This project will focus on carefully calibrating and validating these methods for well-known contemporary eruptions, and will compare and contrast the sulphur isotope signatures of two of the largest eruptions in recent history: the 1875 Askja (Öskjuvatn Caldera) eruption (Iceland), cataclysmic 1815 Plinian eruption of Tambora (Indonesia). These events will provide a fascinating contrast because their magma composition, eruption style and location is fundamentally different. The Askja eruption had significant regional impacts, while the Tambora eruption caused prolonged Earth surface cooling and had global impacts (Sigl et al. 2015).

The main objectives of this project are:

1) **the sulphur isotope values of the magma source.** To understand how atmospheric chemical processing of the plume affects its isotope composition, it is important to constrain the initial $S$ isotope value for these eruptions. To achieve this, we will undertake detailed petrography and microanalysis of volcanic eruption deposits to constrain $S$ speciation, concentration and isotopes in pre-eruptive melts, $S$-bearing minerals (apatite) and use this to reconstruct $S$ isotopes in co-existing gas phase (e.g. McKibben et al. 1996).

2) **Create high temporal resolution records of plume fallout using ice core records.** To fully understand the time-evolving plume chemistry, ice core records will be analysed for quadruple sulphur isotopes using new MC-ICP-MS methods (under active development at St Andrews, Burke et al. 2019). These measurements will provide isotope fingerprints for the key eruptions (at bi-monthly resolution) and will be used to evaluate the proportions of tropospheric to stratospheric sulphate deposited through time (Martin, 2018).

3) **Calibrate and validate models of the isotopic evolution of volcanic plumes.** Having generated detailed isotopic constraints on the plume sources (Objective 1) and high temporal resolution records of their evolution and fall out (Objective 2), the final goal of the project is to use isotope modelling to link these measurements and quantify isotope fraction in an evolving volcanic plume. We will use existing photochemical models (e.g. Claire et al. 2014) to simulate plume dispersal and track the redistribution of $S$ isotopes as a consequence of both photochemical oxidation and distillation processes.

The overarching goal of the project is to unite the time resolved model predictions with the new source and ice core isotope measurements. Evaluating model findings in this way will provide a powerful demonstration that our understanding of the processes that generate and preserve volcanic sulphate isotope signals for these key eruptions is sound.

We expect the project to be of wide significance to volcanology and ice core science communities. The project will yield fascinating insights into the magmatic processes that took place at Askja and Tambora and initiated these climate-changing eruptions. It will also be one of the first attempts to quantify the atmospheric processes that modify the erupted
S isotope signal and will provide an invaluable template for future investigations of unknown eruption ice core signals.

Figure 2. The Öskjuvatn Caldera lake (background) formed during the 1875 Askja eruption (A) and the 1815 eruption of Tambora (B) had profound environmental and societal impacts and will be the targets of this study (images by NASA and Henrik Thorburn, CC BY 3.0).

Methodology

Objective 1:
- Fieldwork and physical volcanology to collect and carefully characterize samples (the project will include at least one dedicated field campaign to Indonesia and/or Iceland)
- Petrography and SEM analysis of igneous textures in thin section
- Electron microprobe analysis of matrix glass, melt inclusions and S-bearing minerals (e.g. sulphides and apatite)
- X-ray absorption near-edge structure (XANES) spectroscopy to constrain the valence states of S in minerals and glasses (Diamond Light Source, UK)
- In-situ S isotopes of selected melt inclusions and S-bearing minerals by SIMS (at the Edinburgh Ion Micro-Probe Facility, EIMF).

Objective 2:
- Multiple S isotopes of ice core sulphate deposits measured by MC-ICP-MS (at the University of St Andrews in the STAiG laboratories).

Objective 3:
- Isotope fractionation and mass balance modelling to evaluate S isotope evolution and speciation in the melt, mineral and gas phase.
- Photochemical modelling to evaluate oxidation reactions and distillation processes, and predict the isotopic evolution of the aerosol fall-out

Timeline

Year 1: Literature review, fieldwork in Iceland and/or Indonesia, petrographic analysis followed by electron microprobe analysis of glass and mineral phases. Training in clean laboratory methods and multiple S isotope analysis of ice core sulphate by MC-ICP-MS at St Andrews. Development of proposals for SIMS and XANES analysis.
Year 2: SIMS analysis of S isotopes in minerals and melt inclusions in close collaboration with experts at EIMF (project partner Dr Cees-Jan de Hoog). XANES spectroscopy to assess valence states of S in glass and S-bearing minerals. Analysis of new data, and draft initial paper(s).

Year 3 to 3.5: Isotope mass balance modelling to evaluate S accumulation and release from the key eruptions. Photochemical modelling to interrogate the ice core signals and link these to S oxidation pathways and plume distillation. Finalize written manuscripts and write thesis.

Training & Skills

This project would suit a student with an excellent BSc/Msci geoscience background and interests in magmatic processes, igneous petrology and geochemistry. Previous laboratory and field work experience is advantageous but not essential.

The student will gain significant new expertise in physical volcanology, climate science, atmospheric chemistry, and isotope geochemistry (working with experts in this field, e.g. Hutchison et al. 2019; Humphreys et al. 2019; Burke et al. 2019 and Claire et al. 2014). They will be trained in all key technical areas (SEM, EPMA, SIMS, XANES, MC-ICP-MS, and modelling) and will be involved in developing proposals for national facilities (e.g. Diamond Light Source). They will also gain transferable skills such as scientific writing, statistics and data analysis, and problem-solving, as well as time management and working towards a long-term goal.

The student will join a burgeoning volcanology group at the St Andrews and will benefit from interactions with this vibrant and supportive team. They will also form strong collaborations with the Durham Volcanology Group and will make frequent exchange visits to discuss their results and tap into the diverse range of volcanological expertise offered by this group. They will be encouraged to attend major international conferences (e.g. AGU Fall meeting, San Francisco) and will be fully supported in forming international research networks with volcanology and ice cores science communities.

References & Further Reading

Martin, Geosciences 8, 198, 1–19 (2018)

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