

## Improved understanding of the behaviour of mercury and other trace metals in basaltic magmas

### Supervisory Team

- Prof. Tamsin A. Mather  
[www.earth.ox.ac.uk/people/mather](http://www.earth.ox.ac.uk/people/mather)
- Prof. Bernie J. Wood  
[www.earth.ox.ac.uk/people/bernie-wood](http://www.earth.ox.ac.uk/people/bernie-wood)
- Prof. David M. Pyle  
[www.earth.ox.ac.uk/people/pyle](http://www.earth.ox.ac.uk/people/pyle)

### Key Words

Magmatic processes, Environmental effects, Ore formation

### Overview

Mercury (Hg) is one of the most important global pollutants circulating in the present-day Earth's ecosystem. Methylmercury is highly neurotoxic, damages the central nervous system, and is highly dangerous for its development. Anthropogenic Hg was recently regulated under the Minamata Convention. The amount of Hg from natural sources is probably close to anthropogenic levels and the amount of Hg released by the degassing of active volcanoes is one of the major components of this flux. Hg has also recently been proposed as a 'fingerprint' in the geological record for periods of heightened volcanism known as large igneous provinces (LIPs), associated with mass extinction events and other periods of rapid global change (Pyle and Mather, 2003; Percival et al., 2018).

Hg behaviour during magma genesis, evolution and degassing is poorly understood due to low concentrations in natural samples and measurement challenges. These analytical issues, especially with *in situ* techniques, include low ionization potential, high number of naturally occurring isotopes and stickiness<sup>1</sup>. Consequently, all previous estimates of present-day and past LIP magmatic Hg emissions are based on modern-day Hg/SO<sub>2</sub> measurements in volcanic plumes. Mercury's volatility and volcanic Hg measurements from fumaroles and diffuse soil emissions associated with CO<sub>2</sub> (rather than SO<sub>2</sub>) degassing (e.g.,

Bagnato et al., 2014) suggest that Hg degasses at relatively high pressures and that scaling with SO<sub>2</sub> release is not appropriate. Sulphide saturation may be common in LIP basalts and, given the stability of Hg sulphide, will likely have an important influence on Hg (Edmonds and Mather, 2017). These knowledge gaps compromise predictions of current Hg emissions and the scale of LIP magmatic degassing. Since we cannot study these processes using natural samples, this project will use experimental petrology.

We will overcome the analytical difficulties by taking an experimental approach using artificial Hg-doped samples. We will start off using compositions characteristic of LIP products (typically tholeiitic basalts) made using high-purity starting materials to exclude interfering elements (e.g., W). We can then use ICP-MS (solution/laser ablation, estimated detection limit 10-100ppm) to constrain our silicate Hg concentrations (as well as SEM and electron microprobe analysis for major elements).

Using our new experimental constraints of Hg degassing and sulphide partitioning, we will build robust conceptual/quantitative models of Hg behaviour during magma evolution. These experiments will also contribute to understanding of Hg in sulphide ore deposits, which is of use to economic geologists and industry. The experiments will open future work to understand Hg inputs into volcanic hydrothermal fluids.

<sup>1</sup>[http://www.agilent.com/cs/library/articlereprints/public/5990\\_7173EN.pdf](http://www.agilent.com/cs/library/articlereprints/public/5990_7173EN.pdf)



Figure showing fissures erupting in Kilauea Iki on November 14, 1959, at 10:30 p.m., Kilauea Volcano, Hawai'i. Photo: USGS

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## Methodology

**Volatilization experiments:** We will use a novel experimental apparatus in Oxford (Norris & Wood, 2017) to study Hg volatility in silicate melts. A crucible containing the melt is lowered into a furnace and heated at atmospheric pressure while being stirred. Oxygen and sulphur partial pressures are controlled to constrain the oxidation state and composition of the magma. After treatment, the sample is rapidly quenched in water. We will determine Hg's volatility by comparing initial and final Hg contents for a suite of experimental charges created under variable oxygen fugacity. In addition to controlling sulphur fugacity, we will dope samples with varying Cl to study the effects of S and Cl ligands on Hg volatility. We plan to develop the methodology further to study the effects of pressure using the piston cylinder apparatus.

**Sulphide-partitioning experiments/model:** In the Oxford lab., Kiseeva & Wood (2013; 2015) developed a simple thermodynamic model for chalcophile/moderately chalcophile element partitioning into sulphide melts. For a range of elements (Cu, In, Tl, Pb, Ag, Mn, Zn, Cr, Co, Ni, Sb, Cd) there is a predictable relationship between sulphide-silicate partitioning and silicate melt FeO content. Mercury is also known to have a strong affinity for sulphide so it is important that we develop an understanding of Hg behaviour in sulphide-bearing melts. We will use the same

experimental approach (50:50 mixtures of synthetic sulphide/silicate held at high pressure and temperatures above the silicate liquidus, varying silicate/sulphide liquid compositions) to develop this model for Hg.

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## Timeline

**Year 1:** Training and initial volatilization experiments.

**Years 2 and 3:** Training and sulphide-partitioning experiments. Extension to volatilization experiments.

**Year 4:** Data integration, thesis completion, papers for international journals/conference presentation.

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## Training & Skills

Oxford offers a full range of advanced courses and transferable skills training as part of its 4<sup>th</sup> year undergraduate course and DTP training programme.

Specialised training foreseen:

- Full training in experimental petrology
- Personalised training in whole-rock and microanalytical geochemistry (possibly including ICP-OES/XRF, ICP-MS, SEM, EPMA, SIMS, XANES)
- Melts, Glasses and Magmas summer course in Munich, Germany
- Conference presentations including conference field trips as appropriate
- Participation in a field excursion to a volcano (e.g., Stromboli or Santorini)

**Key external collaborators include Kate Kiseeva** (University College, Cork, Ireland - [www.ucc.ie/en/bees/staff/kiseeva](http://www.ucc.ie/en/bees/staff/kiseeva)).

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## References & Further Reading

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## Further Information

Contact: Tamsin Mather

[Tamsin.Mather@earth.ox.ac.uk](mailto:Tamsin.Mather@earth.ox.ac.uk)