

Valence state of arsenic and antimony in basalts: an experimental and synchrotron study

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Arsenic (As) and antimony (Sb) are trace elements that have multiple redox states (-III, III, V) in geological systems. This variability in valence state grants these elements a diverse geochemical behaviour, which could be exploited as a tracer of magmatic processes, such as crustal assimilation or monitoring redox state. Furthermore, in many magmatic platinum group element (PGE) deposits, platinum and palladium preferentially partitioning into a coexisting arsenide phase over the sulphide phase, which suggests that arsenic may play an important role in PGE sequestration. Unfortunately, there is a lack of information on the redox state of As and Sb in magmas, with conflicting results in some cases for As. These will be the first quantitative measurements for Sb valence state in a magmatic system. Preliminary thermodynamic calculations predict changes in the valence state of As and Sb over the range of terrestrial oxygen fugacities (fO_2), but these calculations require experimental calibration.

To assess the valence state of these elements we synthesized a suite of Sb- and As-bearing basaltic glasses in chromite crucibles encapsulated in vacuum-sealed silica ampoules over a range in fO_2 (FMQ -3.3 to FMQ +5.7) at 0.1 MPa and 1200°C. We measured the oxidation state of As and Sb in the glasses by x-ray absorption near edge structures (XANES) at the Canadian Light Source (CLS) using the HXMA beamline for Sb and the VESPERS beamline for As. Preliminary analysis of the XANES spectra indicates that the trivalent oxidation state of As and Sb is dominant over the range of fO_2 investigated. Additionally, at higher oxygen fugacities pentavalent As and Sb are present in addition to the trivalent form.