Speaking Speciation: An Experimental Study of Arsenic and Antimony in Basalts

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Arsenic (As) and Antimony (Sb) are redox sensitive elements known to have both anionic and cationic chemical forms (-III, III, V). These elements are normally trace constituents in the mantle and crust, yet they can be concentrated in some sedimentary environments, as well as in magmatic and hydrothermal ore systems. Such diverse geochemical behavior suggests that As and Sb could serve as tracers for magmatic processes, such as crustal assimilation, and as a monitor of magma redox state. Despite this potential utility, there is a relative dearth of information on the speciation of As and Sb in magmas, with conflicting results in some cases for As. Preliminary thermodynamic calculations predict changes in the speciation of As and Sb over the range of terrestrial oxygen fugacities (fO_2), but these calculations require experimental validation.

Experiments to assess the speciation of these elements at magmatic conditions involved the synthesis of a suite of Sb- and As-bearing basaltic glasses in chromite crucibles encapsulated in vacuum-sealed silica ampoules over a range of fO_2 from FMQ-3.3 to FMQ+5.7 at 0.1 MPa and 1200°C. Speciation of As and Sb in run-product glasses was measured using x-ray absorption near edge structures (XANES) and extended x-ray absorption fine structures (EXAFS) at the Canadian Light Source (CLS).

Linear combination least squares fitting (LCF) of the XANES portion of the spectra reveals that the oxidation state of Sb changes from dominantly Sb^{3+} at fO_2 less than FMQ +0.7, to a mixed Sb^{3+}/Sb^{5+} region at higher fO_2, with the Sb^{5+} oxidation state reaching ~50% of total Sb at FMQ +5.3. The oxidation state of arsenic is dominantly As^{3+} over the entire range of fO_2 investigated, although minor amounts (up to 15%) of As^{5+} are present in the most oxidized samples. Reduced forms of As or Sb (e.g. As^{0} or As^{3-}) were not observed, even for the samples equilibrated at the lowest fO_2. The presence of both 3+ and 5+ oxidation states of As and Sb in run product glasses suggests that selective partitioning of these elements into minerals with a strong affinity for a single valence state (e.g. As^{5+} into apatite) may be useful for oxygen barometry.

Modelling of the EXAFS portion of the spectra is in progress, and results will be presented at the conference.