XANES investigation of selenium speciation in silicate glasses

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The speciation of sulfur in silicate melts as a function of oxygen fugacity is an important factor in volcanic degassing and ore deposition. Due to the large number of electrons involved in the 2- to 6+ transition, sulfur changes from 2- to 6+ over a very narrow fO_2 interval, <2 log units. The 4+ valence state of sulfur does not appear to be an important species in silicate melts. Selenium lies directly below sulfur in group 16 of the periodic table and is considered to display similar geochemical behavior. However, differences in redox speciation between sulfur and selenium, either in the fO_2 of Se^{2-} to Se^{6+} relative to S^{2-} to S^{6+} transitions, or the existence of a Se^{4+} stability field will result in fractionation of Se from S in magmatic systems [1].

We have conducted high pressure, high temperature experiments under controlled fO_2 conditions to investigate the speciation of Se in silicate melts. Oxide mixes of basaltic composition were doped with 500 to 2500 ppm Se and equilibrated in Pt or graphite-Pt capsules at 1400°C for 36 hours. Chemical potential of oxygen was controlled by the addition of $Ru\text{-}RuO_2$, PtO_2 and the presence of graphite, to produce experiments reflecting reduced (graphite $\approx$ FMQ-2.2; [2]), oxidising ($Ru\text{-}RuO_2 \approx$ hematite-magnetite at 1400°C) and very oxidising conditions (PtO_2 produces O_2 gas phase).

Quenched glasses were recovered from the piston-cylinder experiments and the selenium K-edge XANES (X-Ray Absorption Near Edge Structure) spectra were collected in fluorescence mode at the Australian National Beamline Facility at the Photon Factory, Tsukuba, Japan.

Glasses from each redox condition produced a distinct Se K-edge spectra, with the absorbtion edge energy increasing with increasing fO_2. The spectra are interpreted to represent Se^{2-}, Se^{4+} and Se^{6+}. Thus, at moderate to high fO_2, selenium exhibits distict redox speciation to sulfur, with the existence of a significant stability field for Se^{4+}, and the Se^{2-} to Se^{4+} transition will occur over a larger fO_2 range than S^{2-} to S^{6+}. We suggest that Se^{6+} is not an important species in silicate metls at geologically relevant oxygen fugacities.

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Geochemical evidence of source and process controls on Mid-Miocene silicic volcanism in the Idaho-Oregon-Nevada Region, USA

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In this study we report results of a geochemical and petrological investigation of Mid-Miocene silicic volcanism in the Idaho-Oregon-Nevada (ION) region aimed at examining models of continental crust formation and modification in the northwestern US. In the late Oligocene to Miocene portions of the northwestern US underwent extension accompanied by bimodal (mafic and silicic) volcanism [1,2]. The ION region resides in the northernmost Basin and Range Province on a "transitional" lithosphere between Mesozoic accreted lithosphere to the west and Precambrian Wyoming Craton to the east as marked by Sr isotopic composition (0.704 and > 0.706 respectivly). It is characterized by bimodal, silicic (~16 to ~13 Ma) and mafic (~17 to 15 Ma) volcanism temporally related to the main volumes of Columbia River flood basalt activity to the north. Mantle upwelling behind an active magmatic arc, mafic magma intrusion into crust, melting of heterogeneous lithosphere and mixing of the melts from heterogeneous sources are contributing to the ION region bimodal volcanism and its continuation in time and space to the NE (Snake River Plain-Yellowstone) and the NW (High Lava Plains-Newberry) [1,3,4].

To investigate the heterogeneity and spatial and temporal relationships between off craton, "transitional", and on craton sources and reservoirs five ION volcanic centers are investigated. We conducted petrological, geochemical and Sr, Nd and Pb isotopic analyses on 23 whole rock-glass separate pairs and Hf isotopic analyses on the glass separates [3]. In addition to the influence of sptaillay and temporally heterogeneous source regions open system behavior in crustal storage chambers plays an important role in ION area silicic magma evolution. This is evident from feldspar dissolution textures and differences in trace element and isotopic compositions between whole rock and glass separate pairs.

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