An fO_2-P-T-X model of sulfur speciation in reduced basaltic melts

BRENDAN A. ANZURES[1]*, STEPHEN W. PARMAN[1], RALPH E. MILLIKEN[1], OLIVIER NAMUR[2], CAMILLE CARTIER[3]

[1]Department of Earth, Environmental and Planetary Sciences, Brown University, Providence, RI 02912, USA (*correspondence: brendan_anzures@brown.edu)
[2]Department of Earth and Environmental Sciences, KU Leuven, 1001 Leuven, Belgium (*olivier.namur@kuleuven.be)
[3]Department de géologie, Université de Lorraine, Nancy, France (*camille.cartier@univ-lorraine.fr)

The NASA MESSENGER mission revealed that lavas on Mercury are enriched in sulfur (1.5-4 wt.%) compared with other terrestrial planets (<0.1 wt.%), a result of high S solubility under its very low oxygen fugacity (estimated fO_2 between IW-3 and IW-7). Due to decreasing O availability at these low fO_2 conditions, and an abundance of S^{2-}, the latter acts as an important anion. This changes the partitioning behavior of many elements, and modifies the physical properties of silicate melts. To further understand S solubility and speciation in reduced magmas, we have analysed 60 high-P experiments that span a range of P (177 bar to 5 GPa), T (1225 to 1850 °C), and fO_2 (IW-0.8 to IW-8.6).

S K-edge X-ray Absorption Near Edge Structure (XANES) spectra were collected at Argonne National Laboratory and fit with a linear mixing model to quantitatively determine S speciation in the silicate glass. We find that in basaltic melts at low fO_2, (1) FeS (+Ni, Na, Cr sulfide in a few experiments) is destabilized, (2) MgS becomes the dominant species, and (3) CaS is a minor species. The FeS to (Mg,Ca)S transition occurs over IW-2 to IW-4. These trends are robust over a compositional range that is relevant to the Mercurian surface (Northern Volcanic Plains, High Mg, Inter-crater Plains and Highly Cratered Terrain), Mercurian mantle (modified CH chondrite), and enstatite chondrite (EH and EL) parent bodies.

Our results also suggest that the dominant control on FeS speciation is fO_2, whereas MgS and CaS speciation depend on fO_2 and pressure. If confirmed, the controlling reactions of sulfur solubility in silicate melt at low fO_2 might be $FeS_{sulfide} + MgO_{melt} \leftrightarrow MgS_{melt} + Fe^0 + ½O_2$ at 0>IW>-3. At IW<-3, exchange reactions for MgS and CaS might follow $MS_{melt} + ½O_{2gas} \leftrightarrow MO_{melt} + ½S_{2gas}$ where M refers to cation Mg or Ca.