

SULFIDE SPECIATION IN MERCURIAN MAGMAS. B. A. Anzures¹, S. W. Parman¹, R. E. Milliken¹, O. Namur², C. Cartier³. ¹Department of Earth, Environmental, and Planetary Sciences, Brown University, Providence, RI, 02906. ²Department of Earth and Environmental Sciences, KU Leuven, 1001 Leuven, Belgium. ³Department de géologie, Université de Lorraine, Nancy, France. Email: brendan_anzures@brown.edu

Introduction: The NASA MESSENGER mission revealed that lavas on Mercury are enriched in sulfur (1.5-4 wt.%) [1] compared with other terrestrial planets (<0.1 wt.%) [2], a result of high S solubility under its very low oxygen fugacity (estimated f_{O_2} between IW-3 and IW-7) [3,4]. Due to decreasing O availability at these low f_{O_2} conditions, and an abundance of S^{2-} , the latter acts as an important anion. This changes the partitioning behaviour of many elements and modifies the physical properties of silicate melts. Studies of low f_{O_2} systems are also applicable to the petrologic evolution of enstatite chondrite parent bodies and perhaps early Earth [5].

S K-edge XANES spectroscopy was used to quantify the coordination chemistry of S species in highly reduced silicate melts. The measured S speciation changes significantly impact physicochemical properties such as viscosity, melting temperature, and mineral stability, which led to Mercury's distinct evolution.

Methods: Experimental samples consistent with the Mercurian surface [2] and estimated mantle composition [6], as well as a crystallizing EL chondrite [7], were prepared in a TZM pressure vessel, internally heated pressure vessel, piston cylinder, and multi-anvil. Experiments ranged from 0.1 to 5 GPa at temperatures of 1225 to 1850 °C and f_{O_2} between IW-0.8 to IW-8.6. Oxygen fugacity was controlled by varying the initial Si^0/SiO_2 ratio in the starting mix. Afterward, the intrinsic f_{O_2} of the experiments were calculated using an empirically derived sulfur solubility-oxygen fugacity model [2] because although all samples were sulfide-saturated, most were not Fe metal-bearing.

Sulfur speciation was measured using S K-Edge XANES spectra collected in a helium environment using an undulator-based, hard X-ray microprobe at Argonne National Laboratory. The spot size for XANES was 1-2 μm with a nominal penetration depth of 2-3 μm for S. XANES spectra were normalized using an automated edge-step normalization algorithm [8]. Quantification of S speciation for the quenched silicate glasses was achieved by linearly unmixing the quenched silicate glass spectra into their component pure sulfide spectra to minimize RMSE and maximize r^2 , keeping in mind chemical constraints as described in [6].

Results: As f_{O_2} decreases from IW-1 to IW-9, S speciation goes through two major changes as shown in qualitatively in **Figure 1** and quantitatively in **Figure 2**. At \sim IW-2, FeS and $FeCr_2S_4$ species are destabilized, and CaS becomes the dominant S species with minor Na_2S and MnS. At \sim IW-4, MgS is the dominant S species with minor CaS. The bonding of S with Fe, Mg, Ca,

Na, Mn, and Cr reduces the concentrations of the cations available to form oxides as shown in **Figure 3** affecting the silicate phase equilibria. Oxide concentrations of FeO, Cr_2O_3 , and MnO will be reduced by 100%. On average, CaO will decrease by 25%. When present, MgO and Na_2O will decrease by 22% and 28% respectively.

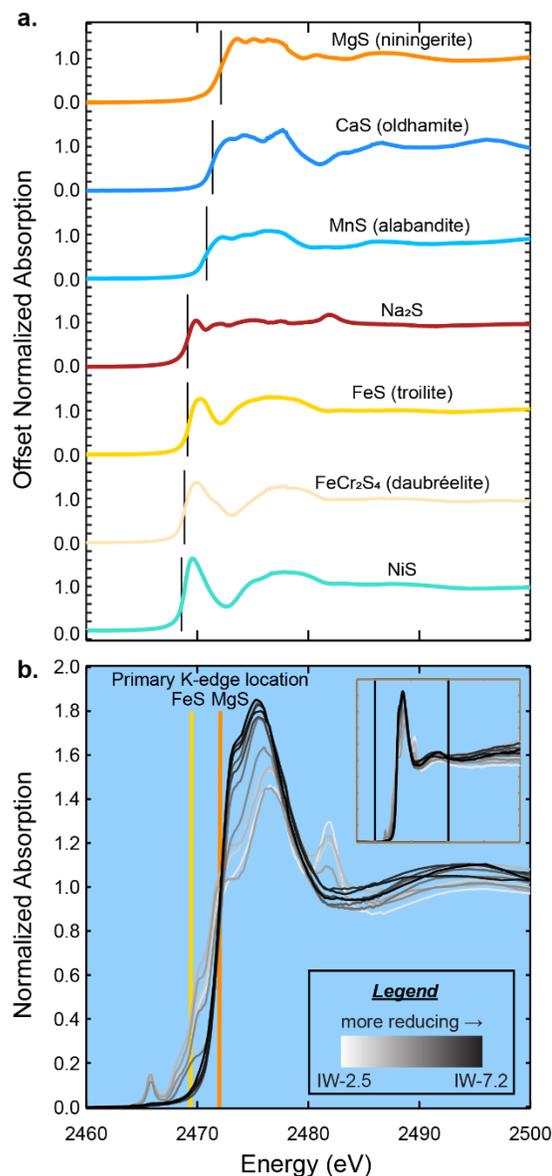


Figure 1. S K-edge XANES spectra for **a.** pure endmember sulfides and **b.** experimental silicate glasses. Silicate glass spectra display a systematic change in shape with f_{O_2} with the spectral shoulder at \sim 2470 eV disappearing and the near-edge structure flattening. The inset brown box shows the complete spectra from 2440 to 2540 eV with black lines showing the expanded region.

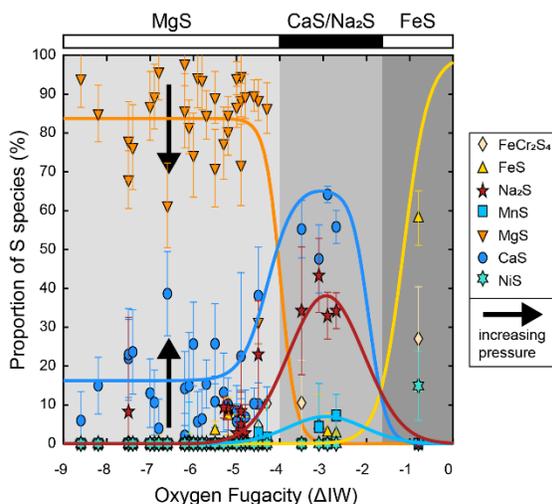


Figure 2. Sulfide speciation in experimental glasses as a function of fO_2 from linear unmixing of XANES spectra. The proportions of FeS, $FeCr_2S_4$, MnS, and Na_2S species decrease and MgS increases with more reducing conditions. CaS reaches a peak at IW-3 and then becomes the minor species. Oxygen fugacity for the melts was calculated using the fO_2 -sulfur solubility model of Namur et al. (2016). Experiments run at 1 GPa and 1250-1475 °C. Error bars indicate standard error during unmixing.

Implications: The sulfide speciation trends as a function of oxygen fugacity have important ramifications for Mercurian magmas and other reduced rocky bodies. The changes in S speciation at low fO_2 affect the activities of SiO_2 , MgO and CaO in the melt, stabilizing enstatite at the expense of forsterite, and destabilizing plagioclase and clinopyroxene. These shifts cause the initial layering of Mercury's solidified magma ocean to be enstatite-rich and plagioclase poor. Also, if S speciation is measured in Mercurian lavas themselves, CaS/MgS may be used to constrain fO_2 between IW-2 and IW-4 or lower than IW-4.

Effect on physical properties: Sulfide complexing increases the activity of SiO_2 , which should increase polymerization and viscosity [9]. However, S may preferentially replace bridging oxygen atoms in the melt, which would produce the opposite effect [10] and lower viscosity has recently been measured in S-bearing Mercurian magmas [11]. The melting temperature of S-bearing magmas also decreases, increasing the depth of melting initiation, with the multiple saturation point of forsterite, enstatite, and melt decreasing by 100 °C [12].

Effect of pressure: Looking at only the High-Mg composition experiments that ranged from 0.1 to 2.0 GPa within a limited range of fO_2 (IW-4.5 to IW-6.1) and temperature (1420 to 1500 °C), pressure seems to have a little effect on sulfide speciation. CaS and Na_2S may both be more stable at ~1 GPa. This may provide a mechanism to consolidate alkali-sulfides (Na-bearing

caswellsilverite and Na-, K-, and Cl-bearing djerfisherite), candidate hollows-forming material, carried to the surface within high pressure magmatic liquids, before exolving and floating during flash melting and low-pressure cooling within shallow impact melt sheets.

Comparing High-Mg experiments (0.1 GPa) to EL chondrite experiments (5 GPa) with similar composition and with fO_2 between IW-4.5 and IW-7.5 displayed an increase in CaS stability at higher pressure even with less total Ca in the silicate melt (>2.62 vs. <2.44 wt.%).

Effect of temperature: Looking at only the Northern Volcanic Plains composition experiments that ranged from 1310 to 1500 °C within a limited range of fO_2 (IW-5.8 to IW-6.8) and constant pressure (0.1 GPa), temperature had a negligible effect on sulfide speciation. Temperature does, however, increase sulfur solubility, while pressure is more difficult to deconvolve from associated changes in temperature and crystallization[2].

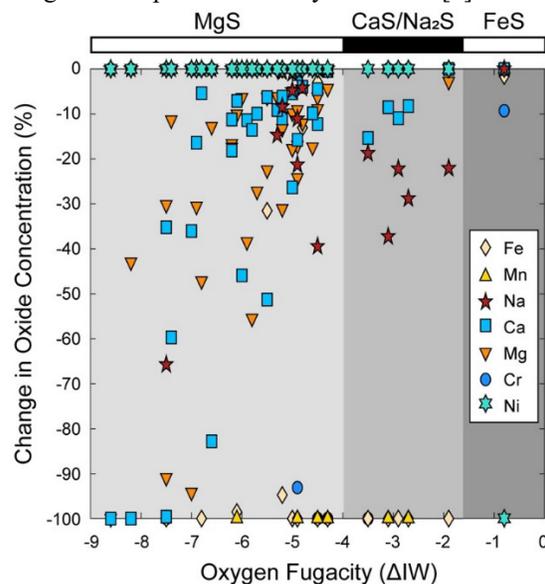


Figure 3. Relative percent decrease in oxide concentration due to cations bonding with S as a function of fO_2 .

Future Work: More experiments are needed in the CaS dominated regime between IW-2 to IW-4, which would place further constraints on the fO_2 of Mercury's mantle. However, alternative experimental methods may need to be used because the addition of any Si^0 in the starting experimental mix seems to drive the fO_2 below this point.

References: [1] Nittler L. R. et al. (2011) *Science*, 333, 1847–1850. [2] Namur O. et al. (2016) *EPSL*, 448, 102-114. [3] McCubbin F. M. et al. (2012) *GRL*, 39, 1-5. [4] Zolotov M. Y. et al. (2013) *JGR-Planets*, 118, 138-146. [5] Javoy M. et al. (2010) *EPSL*, 293, 259-268. [6] Anzures B. A. et al. (2020) *GCA*, 286, 1-18. [7] Cartier C. et al. (2014) *GCA*, 130, 167-187. [8] Anzures B. A. et al. (2020) *AmMin*, 105, 375-381. [9] Fogel R. A. (2005) *GCA*, 69, 1633-1648. [10] Holzheid A. & Grove T. L. (2002) *AmMin*, 87, 227-237. [11] Mouser M. D. et al. (2020) *LPSC LI, Abstr #2098*. [12] Namur O. et al. (2016) *EPSL*, 439, 117-128.