

**MERCURY SILICATE PHASE EQUILIBRIA CHANGES DUE TO S SPECIATION.** B. A. Anzures<sup>1</sup>, S. W. Parman<sup>2</sup>, R. E. Milliken<sup>2</sup>, O. Namur<sup>3</sup>, C. Cartier<sup>4</sup>, F. M. McCubbin<sup>5</sup>, K. E. Vander Kaaden<sup>6</sup>, K. Prissel<sup>7</sup>, K. Iacovino<sup>1</sup>, A. Lanzirotti<sup>8</sup>, M. Newville<sup>8</sup>. <sup>1</sup>Amentum, NASA Johnson Space Center. <sup>2</sup>Brown University. <sup>3</sup>KU Leuven. <sup>4</sup>Université de Lorraine. <sup>5</sup>ARES, NASA Johnson Space Center. <sup>6</sup>NASA Headquarters. <sup>7</sup>Purdue University. <sup>8</sup>Center for Advanced Radiation Sources, The University of Chicago. Email: brendan.a.anzures@nasa.gov

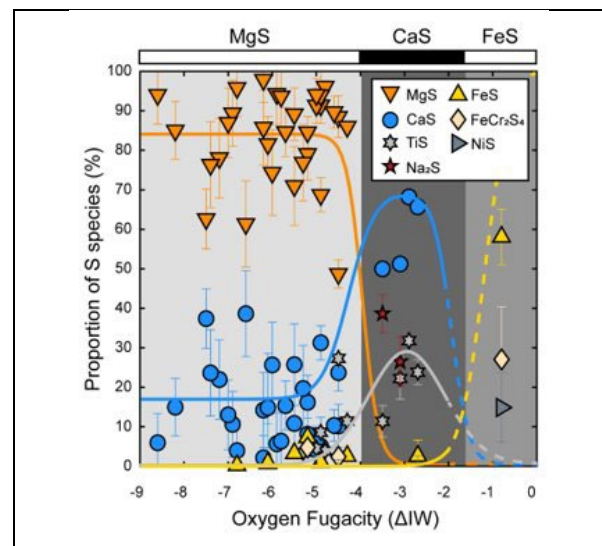
**Introduction:** The NASA MESSENGER mission revealed that lavas on Mercury are enriched in sulfur (1.5-4 wt.%) compared with other terrestrial planets (<0.1 wt.%) due to high S solubility in silicate melt under its very low oxygen fugacity ( $fO_2$ ) [1]. However, the speciation of that S remains poorly constrained. In this study, we evaluate the role of pressure, temperature, and melt composition on S solubility and speciation in reduced magmas relevant to Mercury. Sulfur speciation was determined by S K-edge XANES spectra collected in 60 experiments that span a range of pressure (0.1 to 5 GPa), temperature (1225 to 1850 °C), and  $fO_2$  (IW-0.8 to IW-8.6). Data were analysed using new relevant XANES standards and XANES spectral unmixing techniques. Stepwise forward regression was used to develop empirical equations for S species (MgS, CaS, and TiS). We found that  $fO_2$ , P/T, and S content in the silicate melt at sulfide saturation (SCSS) exert the main controls on MgS content (wt.%) in the silicate melt, and that  $fO_2$  and MgS content in the silicate melt exert the main controls on SCSS.

$$[MgS_{iiq} \text{ wt. \%}] = a + \frac{bP}{T} + c \log fO_2 + d[S \text{ wt. \%}]_{SCSS}$$

We find that as  $fO_2$  decreases from IW-2 to IW-7, S speciation in silicate melt goes through two major changes. Between IW-2 and IW-4, FeS and  $FeCr_2S_4$  species are destabilized, and CaS becomes the dominant S species with minor TiS. Below IW-4, MgS is the dominant S species with minor CaS. At low  $fO_2$ , S bonding with Fe, Mg, Ca, Ti, Na, and Mn affect the activities of  $SiO_2$ , MgO, CaO, TiO,  $Na_2O$ , and MnO in the silicate melt. This stabilizes enstatite at the expense of forsterite, destabilizes the Ca-bearing minerals plagioclase and clinopyroxene, and shifts plagioclase chemistry from the Ca-rich endmember anorthite to the Na-rich endmember albite as understood by reprojecting silicate ternary diagrams incorporating S speciation data. At the expense of MgS, CaS is more stable in the silicate melt at higher pressures at  $fO_2$  below IW-4, creating a pathway for CaS to be carried in the silicate melt from depth to the surface before oldhamite (CaS) crystallization. These S speciation changes have substantial impacts on physicochemical properties of silicate melt such as viscosity [2], melting temperature [3], and mineral stability, which led to the distinct evolution of Mercury and other reduced planetary interiors. This work is published in Anzures et al. (2025) [4].

**Methods:** Sulfur speciation in silicate melt were measured using S K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy. Spectra were

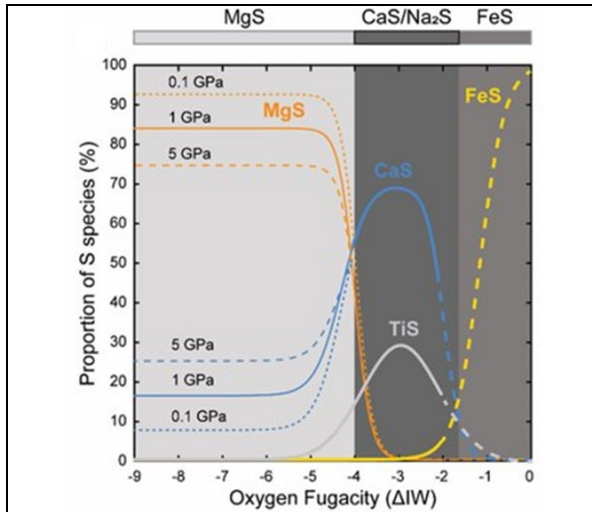
collected in a helium environment using an undulator-based, hard X-ray microprobe at Argonne National Laboratory. The spot size was 2  $\mu\text{m}$  with a nominal penetration depth of 2-3  $\mu\text{m}$  for S. XANES spectra were normalized using an automated edge-step normalization algorithm. Quantification of S speciation in the silicate glass spectra into their component pure sulfide spectra was completed through linear unmixing with chemical constraints.



**Figure 1.** Sulfide speciation in very reduced experimental silicate glasses as a function of oxygen fugacity. The proportion of MgS increases with more reducing conditions below IW-4. CaS and TiS reach peaks at IW-3 and then becomes the minor species below IW-3.  $Na_2S$  is stable at IW-3 and seems to become less stable at more reducing and more oxidizing conditions. The  $fO_2$  regions where FeS, CaS, and MgS are the dominant S species are highlighted in different shades of gray. The large scatter in the proportions of MgS and CaS in the Mg-dominated region hint at additional controls on S speciation aside from  $fO_2$ . Nevertheless, these S speciation trends are consistent even within the large range of temperature (1225 to 1850 °C), pressure (0.1 to 5 GPa), and composition, implying  $fO_2$  is the primary control on S speciation in very reduced silicate melts. Error bars indicate standard error during unmixing.

**Results:** Sulfur speciation in a wide range of experiments were measured (Figure 1) and confirms S speciation trends with  $fO_2$  observed in reduced silicate melts on a single composition [5] over a wider range of temperature, pressure, and composition. At IW-2, FeS and  $FeCr_2S_4$  species in the melt are destabilized, and CaS becomes the dominant S species with minor TiS. At IW-

4, MgS is the dominant S species with minor CaS. Stepwise forward regression was used to develop empirical equations for S melt species (MgS, CaS, and TiS) and S content at sulfide saturation (SCSS). We found that  $fO_2$ , P/T, and S content in the silicate melt exert the main controls on MgS content (wt.%) in the silicate melt (**Figure 2**), and that  $fO_2$  and MgS content in the silicate melt exert the main controls on SCSS. At the expense of MgS, CaS is more stable in the silicate melt at higher pressures at  $fO_2$  below IW-4, creating a pathway for CaS to be carried in the silicate melt from depth to the surface before crystallizing oldhamite (CaS).



**Figure 2.** Modelled sulfide speciation as a function of oxygen fugacity. Outside of  $fO_2$ , pressure exerts a strong effect on MgS and CaS proportion with higher pressures leading to higher % CaS (and proportionally lower MgS).

**Implications:** The changes in S speciation at low  $fO_2$  affect the activities of  $SiO_2$ , MgO and CaO in the silicate melt by reducing their effective oxide concentrations in the silicate melt [5]. Silicate melt compositions were broken down into their mineral components using expressions from [6]. Silicate glass S speciation data used to normalize silicate melt compositions for projection onto sulfur-free phase diagrams such as FOPL-QZ were plotted in **Figure 11** after [7].

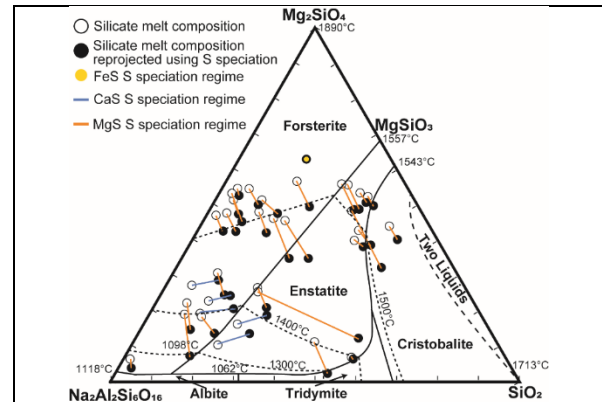
These speciation changes stabilize enstatite at the expense of forsterite and destabilize Ca-bearing minerals such as plagioclase and clinopyroxene. A decrease in CaO also shifts plagioclase compositions from the Ca-rich endmember anorthite toward the Na-rich albite, which is also observed in enstatite chondrite and aubrite meteorites [7]. In some of our experiments, all Ca present in the silicate glass appears to be bonded with S, causing a nearly 100% decrease in the silicate melt CaO component, resulting in the destabilization of any CaO-bearing minerals from oxides to phosphates. These shifts in melt speciation at low  $fO_2$  would be expected to cause the initial layering of Mercury's solidified magma ocean to be more enstatite-rich and plagioclase

poor compared to a S-free magma ocean. The extent to which forsterite and plagioclase were suppressed during magma ocean crystallization on Mercury likely depends on the initial S abundance in bulk silicate Mercury and the depth at which crystallization occurred, as forsteritic olivine would likely be more stable at higher pressure than lower pressure for a given S abundance, given the pressure effects on MgS and CaS speciation in silicate melts. However, forsterite has been predicted to be present at the surface and in the mantle of Mercury [8-10]

(Namur and Charlier, 2017; Vander Kaaden et al., 2017; McCubbin and Anzures, 2025), which may be due to cumulate mantle overturn [2,11].

We will further investigate melt speciation by analyzing already collected Ti, Cr, Cl, and P XANES spectra. These particular heterovalent elements are important because at low oxygen fugacity various anions may bond with these elements rather than just oxygen, impacting metal and sulfide complexing and transport.

**References:** [1] Nittler et al. (2011) *Science*, 333, 1847-1850. [2] Mouser et al. (2021) *JGR: Planets*, 126.11. [3] Namur et al. (2016) *EPSL*, 439, 117-128. [4] Anzures et al. (2025) *GCA*, 388, 61-77. [5] Anzures et al. (2020) *GCA*, 286, 1-18. [6] Grove (1993) *Contrib. to Min. & Pet.*, 80, 160-182. [7] Fogel (2005) *GCA*, 69(6), 1633-1648. [8] Namur & Charlier (2017) *Nature Geoscience*, 10(1), 9-13. [9] Vander Kaaden et al. (2017) *Icarus*, 285, 155-168. [10] McCubbin & Anzures (2025) *Treatise on Geochemistry 3<sup>rd</sup> Edition*, 7, 257-287. [11] Mouser & Dygert (2023) *JGR: Planets*, 128(7).



**Figure 3.** Forsterite-albite-silica phase diagram. Mercurian silicate melt compositions are reprojected using knowledge of cations bonding with S rather than O. Silicate phase equilibria change little at oxidizing conditions where FeS is the dominant S species, but substantially change at reducing conditions where CaS or MgS are the dominant S species and S solubility increases greatly.