EFFECT OF SULFUR SPECIATION ON CHEMICAL AND PHYSICAL PROPERTIES OF HEAVILY REDUCED MERCURIAN MELTS.

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Introduction: Mercury evolved as a geochemical and mechanical endmember among the terrestrial planets, largely due to its low oxygen fugacity. The Earth, Moon, and Mars have similar mantle fO_2 between IW-2 and IW+2 [1]. S solubility in magmas is low at these conditions and is present as an important but minor element (<0.1wt%) [2]. In contrast, the Mercurian surface exhibits high S concentrations (1.5-4wt%) [3], and if these values reflect magma compositions then a mantle fO_2 between IW-3 and IW-7 is implied from silicate-metal-sulfide equilibria [4]. Studies of low fO_2 systems also are also applicable to the petrologic evolution of enstatite chondrite parent bodies [5] and perhaps early Earth [6] and exoplanets orbiting C-rich suns.

High S solubility has been observed in numerous experimental melts [2,5,7-12] at highly reducing conditions. Due to the decreasing O at these low fO_2 conditions, S^{2-} fills in as a 2nd major anion, changing the partitioning behavior of many elements and modifying the structure and physical properties of the silicate melt. Enstatite chondrite-derived thermodynamic models [13] and Raman spectra [2] suggest S bonds with Fe, Mg, and Ca in silicate melts at these reducing conditions.

In this study, we use S K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy to quantify the coordination chemistry of S in silicate melts at heavily reduced conditions [14,15]. The results provide insights into the effect of S on the chemical and physical properties of Mercurian melts.

Methods: Experimental samples consistent with Mercurian surface [3] and estimated mantle compositions were prepared in the TZM pressure vessel and piston cylinder (PC) at Brown University. MESSENGER-derived Northern Smooth Plains (NSP) [3] composition was used for the surface and CH chondrite Allan Hills 85085 [16] was used as a primitive Mercurian mantle analog. Experiments ranged from 177-196 bar and 1225-1400 °C in the TZM for the surface, and 1-2 GPa and 1250-1475 °C in the PC for mantle studies, with fO_2 in the range estimated for Mercury (IW-3 to IW-7). Pure sulfide standards for XANES were synthesized by reaction of the elements at high T in a sealed evacuated silica tube (MgS, FeS, $Ni_{1-x}S$, NiS_2, Ni_7S_6, Ni_3S_2) or purchased from Alfa Aesar© (CaS, MnS, Na_2S, Al_2S_3). Glass compositions were measured using the SX100 elecron microprobe at Brown University. For a more detailed description of experimental methods see [22].

S K-edge XANES spectra were collected in a helium environment using an undulator-based, hard X-ray microprobe at Argonne National Laboratory. Data collection and creation of micro-X-ray fluorescence (XRF) maps were performed in Larch [17]. Processing and linear combination fitting (LCF) of the resultant XANES spectra were performed in Athena[18] to calculate proportions of S species in the sulfide saturated Mercurian glasses. The set of endmembers used in the LCF was narrowed down through statistical analysis
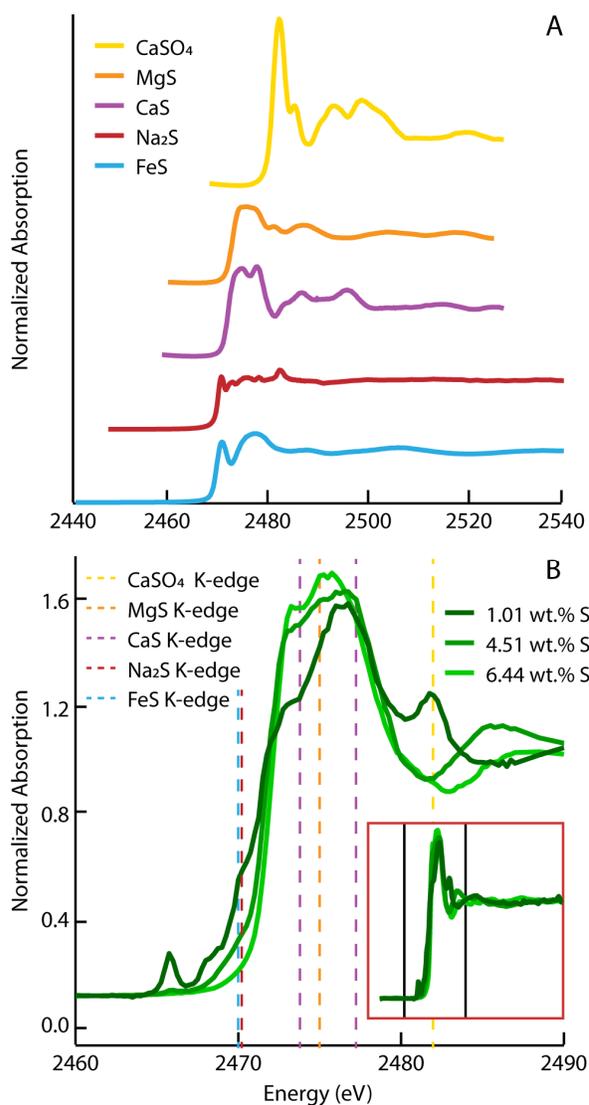

Figure 1. A. *New S K-edge XANES spectra standards for FeS (troilite), Na_2S, MgS (niningerite), CaS (oldhamite), and $CaSO_4$ (anhydrite).* **B.** *XANES spectra for experimental glasses change shape with fO_2 due to changes in S speciation. Inset red box shows the complete spectra with the black lines showing expanded region. Adapted from [22]*

keeping in mind results from thermodynamic predictions [13] and previous Raman measurements [2].

Results: New S K-edge XANES standards were collected for a number of sulfides including FeS, MgS, CaS, and MnS to take advantage of improvements in detectors, while Na_2S, $Ni_{1-x}S$, NiS_2, Ni_7S_6, Ni_3S_2, and Al_2S_3 were analyzed for the first time (Fig 1a). Surprisingly, FeS (troilite) and Na_2S have the same K-edge energy at 2469.25 eV indicating Na_2S is very metallic. A slight sulfate contribution at 2481.9 eV is observed in the Na_2S spectra due to its high reactivity in air (Fig 1a).

XANES analysis of the experimental glasses exhibit a positive K-edge shift due to the decrease in the FeS and Na_2S peak as fO_2 decreases (Fig 1b). The contribution of MgS is seen in all spectra, and CaS is obvious only at the lowest fO_2 (Fig 1b). The XANES analyses demonstrate that FeS and Na_2S are destabilized at low fO_2, MgS becomes the dominant species, and CaS is a minor species in heavily reduced basaltic melts (Fig 2). These trends are robust over the the compositional range (FeO = 0.01-0.12wt%, MgO = 8.91-29.25wt%, CaO = 6.19-11.20wt%, Na_2O = 0.46-4.61wt%), and they show a correlation with Fe, Mg, and Na, but not Ca content. FeS, MgS, and CaS trends are consistent with previous Raman results [2] and a prediction of Na^+ as a charge-balancing cation [19].

Discussion: The sulfide speciation trend has important ramifications for Mercurian magmas and other reduced rocky bodies. The bonding of S with Fe, Mg, Ca, and Na will reduce the activites of FeO (when present), MgO, CaO, and Na_2O affecting the silicate phase equilibria. Applying the S speciation trends to Mercurian melt chemistry, any iron in the silicate melt exists as FeS rather than FeO at these reducing conditions. The effective concentrations of MgO, CaO, and Na_2O are reduced by up to 28%, 53%, and 20% respectively. Sulfide complexing also increases the activity of SiO_2. As such, S speciation must be accounted for in thermodynamic models at these reducing conditions, including those calculating fO_2 from activities of FeO [4] or SiO_2 [7].

These changes in activity stabilize pyroxene with respect to olivine [21], and destabilize Ca-bearing silicates like feldspar and clinopyroxene. This implies enstatite may be enriched in the Mercurian mantle. Likewise, the increased stability of (Mg,Ca)S in the melt structure suggests it may be the dominant sulfide in Mercury's crust.

Changing S speciation should also affect the physical properties of the melts. Sulfide complexing increases the activity of SiO_2, which should increase polymerization and viscosity [20,21]. However, S may preferentially react with non-bridging oxygen atoms in
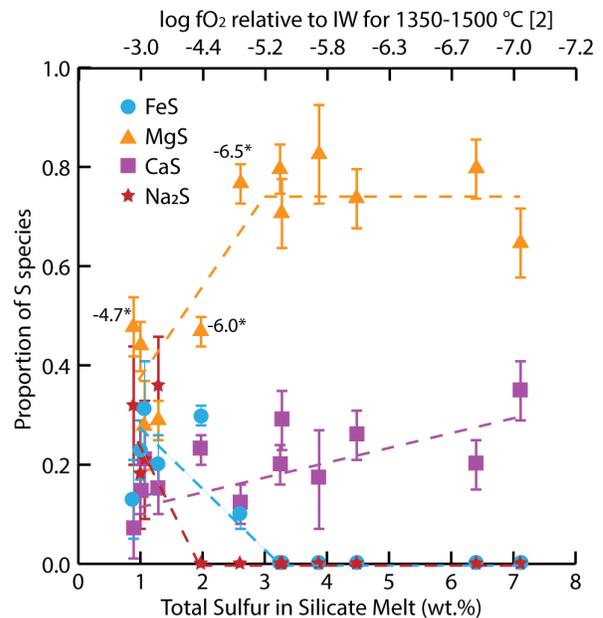

Figure 2. *Sulfide speciation in experimental glasses from LCF analyses of the XANES spectra. The proportion of the S species in the melt represented by FeS and Na_2S decreases, MgS increases, and CaS increases as S content increases and fO_2 decreases. Experiments run at 1GPa and 1250-1475 °C. Error is RSS of the 1σ SD and fitting error. *fO_2 recalculated for lower T*

the melt, which would produce the opposite effect [10]. Melt density should also be affected by what S species form in the melt: (density Na_2S < CaS, MgS < FeS). Changing viscosity and density will have substantial influences on both magma eruption dynamics, as well as the evolution of a Mercurian magma ocean.

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