

SULFUR SPECIATION IN HEAVILY REDUCED MERCURIAN MELTS BY K-EDGE XANES SPECTROSCOPY. B. A. Anzures¹, S. W. Parman¹, R. E. Milliken¹, ¹Department of Earth, Environmental, and Planetary Sciences, Brown University, Providence, RI, 02906. Email: brendan_anzures@brown.edu

Introduction: Oxygen fugacity has a large effect on sulfur solubility. The Earth, Moon, and Mars have typical mantle fO_2 between IW-2 and IW+2 [1,2] (Fig 1a). At these conditions, sulfur is present as an important minor element. On Mercury and in enstatite chondrites, high S abundances [3,4] imply substantially lower fO_2 values. Mercurian surface sulfur contents range from 1.5 to 4 wt. % [3], correlating with a mantle fO_2 between IW-3 and IW-7 from silicate-metal and silicate-sulfide equilibria [5].

An increase in sulfur solubility implies a change in sulfur speciation. High sulfur solubility has been observed in numerous experimental melts [6,7] at highly reducing conditions due to sulfide stability (Fig 1b). Thermodynamic models have predicted that sulfur bonds with Fe, Mg, and Ca in silicic melts under the heavily reduced conditions expected on Mercury. Such sulfides are found as phases in enstatite chondrites

[4,9]. However, sulfur speciation in basaltic melts at such low fO_2 is poorly constrained.

In this study we apply K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy to heavily reduced Mercurian experimental samples. K-edge XANES is a powerful method in determining S speciation in S-bearing phases and silicic glasses [10,11] and can provide direct insights into the oxidation state and coordination chemistry of various elements [12]. This experimental study looks to confirm and expand upon models linking sulfide speciation, sulfur solubility, and oxygen fugacity under heavily reduced conditions.

Methods: Experimental samples consistent with Mercurian surface measurements [3] and mantle estimates were prepared using the TZM pressure vessel and piston cylinder (PC) at Brown University. Experiments ranged from 177-196 bar and 1225-1400 °C in the TZM for the surface and between 1-2 GPa and 1300-1475 °C in the PC for mantle studies, with fO_2 in the range estimated for Mercury (Fig 1b). A composition similar to CH chondrite Allan Hills 85085 [13] was used as a primitive Mercurian mantle analog for PC experiments and a MESSENGER-derived Northern Smooth Plains (NSP) composition [3] was used for TZM. ALH 85085 was chosen as an Mercurian analog due to its similarities in major element ratios to an estimated bulk composition derived from Mercurian surface measurements. Sulfur was added to ensure sulfide saturation and fO_2 was controlled by initial Si/SiO₂ ratio. To produce standards for XANES, pure MgS was synthesized from Mg metal powder and excess S in a sealed evacuated silica tube [14] and 99.9% pure CaS was purchased from Alfa Aesar®. Glass compositions were obtained from WDS measurements using the microprobe at Brown University.

S K-edge XANES analyses were performed in a helium environment using an undulator-based, hard X-ray microprobe at beamline 13 IDE of the Advanced Photon Source (APS) at Argonne National Laboratory. Data collection and creation of micro-X-ray fluorescence maps were performed in Larch [15], an open source software designed for X-ray spectroscopy at modern synchrotron sources.

Processing and linear combination fitting of the resulting XANES spectra were performed within the Athena software package [16] to calculate proportions of FeS, MgS, and CaS in the sulfide saturated Mercurian glasses.

Results: New S K-edge XANES spectra standards were collected for pure Niningerite (MgS) and Old-

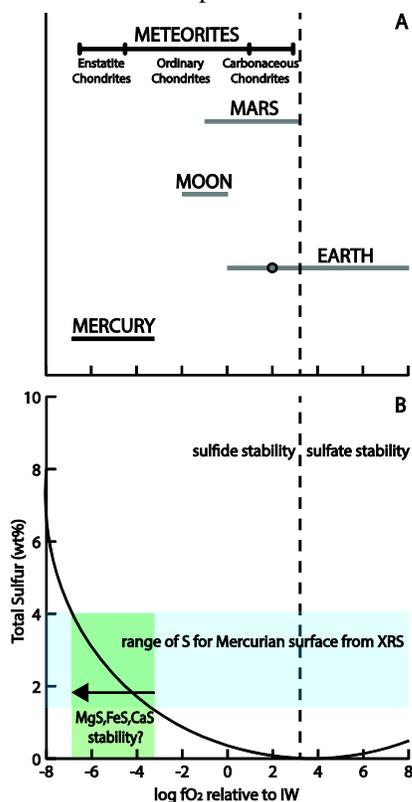


Figure 1. A. Terrestrial planets and meteorites cover a range of fO_2 [1,2]. The fO_2 for typical magmas on Earth is denoted by a gray circle B. S content at saturation in a silicic melt depends on fO_2 [4,8], which controls S speciation. The dotted line marks the division between sulfate and sulfide stability in silicic melts from experimental [6] studies. The range of S content for the Mercurian surface from XRS [3] is highlighted in blue, while the experimental range is highlighted in green.

hamite (CaS) and our results compare favorably with previous studies [11] (Fig 2a). FeS and MgS have K-edge energies at 2470.0 and 2475.1 eV, respectively, and CaS has two K-edge energies at 2474.0 and 2477.4 eV [11] (Fig 2b). CaSO₄ has the highest K-edge energy at 2481.9 eV [11] (Fig 2b).

XANES analysis of the Mercurian glasses exhibit a positive K-edge shift in observed mixed spectra due to a decrease in the FeS peak as fO_2 decreases (Fig 2b). MgS is seen in all spectra. A kink in the spectra at 2470.0 eV, the location of the FeS K-edge peak [11], is only observed in higher fO_2 experiments and disappears as fO_2 decreases (Fig 2b). The contribution of CaS is only obvious in a few experiments at the lowest fO_2 (Fig 2b). Linear combination fitting of the XANES spectra confirm that MgS is the dominant S-bearing species in silicic melts under Mercurian conditions. As total sulfur content in the glass increases and fO_2 decreases, the solubility of FeS decreases, MgS increases, and CaS increases (Fig 3). This is consistent with predictions from a previous study into S speciation at reducing conditions by Raman spectroscopy [17].

Discussion: The sulfide speciation trend has important ramifications for Mercurian magmas and other

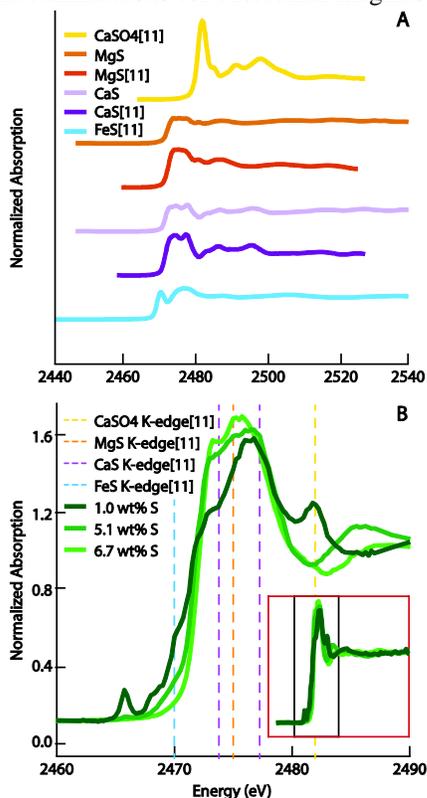


Figure 2. A. S K-edge XANES spectra standards for FeS (troilite), MgS (Niningerite), CaS (oldhamite), and CaSO₄ (gypsum) [11] and MgS and CaS from this study. B. XANES spectra for Mercurian mantle glasses change shape with fO_2 due to changes in S speciation. The red box shows the complete spectra with the black inset shown in large.

reduced rocky bodies including enstatite chondrites. It demonstrates that FeS is destabilized at low fO_2 . In addition, MgS is the dominant species and CaS is a minor species in heavily reduced basaltic melts. The bonding of S with Mg and Ca will change the activities of MgO and CaO and thus affect the silicate phase equilibria. Speciation will also affect the viscosity and density of the melt as both MgS and CaS are less dense than FeS, influencing both erupted magma and magma ocean dynamics [8].

The predominance of MgS in the melt is consistent with the Mg-rich nature of sulfide liquids seen in experimental studies at low fO_2 [4,17]. This implies MgS may be the dominant sulfide on Mercury's surface.

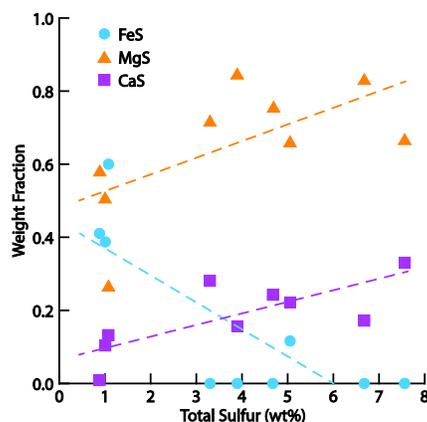


Figure 3. Sulfide speciation in Mercurian mantle glasses as revealed by linear combination fitting of the XANES spectra. The proportion of the sulfur bearing species in the melt represented by FeS decreases, MgS increases, and CaS increases as sulfur content increases. Experiments run at 1GPa and between 1300 and 1475 °C.

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References: [1] Righter K. et al. (2006) *Meteorites and the early solar system II*, 943, 803-828. [2] Wadhwa M. (2008) *RIMG*, 68, 493-510. [3] Nittler L. R. et al. (2011) *Science*, 333, 1847-1850. [4] Berthet S. et al. (2009) *GCA*, 73, 6402-6420. [5] Zolotov M. Y. et al. (2013) *JGR-Planets*, 118, 138-146. [6] Backnaes L. et al. (2011) *RIMG*, 73, 143-165. [7] Baker D. R. et al. (2011) *RIMG*, 73, 167-213. [8] Parman et al. (2016) *LPSC XLVII*, Abstract #2990 [9] Ebel D. S. et al. (2011) *Planet. & Space Sci.*, 59, 1888-1894. [10] Jugo P.J. et al. (2010) *GCA*, 74, 5926-5938. [11] Fleet M. E. (2005) *CANMIN*, 43, 1811-1838. [12] Newville M. (2014) *RIMG*, 78, 34-74. [13] Weisberg M. K. et al. (1988) *Earth & Planet. Sci.*, 91, 19-32. [14] Osborne M. D. et al. (1984) *Physics & Chemistry of Minerals*, 10, 245-249. [15] Newville M. (2013) *Physics*, 430. [16] Ravel B. et al. (2005) *Synchrotron Radiation*, 12, 537-541. [17] Namur O. et al. (2016) *Earth & Planet. Sci.*, 448, 102-114.