Sulfur Speciation in Heavily Reduced Mercurian Melts by K-Edge XANES Spectroscopy

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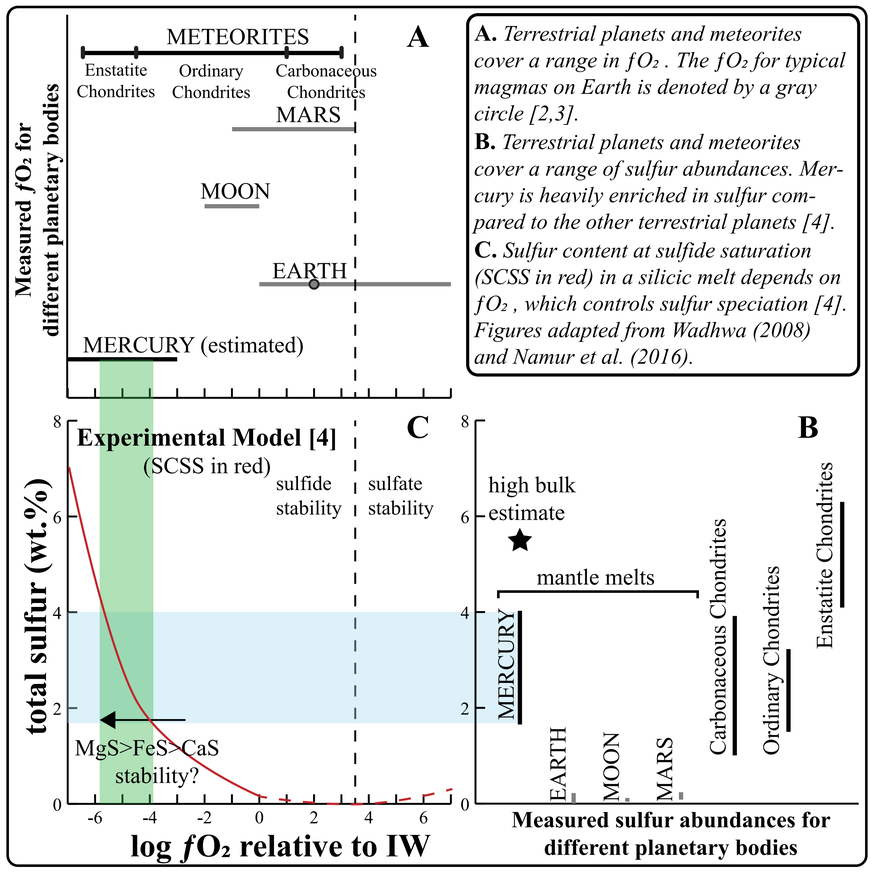
Abstract #2039

INTRODUCTION

What is the relationship between sulfide speciation, sulfur solubility, and oxygen fugacity in heavily reduced basaltic melts?

- Mercury's low oxygen fugacity (fO_2) is primarily inferred from its high surface sulfur abundance as revealed by the MESSENGER X-Ray Spectrometer (XRS) [1,2]
- High sulfur solublity in melts implies a change in sulfur speciation, which is poorly constrained
- S K-Edge XANES spectroscopy provides direct insights into sulfur speciation

We provide the first application of this method to basaltic melts at fO_2 relevant for Mercury

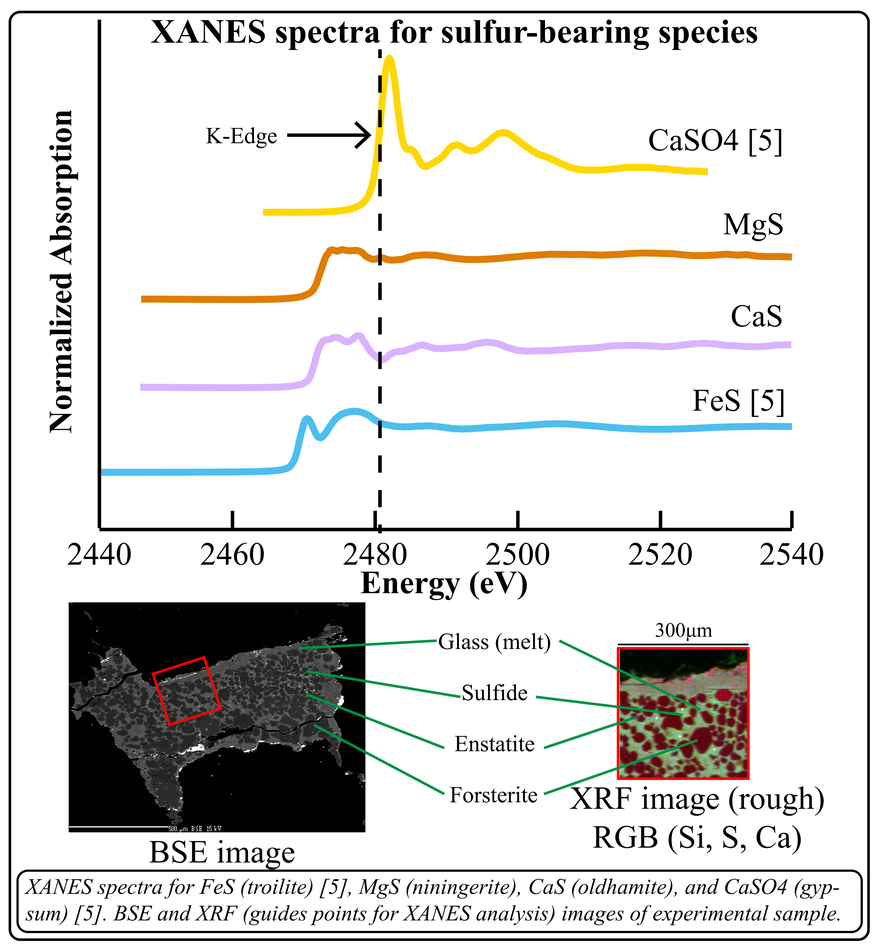


A. *Terrestrial planets and meteorites cover a range in fO_2. The fO_2 for typical magmas on Earth is denoted by a gray circle [2,3].*
B. *Terrestrial planets and meteorites cover a range of sulfur abundances. Mercury is heavily enriched in sulfur compared to the other terrestrial planets [4].*
C. *Sulfur content at sulfide saturation (SCSS in red) in a silicic melt depends on fO_2, which controls sulfur speciation [4]. Figures adapted from Wadhwa (2008) and Namur et al. (2016).*

METHODS

S K-Edge XANES Spectroscopy can directly characterize sulfur speciation

Remote Sensing (XRS,GRS) → Experimental Analog (PC,TZM) → Lab Spectroscopy (XANES)



XANES spectra for FeS (troilite) [5], MgS (niningerite), CaS (oldhamite), and CaSO4 (gypsum) [5]. BSE and XRF (guides points for XANES analysis) images of experimental sample.

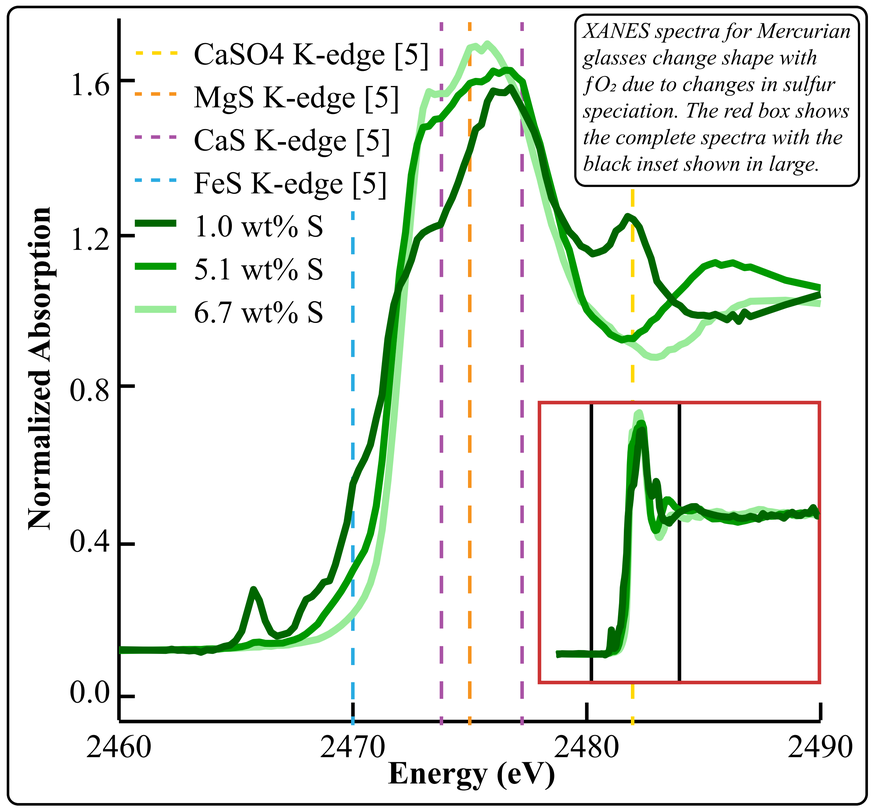
- Experimental samples consistent with Mercurian surface (XRS/GRS measurements) and mantle estimates (ALH85085), were prepared in a TZM (177-196 bar and 1225-1400 °C) and Piston Cylinder (1-2 GPa and 1300-1475 °C)
- XANES spectra collected using an undulator-based, hard X-ray microprobe at Argonne
- Processing and linear unmixing of XANES spectra performed using sulfur-bearing species as endmembers

RESULTS

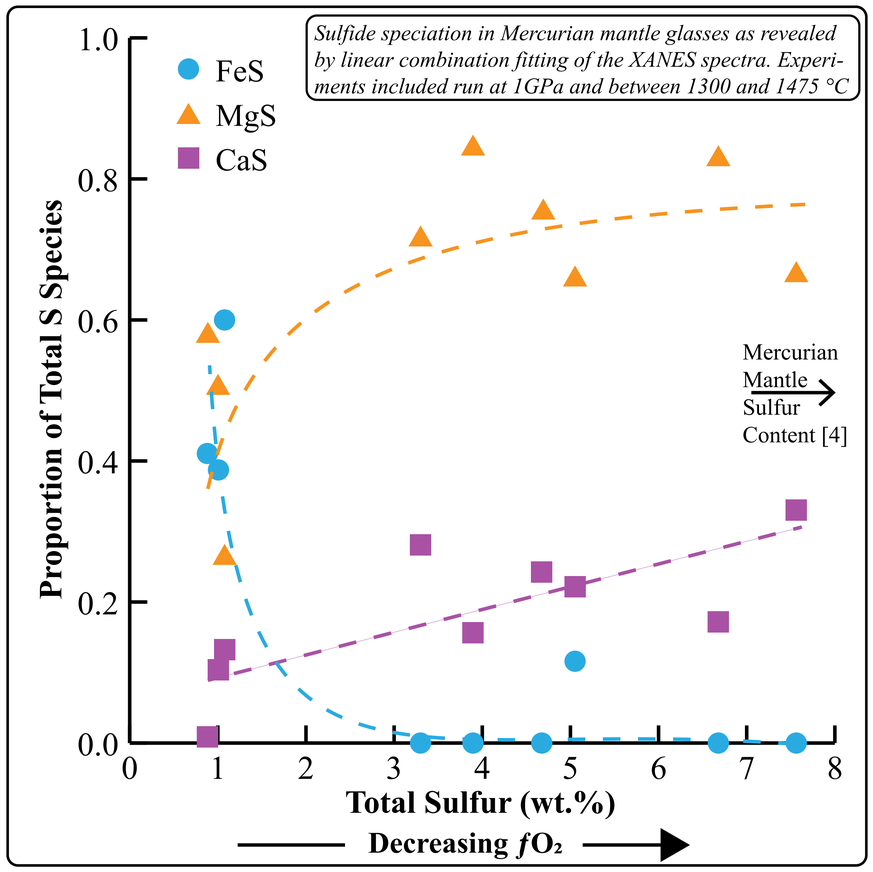
As total sulfur solubility increases due to decreasing oxygen fugacity, the relative proportions of each sulfur species changes

Visual examination of the specta reveals...

- The contribution from FeS disappears as fO_2 decreases (kink in spectra by the blue FeS K-edge)
- Spectra most closely resemble that of MgS
- The presence of CaS is only obvious in samples at the lowest fO_2 (double peak by purple CaS K-edges)
- Some sulfate contribution due to high reactivity of samples in air



XANES spectra for Mercurian glasses change shape with fO_2 due to changes in sulfur speciation. The red box shows the complete spectra with the black inset shown in large.



Sulfide speciation in Mercurian mantle glasses as revealed by linear combination fitting of the XANES spectra. Experiments included run at 1GPa and between 1300 and 1475 °C

Linear unmixing of the spectra reveals...

- FeS is destabilized at low fO_2
- MgS becomes the dominant species and CaS is a minor species in heavily reduced basaltic melts

Findings are consistent with sulfide speciation predictions from Raman spectra [4]

Further work is needed to confirm trends and ensure all endmember sulfides are included in linear unmixing (MnS, Na_2S, K_2S, etc.)

IMPLICATIONS

- Sulfur speciation will affect the viscosity and density of melts, influencing both erupted magma and magma ocean dynamics
- Bonding of S with Fe, Mg, and Ca changes the activites of FeO, MgO, and CaO and will affect silicate phase equilibria
- Results further constrain Mercurian mantle fO_2 and predicts that MgS is the dominant sulfide on Mercury's surface

References: [1] Nittler L. R. et al. (2011) Science, 333, 1847–1850. [2] Zolotov M. Y. et al. (2013) JGR-Planets, 118, 138-146. [3] Wadhwa M. (2008) RIMG, 68, 493-510. [4] Namur O. et al. (2016) Earth & Planet. Sci., 448, 102-114. [5] Fleet M. E. (2005) CANMIN, 43, 1811-1838.
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