**TEMPERATURE EFFECT ON SILICATE MELT-SULFIDE-METAL TRACE ELEMENT PARTITIONING IN THE PRESENCE OF SULFUR UNDER REDUCED CONDITIONS.**

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Introduction:. The reduced nature of Mercury, enstatite chondrites, and the aubrite parent bodies (APB) have raised many questions regarding the geochemical behavior of typically lithophile, heat-producing, and rare-earth elements (REE) in magmas at low oxygen fugacity (fO_2). Observations from experiments suggest that major and minor elements exhibit different geochemical affinities in highly reduced, S-rich systems compared to terrestrial rocks [1-6]. Due to decreasing O availability and an abundance of S^{2-} at low fO_2, sulfur (S) acts as an important anion that changes the partitioning behavior of many elements and modifies the physical properties of silicate melts. The speciation and bonding environment of S dictated by P-T-X-fO_2 may strongly influence the degree to which S affects partitioning behavior and silicate phase equilibria.

We have investigated the partitioning behavior of major, minor, and trace elements between silicate melt, sulfide melt, and metal, as well as the coordination chemistry of S, in highly reduced silicate melts. Our work is focused on investigating solely the entropy-dependent temperature effect on partitioning of elements for which we currently have MESSENGER data (K, Na, Th, U, Si, Mg, Fe, Ti, Ca, Al, Cr, Mn, S, Cl) as well as a host of geochemically relevant trace elements such as REEs (P, Co, Ni, Mo, Ce, Nd, Sm, Eu, Gd, Dy, Yb). Previous studies in which temperature, pressure, and fO_2 were co-varied found that as fO_2 decreases, heat-producing elements U and Th become more chalcophile, while K becomes less chalcophile [1-4]. Concurrently, nominally lithophile elements Mg and Ca become more chalcophile and were observed exsolved sulfides [7] and bonded with S species in silicate melt [8]. These studies, however, could not disentangle entropic T effects from changes in fO_2. New temperature-dependent partitioning data from our work will be used to determine which elements are most likely to retain their lithophile character and hence be incorporated into silicates, and which elements are likely contained within the sulfide (chalcophile) and metal core (siderophile), setting the stage for the thermal and magmatic evolution of reduced planetary bodies.

Methods: Experimental samples of silicate melt, iron sulfide, iron-silicon metal consistent with a predicted mercurian mantle and core composition were prepared in a piston cylinder at NASA Johnson Space Center (JSC). Sulfide-saturated experiments were conducted at 1 GPa at temperatures of 1500 to 1650 °C with an initial vol.% ratio of silicate melt, iron sulfide, and
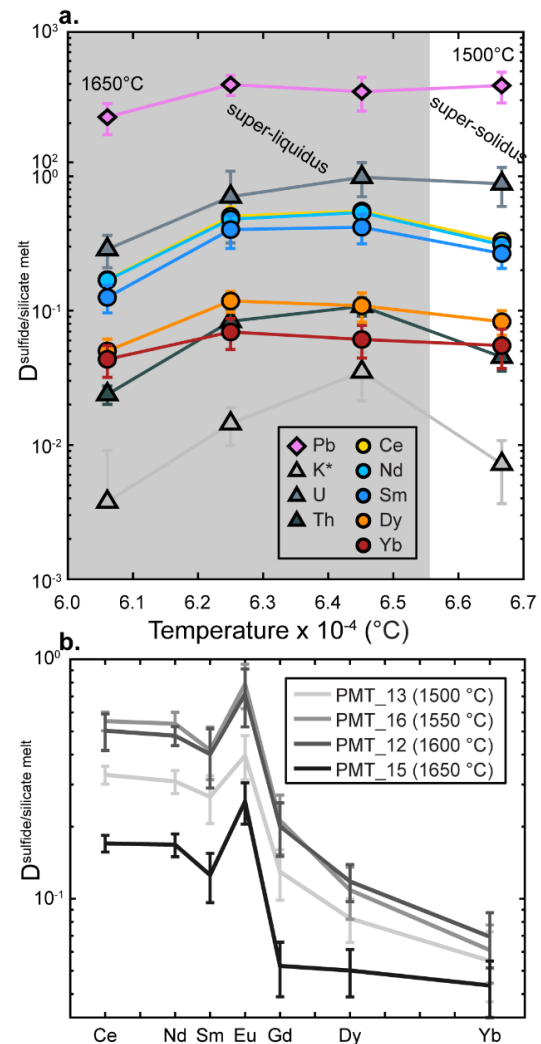

Figure 1. *Sulfide-silicate partition coefficients vs. a) temperature and b) atomic number. *K partition coefficients calculated from EPMA rather than LA-ICP-MS data.*

iron silicon metal of 50:35:15. fO_2 was varied from IW-4.5 to IW-6.5 by changing the Si content of the initial metal (e.g. wt.% Fe:Si 95:5 and 90:10). Major element compositions of silicate melt, sulfide, and metal were measured using the JEOL 8530 field emission electron microprobe (EPMA) at NASA JSC. Trace element compositions including REEs, K, U, Th, and Pb were measured by Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) using the 193 nm wavelength PhotonMachine Excite coupled to a Analytik Jena quadrupole ICP-MS at the University of Houston (laser

fluence of ~3.95 J/cm^2 at 35% laser energy, 10 Hz and spot size of 20–50 µm). Uncertainties were calculated as propagated 1σ weighted mean error.

Sulfur and chromium speciation in silicate melt were measured using S K-edge and Cr K-edge X-ray Absorption Near Edge Structure (XANES) spectra collected in a helium environment using an undulator-based, hard X-ray microprobe at Argonne National Laboratory. The spot size was 2 µm with a nominal penetration depth of 2–3 µm for S and 10 µm for Cr. 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 by linearly unmixing minimizing root mean squared error and maximizing r^2, keeping in mind chemical constraints as described in [8].
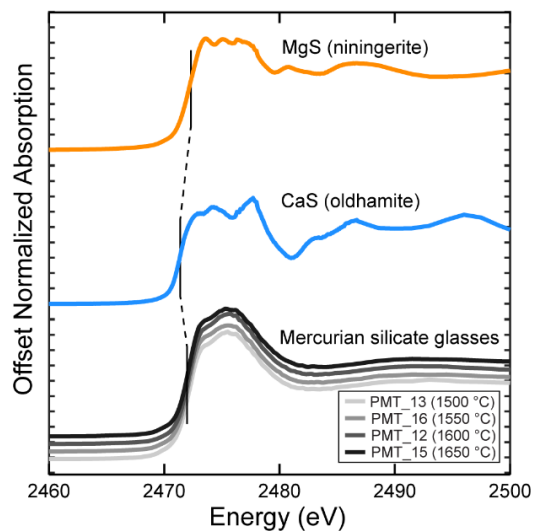
Figure 2. S K-edge XANES spectra of silicate glass from Mercurian temperature series experiments (1500 – 1650 °C) along with MgS and CaS standards.

Trace Element Results: Trace element results show that REEs, K, U, Th, and Pb are more chalcophile than siderophile, with metal trace element concentrations largely below the detection limit unlike sulfide and silicate melt, consistent with previous experiments at similarly reducing conditions [1-6]. Previous experiments at 1.5 GPa show increasing chalcophile behavior for these elements with increasing temperature from 1635 to 2100 °C [3]. However, we observe decreasing sulfide-silicate partition cofficients for REEs, K, U, Th, and Pb for super-liquidus experiments at 1 GPa and a temperature range of 1550 to 1650 °C (**Fig. 1**). Additional experiments will assess whether these conflicting results could be kinetically driven, as the experiments of [3] were run for 10–60 minutes and ours for 2–8 hours.

S Speciation Results: Unlike oxygen fugacity, pressure, and composition [8,9], temperature appears to have a negligible effect between 1310 and 1650 °C on sulfide speciation under very reducing conditions as revealed by S XANES spectral unmixing. The super-

solidus experiment at 1500°C and super-liquidus experiments from 1550 to 1650 °C have consistent S speciation at $(Mg_{80\pm10}Ca_{20\pm10})S$ (**Fig. 2**). This is consistent with another super-solidus temperature series using mercurian Borealis Plantatia composition from 1310 to 1500 °C within a limited range of fO_2 (IW-5.8 to IW-6.8) and lower pressure (0.1 GPa) [9]. Temperature does, however, increase sulfur solubility in very reduced silicate melts at temperatures of 1200 to 1750 °C [e.g. 10].

Implications: In contrast with [3], our preliminary experiments show decreasing sulfide-siliciate partitioning coefficients for rare earth elements and heat-producing elements with increasing temperature. More experiments are needed to expand the experimental T range and assess steady state behavior.

New S speciation results can be used to re-project data in silicate ternaries by apportioning Mg and Ca to bond with S and O. In a forsterite-albite-silica ternary using $(Mg_{80}Ca_{20})S$ as the S speciation in the silicate melt, silicate compositions move away from forsterite and anorthite, and toward silica and albite (**Fig. 3**). For enstatite chondrite and aubrite meteorites, all S dissolved in the silicate melt has been assumed to bond with Ca [11]. Correcting the re-projection with current S speciation results for aubrite basalt vitrophyres moves compositions towards tridymite, consistent with the abundance of silica polymorphs in aubrites and enstatite chondrites. Further work will explore how S bonding environment changes mercurian phase equilibria.

We will further investigate melt speciation by Cr and Cl XANES. These particular heterovalent elements are important because at low fO$_2$ various cations (e.g. Fe, Ca, Cr, Mg, Na, K) may bond with S and Cl rather than just O, impacting metal and sulfide complexing and transport.
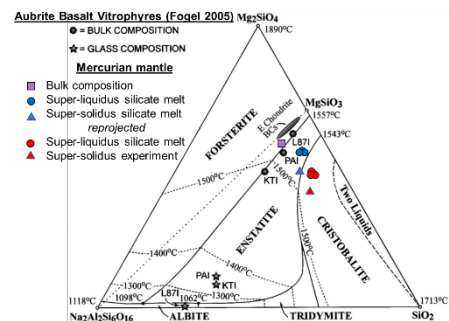
Figure 3. *Forsterite-albite-silica phase diagram annotated from [11]. Mercurian lava compositions are reprojected in red taking into account S bonding as $Mg_{80}Ca_{20}$.*

References: [1] McCubbin et al. (2012) *GRL, 39*, 9. [2] Vander Kaaden et al. (2016) *GCA, 173*, 246-263. [3] Wohlers & Wood (2017) *GCA, 205*, 226-244. [4] Boujibar et al. (2019) *AmMin, 104*, 1221-1237. [5] Steenstra et al. (2020) *Icarus, 335*. [6] Wilbur et al. (2022) *MAPS*. [7] McCoy et al. (1999) *MAPS, 34*, 735-746. [8] Anzures et al. (2020) *GCA, 286*, 1-18. [9] Anzures et al. (2021) *LPSC LII, Abstr # 2238*. [10] Namur et al. (2016) *EPSL, 448*, 102-114. [11] Fogel (2005) *GCA, 69*, 1633-1648.