A SYNTHESIS OF EXPERIMENTAL DATA DESCRIBING THE GEOCHEMICAL BEHAVIOR OF LITHOPHILE ELEMENTS AT EXTREMELY REDUCING CONDITIONS SEEN ON MERCURY

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Introduction: Returned data from the **Me**rcury **S**urface, **S**pace **En**vironment, **Ge**ochemistry and **R**anging (MESSENGER) spacecraft are showing interesting results for the planet Mercury. One of the most interesting features on the surface of the planet is the relatively high amount of S as well as the relatively low amounts of FeO, both up to ~4 wt% [1-3]. The most recent estimates of the oxygen fugacity of Mercury from S and Fe contents on the surface are between 2.6 and 7.3 $\log_{10}$ units below the Iron-Wustite (IW) buffer [4, 5]. These values are at least 2 orders of magnitude more reducing than the Moon [6-8], and are many orders of magnitude more reducing than the Earth [9] or Mars [10, 11]. Much of our geochemical understanding of elements in natural systems comes from empirical observations of rocks on Earth and from other planetary bodies; however Mercury's oxygen fugacity lies outside the norm of these observations, so any broad geochemical interpretations that are rooted in these empirical observations may be misguided.

The reducing nature of Mercury has raised many questions in regards to geochemical behavior and magmatism on not only this planet, but all reducing bodies in our solar system. In fact, interpretations of magmatic processes on Mercury are difficult at present because the numbers of experimental studies relevant to the extremely low fO_2 and high sulfur content of Mercury are very limited. At such reducing conditions, elements are likely to deviate from their typical geochemical behavior displayed at higher oxygen fugacity. For example, lithophile elements such as Mg and Ca display chalcophile behavior in some highly reduced chondrites and achondrites forming the minerals oldhamite [(Ca,Mg,Fe,)S] and niningerite [(Mg,Fe,Mn)S]. The main goal of this project is to experimentally determine the geochemical behavior of typically lithophile elements as a function of decreasing oxygen fugacity to gain a better understanding of the geochemical behavior of elements during Mercury's thermal and magmatic evolution.

Current Experimental Studies: The abundance of oxygen in most planets and planetary materials allows for the existence of lithophile elements. However, without oxygen, lithophile elements would change their behavior to chalcophile or siderophile. It is also possible some elements will exhibit homonuclear diatomic element behavior where they become predominantly self-bonding, a behavior we term here as egophilic. Mercury may be a case where this transition occurs in a geologically significant way. Other than the highly reduced enstatite chondrites and achondrites, we do not have many examples of how we should expect elements to behave in such oxygen-starved systems. Fortunately, a number of studies have reported on the distributions of elements among various phases at a range of oxygen fugacities, so it is possible to make some predictions about how, and under what conditions, certain elements would lose their lithophile behavior. [12] looked at the speciation of sulfur in basaltic glasses as a function of oxygen fugacity and found sulfur is present as sulfite and sulfate in oxidized silicate melts. [13] developed a model to predict sulfur concentrations at sulfide saturation in silicate melts after conducting experiments from 1150-1450 °C from pressures of 500 MPa to 1 GPa. [14] looked at the effect of pressure, temperature, and oxygen fugacity on metal-silicate partitioning of numerous elements including S and found S becomes more siderophile with increasing P and less siderophile with increasing T. More recently [15-17] have examined partitioning behavior in the Fe-S and Fe-S-O system. These studies, conducted at 9 GPa and 1 atm between temperatures of 1050-1600 °C concluded pressure affects solid metal/liquid metal partitioning, most elements show O-avoidance similar to their S-avoidance tendencies, and none of the experiments were able to match the MESSENGER results for the Fe and S on Mercury's Surface. Each of these studies has advanced our field in providing additional constraints on sulfur solubility and elemental partitioning during planetary differentiation; however they have not explored reducing, sulfur bearing conditions that are as extreme as those seen on Mercury.

Available Data: We have compiled sulfide solubility data as well as metal-silicate, sulfide-silicate, and metal-sulfide partitioning data that is currently available [14, 18-33] (Figure 1). We only included data for which oxygen fugacity was defined for each experiment or it could be reasonably estimated from the information provided. We acknowledge that there are other data available in the literature; however these are the most relevant to our work. Some trends are seen in the current available data. For example, sulfur solubility increases with decreasing fo_2 in silicate melts and $D^{Metal/Silicate}$ increases with decreasing fo_2 for Cr, Mn, and Co however, $D^{Metal/Silicate}$ decreases with decreasing fo_2 for S. There are also discrepancies seen within the data from study to study. For instance, $D^{Sulfide/Silicate}$ of

Mn and U is inconsistent at low fo_2. Additionally, numerous elements relevant to Mercury do not have any data available (ex. Ti, Ca), and metal-sulfide data is scarce. Furthermore, $D^{\text{Sulfide/Silicate}}$ values are only available for the uppermost estimate of Mercurian oxygen fugacity.

Future Work: Experiments are being conducted that will have a metal phase, silicate liquid phase, and a sulfide liquid phase present. Each experiment will be at superliquidus temperatures (1825-2200 °C) and pressures relevant to the CMB of Mercury (4-7 GPa) at highly reducing conditions. We expect the partitioning behavior of the elements of interest to change as a function of pressure and temperature. However, we expect that oxygen fugacity will play the largest role in controlling the partitioning of these elements. At lower fO_2’s we anticipate the lithophile elements will become chalcophile, siderophile, or egophile in nature. This partitioning behavior will give us insight into the distribution of elements between the silicate mantle, the core, and the proposed FeS layer at the core-mantle boundary on Mercury. These results may also prove relevant to exoplanets as the high metallicity of these planets imposes a low oxygen fugacity. Therefore, one would expect high Si in the core of these planets and our experimental results will help us better predict the mantle and crustal composition of such exoplanets.

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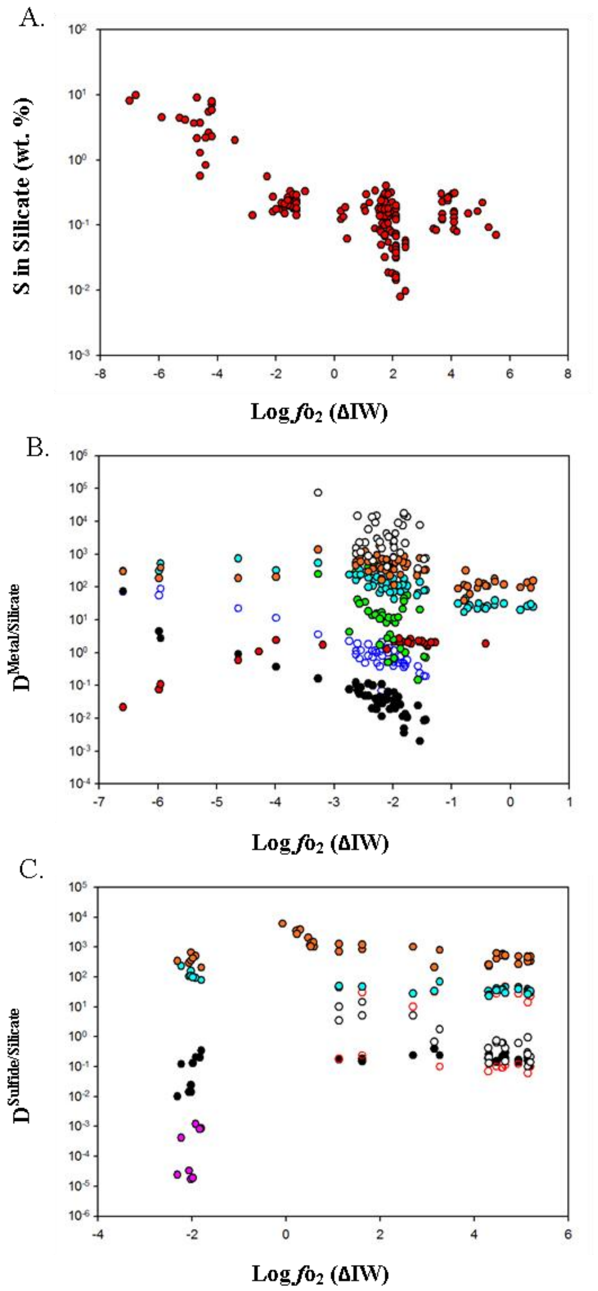

Figure 1. *Compilation of experimental data for sulfide bearing melts as a function of oxygen fugacity relative to the Iron-Wustite buffer (IW).* Symbols refer to different elements: P (green fill), S (red fill), Cr (blue edge), Mn (black fill), Co (cyan fill), Ni (orange fill), Pb (red edge), and U (pink fill). Experiments are from [14, 18-33]. Temperature range: 1050-2600 °C. Pressure range: 0.0001-25 GPa.