CAN SILICON-SMELTING CONTRIBUTE TO THE LOW O/Si RATIO ON THE SURFACE OF MERCURY?
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Introduction: The MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) spacecraft collected data that provided important insights into the structure, chemical makeup, and compositional diversity of Mercury. Among the many discoveries about Mercury made by MESSENGER, several surprising compositional characteristics of the surface were observed. These discoveries include elevated sulfur abundances (up to 4 wt.%), elevated abundances of graphitic carbon (0–4.1 wt.% across the surface with an additional 1–3 wt.% graphite above the global average in low reflectance materials), low iron abundances (less than 2 wt.%), and low oxygen abundances (O/Si weight ratio of 1.20±0.1) [1-6]. These exotic characteristics likely have important implications for the thermochemical evolution of Mercury and point to a planet that formed under highly reducing conditions [6-8].

In the present study, we focus specifically on the low O/Si ratio of Mercury, which is anomalous compared to all other planetary materials [e.g., 6]. A recent study that considered the geochemical implications of the low O/Si ratio reported that 12–20% of the surface materials on Mercury are composed of Si-rich, Si-Fe alloys [6]. They further postulated that the origin of the metal is best explained by a combination of space weathering and graphite-induced smelting that was facilitated by interaction of graphite with boninitic and komatiitic parental liquids. The goal of the present study is to assess the plausibility of smelting on Mercury through experiments run at the conditions that McCubbin et al. [6] indicated would be favorable for Si-smelting.

Rationale for Si-Smelting Model: First, we considered the chemical reactions that would need to occur in order to form Fe and Si metal. At the liquidus temperatures for mercurian magmas, graphite hosted by lavas would react with melt species to form CO through the following reactions:

$$C_{graphite} + FeO_{melt} \leftrightarrow CO_{gas} + Fe^{0}_{metal} \quad (1)$$

$$2C_{graphite} + SiO_{2melt} \leftrightarrow 2CO_{gas} + Si^{0}_{metal} \quad (2)$$

In a system with graphite and silicate melt, the degree to which these reactions proceed to the right depends on the partial pressure of CO (fCO) in equilibrium with graphite, which can be calculated as a function of temperature relative to each of the respective metal-oxide reactions. Importantly, the computed CO pressure using the metal-oxide reactions represents an upper limit because it assumes the activity of the oxide component in the silicate melt is unity, which is not directly applicable to silicate melts from Mercury.

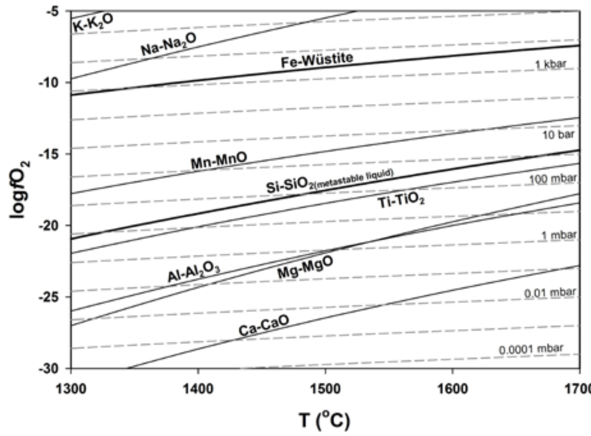

Figure 1. Plot of oxygen fugacity (fO_2) vs. temperature (T) over the range of estimated liquidus temperatures of lavas on Mercury. Dashed lines represent the fO_2 of the GCO buffer at specified partial pressures of CO. The solid black lines represent the oxygen fugacities of various metal-metal oxide reactions at 1 bar. The wüstite in the iron-wüstite reaction represents $Fe_{0.947}O$, and the SiO_2 in the Si-SiO_2 reaction represents a metastable SiO_2 melt. Thermodynamic data for all of the calculations obtained from JANAF tables [9].

Figure 1 illustrates the pressure-dependence of CO on the fO_2 of the graphite-CO (GCO) buffer relative to the fO_2 of numerous metal-metal oxide reactions as a function of temperature. Based on these calculations and liquidus temperatures for mercurian lavas of ~1320–1650 °C [10-12], confining pressures in the range of 10 millibars to 1 bar of CO are needed to prevent the formation of Si metal in the presence of graphite, and pressures of about 1 to 8 kilobars are needed to prevent the formation of Fe metal (Figure 1). When these pressures are adjusted based on the activities of SiO_2 and FeO in mercurian magmas (activities were estimated based on the mole fractions of the oxides in each of the nine geochemical terranes from [13]), confining pressures in the range of approximately 5 to 700 millibars of CO are needed to prevent the production of Si^0 by smelting, and confining pressures of approximately 10 to 400 bars of CO are needed to prevent the production of Fe^0 by smelting. These pressures indicate that smelting of Fe can occur in the shallow subsurface (up to a maximum depth of approximately 4 km below the surface) of Mercury during magma ascent, but smelting of Si would be limited to the surfaces of erupted lava flows provided CO pressure could not build overtop erupted lava flows. It was pointed out by [6] that the kinetics of reactions

(1–2) relative to the cooling rates of lavas on the surface of Mercury need to be assessed to determine the abundances of metallic phases that could reasonably form as a result of the smelting process. Consequently, our experimental study will assess whether or not Si-smelting can occur as described here and by [6].

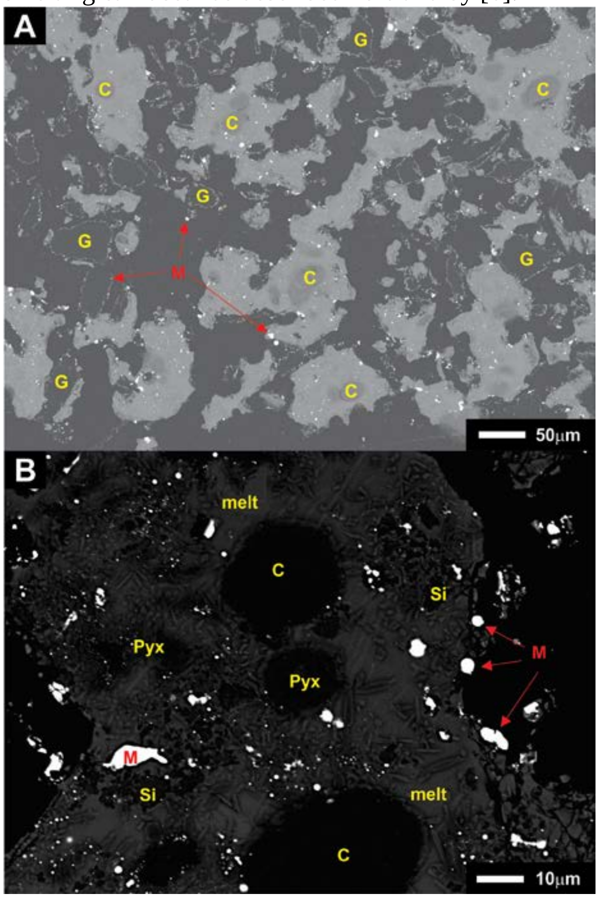

Figure 2. Back-scattered electron images of experimental run product at 1300 °C, with silica (Si), corundum (C), silicate melt (melt), Al-rich pyroxene (Pyx), graphite (G), and metal alloy (M).

Methods: We used the alkali- and S-free northern volcanic plains starting materials used by [12–13] as the silicate base for our experiments, and we mixed that composition with 15 wt.% graphite. ~30 mg of the starting material was placed in an alumina ceramic crucible. The sample crucible and an identical empty crucible were placed in a Labsys EVO differential scanning calorimeter (DSC) furnace/thermal gravimeter (TG) connected to a Pfeiffer GSD 320 quadrupole mass spectrometer (QMS) configured to operate similarly to the Sample Analysis at Mars (SAM) oven/QMS system. The DSC furnace was purged with helium gas and set to a pressure of approximately 30 mbar He. The crucibles were heated from room temperature to 1300 ºC at a heating rate of 35 ºC/min and at a flow rate of 10 sccm He. Masses 1-100 AMU were recorded throughout the entire experiment. Our initial experiments were run without a dwell step, so power was cut off to the system once we reached the maximum *T*. These short runs were designed to assess whether or not Si-rich metal nucleation is rapid, and we acknowledge that the experiments were not designed to approach equilibrium.

All experimental run products were polished to a 0.3 µm finish, carbon coated, and analyzed using a JEOL 8530F microprobe at NASA's JSC using the same procedures and protocols as outlined in [14].

Results: The experimental run product consisted of a mixture of phases, including Al-rich pyroxenes, melt, silica, corundum, and numerous Fe-rich metallic phases. The metallic phases range in Si abundance from 5.89 to 24.15 wt.% Si, which corresponds to 11.3 to 38.5 mol.% Si in the alloys. The alloys also contain Cr (2.5–16.4 wt.%) and Mn (0.06-2.05 wt.%). The metallic phases typically ranged in size from sub-µm to approximately 10 µm in diameter (Figure 2), and many of the metallic phases exhibit a circular habit (Figure 2B). Although the metallic phases occur within melt pools, they also line the edges of graphite, indicating that some of the metallic phases are forming through smelting processes (Figure 2A). Smelting is further supported by the evolved gas data that indicate high temperature releases of CO and CO_2.

Discussion: Our preliminary experimental results indicate that smelting is a kinetically fast process, even for Si-bearing Fe metallic alloys. The Fe-alloys produced in our experimental run product are more Fe-rich than those predicted to occur on Mercury in [6], although this is likely due, at least in part, to the FeO abundance of our starting composition, which had 5.2 wt.% FeO. Regardless, this data indicates that graphite-induced Si-smelting on the surface of Mercury is plausible, but future experiments will need to address if the same nucleation kinetics apply to systems with much less Fe. Additionally, we will conduct experiments for longer periods of time to better characterize how the smelting process and residual silicate mineralogy evolves to place better constraints on the mineralogy of Mercury's surface.

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