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Experimental constraints on Mercury's core composition

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A B S T R A C T

The recent discovery of high S concentrations on the surface of Mercury by spacecraft measurements from the MESSENGER mission provides the potential to place new constraints on the composition of Mercury's large metallic core. In this work, we conducted a set of systematic equilibrium metal–silicate experiments that determined the effect of different metallic compositions in the Fe–S–Si system on the S concentration in the coexisting silicate melt. We find that metallic melts with a range of S and Si combinations can be in equilibrium with silicate melts with S contents consistent with Mercury's surface, but that such silicate melts contain Fe contents lower than measured for Mercury's surface. If Mercury's surface S abundance is representative of the planet's bulk silicate composition and if the planet experienced metal–silicate equilibrium during planetary core formation, then these results place boundaries on the range of possible combinations of Si and S that could be present as the light elements in Mercury's core and suggest that Mercury's core likely contains Si. Except for core compositions with extreme abundances of Si, bulk Mercury compositions calculated by using the newly determined range of potential S and Si core compositions do not resemble primitive meteorite compositions.

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1. Introduction

Mercury is a planet of extremes. It is the smallest, the closest to the Sun, and also the densest when the uncompressed density is considered. Mercury's high density (Anderson et al., 1987) indicates the presence of a large metallic core that comprises roughly two-thirds of the planet, a much larger fraction than the other terrestrial planets of Venus, Earth, or Mars (Goettel, 1988). Additionally, Earth-based radar measurements showed that Mercury's core is at least partially molten (Margot et al., 2007). Earth-based and spacecraft spectral observations of Mercury's surface indicated the surface silicates are Fe-poor due to lack of absorption features, suggesting < ~3% FeO in the surface silicates (Blewett et al., 1997; McClintock et al., 2008; Robinson and Taylor, 2001; Vilas, 1988).

In March 2011, the MESSENGER (MErcury Surface, Space ENvironment, GEochemistry, and Ranging) spacecraft became the first ever to orbit Mercury, and as such is providing a wealth of new data about the Solar System's innermost planet (Bedini et al., 2012). In particular, MESSENGER's X-ray and gamma-ray spectrometers have yielded the first measurements of the elemental composition of Mercury's surface (Evans et al., 2012; Nittler et al., 2011; Peplowski et al., 2011, 2012a, 2012b; Starr et al., 2012; Weider et al., 2012). The composition shows variability across the surface, and for Fe and S, two elements pertinent to our study, Mercury's

surface ranges from roughly 1–4 wt% for both the Fe and S content (Evans et al., 2012; Nittler et al., 2011; Starr et al., 2012; Weider et al., 2012). There is general agreement between the X-ray and gamma-ray results, which sample the top ~100 µm (Weider et al., 2012) and ~tens of centimeters (Evans et al., 2012) of the surface respectively, suggesting that Mercury's regolith is homogeneous to at least a depth of ~tens of centimeters. Based on the measured surface Fe and S contents, the oxygen fugacity of Mercury's interior is quite reducing, with estimates ranging from −2.6 to −7.3 in log units relative to the iron–wüstite buffer (McCubbin et al., 2012; Zolotov et al., 2013).

MESSENGER's gravity data have also provided additional insight into Mercury's internal structure. The results suggest that the depth to Mercury's liquid core is ~400 km (Smith et al., 2012). Additionally, the first models of Mercury's solid layer above the liquid core suggested a higher density than that expected for Fe-poor silicates; this led to the proposal that a solid layer of FeS could be buoyantly stable at the top of the metallic core and thus provide a higher density solid material at the base of the mantle to explain the MESSENGER gravity measurements (Smith et al., 2012). Based on Mercury's reduced conditions, Malavergne et al. (2010) had previously suggested the possibility of Mercury's core containing both S and Si, and explored a variety of core crystallization scenarios that could arise, including the formation of a buoyant solid FeS layer. Chen et al. (2008) and Riner et al. (2008) also examined a variety of crystallization and layered core scenarios for Mercury in the Si-free Fe–S system, which were dependent on Mercury's unknown core S composition. Utilizing the latest determinations of

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Mercury's gravity field and Earth-based radar observations of the planet's spin state, Hauck et al. (2013) modeled Mercury's internal structure and considered core compositions in the Fe–S–Si system, including scenarios with a solid FeS layer at the top of the core.

Enstatite chondrites are primitive meteorites with Fe-poor silicates, suggesting their formation in highly-reduced conditions (Keil, 1989) and therefore their potential applicability as analog material for understanding Mercury's evolution. Partial melting experimental studies that used the Indarch enstatite chondrite as the starting composition created multiple sulfides, Fe-poor silicates, S-bearing silicate melts, and Si-bearing metals (Berthet et al., 2009; McCoy et al., 1999); these enstatite chondrite melting experiments thus offer intriguing potential for implications to Mercury's surface, given in particular the high S content of ~1–4 wt% from MESSENGER measurements. Metal–silicate partitioning experiments with applications for Earth's core formation concluded that S and Si were mutually exclusive in the metal phase, as the reducing conditions required to put Si in the metallic core would cause S to partition into the silicate melt (Kilburn and Wood, 1997), raising the question of whether Mercury's core could contain both S and Si. Other metal–silicate experimental studies have explored the partitioning behavior of S under a variety of pressure, temperature, oxygen fugacity, and composition conditions (Holzheid and Grove, 2002; Li and Agee, 2001; Rose-Weston et al., 2009). These previous experimental studies naturally were focused on conditions relevant to Earth, rather than the highly-reduced conditions experienced on Mercury, given the lack of chemical data for Mercury prior to MESSENGER's orbital measurements.

In this work, we conduct a set of systematic metal–silicate partitioning experiments designed to examine the effect that different metallic compositions in the Fe–S–Si system would have on the co-existing silicate. For Mercury, we have measurements of the planet's silicate surface, so we examine what constraints the chemical signatures measured in the silicate can provide on the composition of Mercury's large metallic core.

2. Methods

All experiments were conducted at 1 atm and 1500 °C in a vertical tube Deltech furnace at the Johns Hopkins University Applied Physics Laboratory using evacuated and sealed silica glass tubes, a technique well-established in previous experimental studies in this lab (Chabot et al., 2010, 2009, 2007).

To systematically examine the effect of varying the metallic composition of Mercury's core, we have restricted our experiments to a single starting silicate composition. This starting composition was based on measurements reported from the MESSENGER spacecraft for the major element surface composition of Mercury (Evans et al., 2012; Nittler et al., 2011; Starr et al., 2012; Weider et al., 2012). Ideally, these metal–silicate partitioning experiments would be conducted with a silicate composition that was representative of Mercury's bulk silicate composition, but the composition of Mercury's mantle is poorly constrained. The starting silicate was produced by mixing commercially purchased powders of SiO_2, $CaCO_3$, Al_2O_3, MgO, and TiO_2 (Table A1) and then decarbonating the mixture at 900 °C for 1 hour prior to the experiments.

The starting metallic material was varied between the experiments and was a mixture of Fe, FeS, and Si commercially purchased powders (Table A2). The different metallic compositions also resulted in different oxygen fugacity conditions between the runs. Starting silicate and metallic materials were mixed in a roughly 1:2 weight ratio and placed into a hard alumina crucible with an outer diameter of 6.5 mm and a wall thickness of 1.1 mm. The crucible was inserted in a high purity silica tube, with an outer diameter of 12 mm and a wall thickness of 2.1 mm. The tube
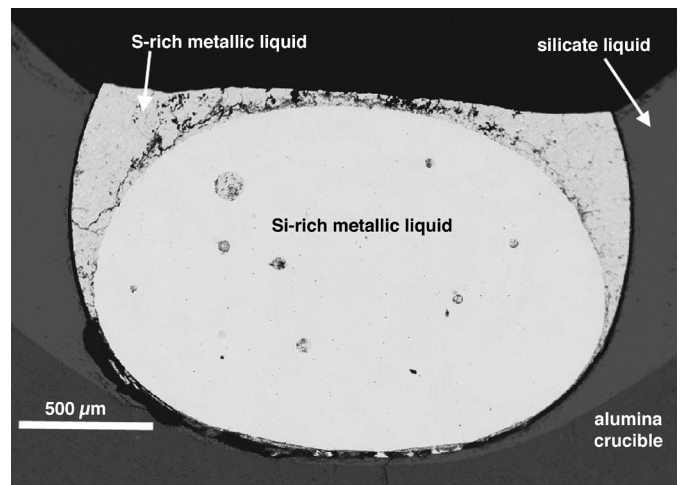

Fig. 1. Back-scattered electron image of experimental run #M1. The silicate was liquid at run conditions and quenched to a glass. In this experiment, two immiscible metallic liquids were present at run conditions, one S-rich and one Si-rich, which exhibit multi-phase textures upon quenching.

was evacuated and then sealed while under vacuum. The evacuated tube was lowered into the Deltech vertical tube furnace and held at 1500 °C for ~4 hours. Tubes were then removed from the furnace and quenched in a water bath. The alumina crucible was removed from the tube, mounted in epoxy, and sliced with a diamond saw to expose a cross-section of the experiment. The cross section was mount in epoxy and polished with alumina powder in preparation for analysis.

Run products consisted of quenched silicate and metallic phases that had been liquid at run conditions. Fig. 1 shows a back-scattered electron image of a typical run product. The silicate liquid quenched to a predominantly glass phase in all experiments. The runs either had one or two metallic liquids, depending on the bulk composition of the metal and whether liquid immiscibility was encountered in the Fe–S–Si system (Raghavan, 1988). If the run encountered the liquid immiscibility field in the Fe–S–Si system, two metallic liquids were present, one S-rich and one Si-rich. Sulfur-rich metallic liquids had a typical dendritic quench texture of Fe dendrites surrounded by predominantly interstitial FeS. Silicon-rich metallic liquids also displayed quench texture but it was more subdued, as reported in previous Fe–S–Si experiments (Chabot et al., 2010).

All experiments were analyzed on a JEOL JSM-6500F field emission scanning electron microscope at the Carnegie Institution of Washington, with settings of 15 kV, 1 nA, and 30 s acquisition time. Standards used were Fe_3O_4, MgO, Al_2O_3, SiO_2, FeS_2, Fe, wollastonite, diopside, orthoclase, and a natural basalt. Analyses were conducted such as to sample rectangular areas between 100 and 200 µm on a side, enabling the bulk composition of phases with quench textures to be determined. At least three measurements were made of each phase and averaged to determine the composition, with errors determined as the standard deviation of the multiple analyses.

3. Results

Tables 1 and 2 summarize the final compositions of the silicate and metallic phases. Five runs with the same starting metallic composition were conducted for durations of 0.5, 1, 2 (#M31), 4 (#M1), and 16 (#M34) hours. The three experiments with durations ⩾2 hours produced run products with consistent silicate and metallic compositions, as reported in Tables 1 and 2. In contrast, the two experiments with durations ⩽1 hour resulted in silicate compositions with slightly higher Si contents (~23 wt%) and