

**WHAT SULFIDES EXIST ON MERCURY?** W. M. Vaughan<sup>1</sup>, J. W. Head<sup>1</sup>, S. W. Parman<sup>1</sup>, and J. Helbert<sup>2</sup>.<sup>1</sup>Department of Geological Sciences, Brown University, Providence, RI 02912, USA, [Will\\_Vaughan@brown.edu](mailto:Will_Vaughan@brown.edu).<sup>2</sup>Institute of Planetary Research, Deutsches Zentrum für Luft und Raumfahrt, Berlin 12489, Germany.

**Introduction:** The planet Mercury has been described as hellish due to its maximum daytime surface temperatures, which exceed 400°C near 0°E and 180°E longitude. Chemical measurements of Mercury's shallow regolith made from orbit by the MESSENGER spacecraft indicate that Mercury is more hellish than anticipated, with brimstone in addition to fire: X-ray spectroscopy (XRS) [1-2] and gamma-ray [3] spectroscopy (GRS) independently indicate that Mercury's shallow regolith (GRS samples the top 10s of cm of regolith [3-4]) contains abundant sulfur (~2 wt. % S on average [1-3]; up to 4 wt. % S [1-2]). (We take this shallow regolith composition to represent the composition of mercurian magmas, following [5-6].)

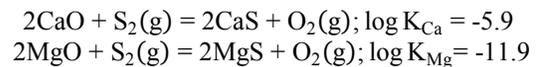
In what phase(s) is this sulfur present? Not in elemental sulfur, which is unstable on most of Mercury's surface (where maximum daytime temperatures of >500 K exceed the melting point of elemental sulfur (~400 K) and imply exceedingly high sulfur evaporation rates [7]); probably not in sulfates, due to Mercury's reduced, oxygen-poor chemistry [5-6]; probably not in quenched silicate melts (although silicate melts can contain up to 10 wt. % sulfur in very reducing conditions (below IW-3) [1,5-6,8], exsolution of sulfide phases from sulfur-rich silicate melt occurs upon even rapid (~10<sup>2</sup> sec) quenching [8]; for comparison, a 1-meter thick lava flow takes ~10<sup>6</sup> sec to cool by conduction). By process of elimination, the most probable sulfur-bearing phases on Mercury are sulfides.

What sulfides exist on Mercury? Likely FeS, as Fe is readily sulfidated in the presence of free S (in reduced conditions where O is wanting). But the shallow regolith is too Fe-poor for all sulfur to be present as FeS: the average Fe/S ratio of shallow regolith is ~0.8 by weight [3], whereas the Fe/S ratio of FeS is ~1.8 by weight. Thus, FeS accounts for only about half of the sulfur observed. Other sulfides must be invoked. Common sulfide-forming elements (e.g., Cu, Zn, Ni, etc.) have not been detected in any abundance [1]. Sulfides of the lithophile elements (e.g., CaS, MgS, MnS, NaCrS<sub>2</sub>, etc.) are common in enstatite chondrites [9], enstatite achondrites, and melts of enstatite chondrites [8], which are thought to be good chemical analogs for Mercury [1,5-6]; thus, lithophile sulfides could also be present on Mercury and account for the rest of the observed sulfur. In this abstract, we (1) present thermochemical and experimental evidence that CaS is the major lithophile sulfide on Mercury and (2) consider some implications of abundant CaS on Mercury.

**Thermochemical evidence for abundant CaS:**

The most abundant lithophile sulfide-forming elements on Mercury are Ca and Mg (Na is also abundant [3], but the major Na-bearing sulfide in enstatite chondrites is NaCrS<sub>2</sub> [9]; low inferred Cr abundances [1] contraindicate abundant Na-bearing sulfides). Thus, the major lithophile sulfide is either CaS or MgS (or both). What are the relative abundances of CaS and MgS likely to be on Mercury?

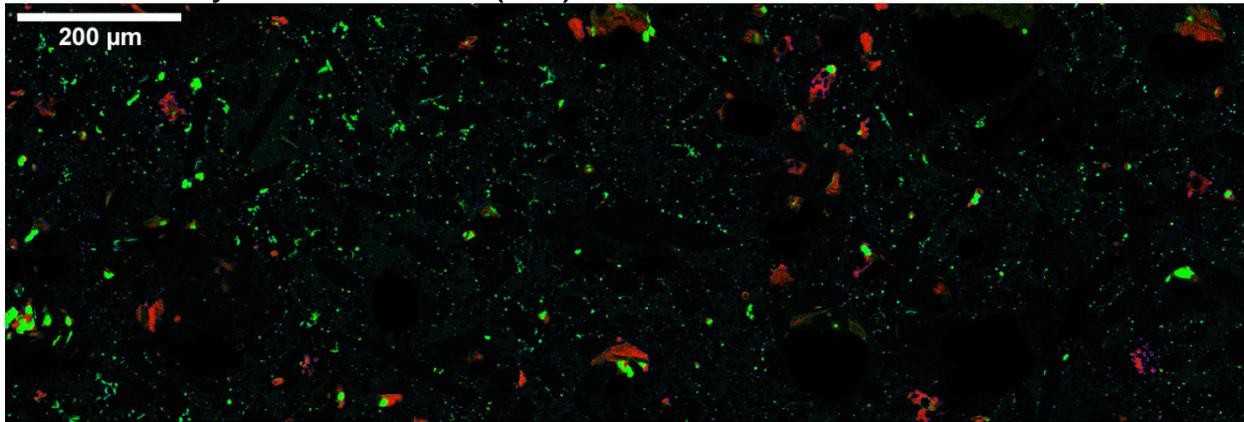
A simple thermochemical argument indicates that CaS ought to be substantially more abundant than MgS. Consider the following sulfidation reactions at 1500 K and 1 bar (tabulated in [5]):



Supposing that these sulfidation reactions occur in a silicate melt with a fixed bulk composition, and taking the activities of CaO and MgO to be equal (the Ca/Mg of Mercury's shallow regolith is ~0.5 [1-3], and normative calculations indicate the presence of both CaO and MgO in silicates [10]) the activity of CaS in the silicate melt at equilibrium is *10<sup>6</sup> times greater* than the activity of MgS. Therefore, a silicate melt with a composition similar to the shallow regolith becomes saturated with (crystallizes) CaS long before MgS.

Moreover, CaS will be saturated at the low fO<sub>2</sub> and high fS<sub>2</sub> conditions probably typical of mercurian magmas [5-6]. Before CaS is saturated, fS<sub>2</sub> in a sulfide-saturated melt is probably buffered by the equilibrium between FeS and Fe (if both phases are pure, log K<sub>Fe</sub> = log fS<sub>2</sub> = -4.8 [5]). Saturation will take place when log fO<sub>2</sub> = log K<sub>Ca</sub> + log fS<sub>2</sub> + 2 log a<sub>CaO</sub>; log a<sub>CaO</sub> is certainly <0 and probably near -2, so CaS is saturated near IW-2 at 1500 K and 1 bar. The fO<sub>2</sub> of mercurian magmas is thought to be somewhat lower [5-6].

A dramatic increase in the sulfur content of sulfide-saturated silicate melts (the SCSS) from ~0.4 wt. % S to ~10 wt. % S is observed near IW-3 to IW-4 [5-6,8]; the coincidence between these fO<sub>2</sub>s and the fO<sub>2</sub> of CaS saturation suggests that CaS saturation may be responsible for the SCSS increase (as previously suggested by [11-12]); i.e., near IW, a silicate melt is saturated with only FeS; several log units below IW, a silicate melt becomes saturated with both FeS and CaS, increasing the SCSS. Lithophile sulfide assemblages may serve as a useful oxybarometer for reduced solar system bodies such as Mercury.



**Figure 1.** X-ray map of run product (brightness: S concentration; R channel: Fe; G channel: Ca; B channel: Mg). All sulfides (bright phases) are FeS (red) or CaS (green). No MgS (blue) is observed, though MgO grains are seen.

**Experimental evidence for abundant CaS:** In order to confirm our thermochemical prediction that CaS is saturated in mercurian magmas, we investigated the sulfide mineralogy of a synthetic mercurian magma. A sulfur-rich, iron-poor Mercury shallow regolith bulk composition based on XRS measurements (flare #5 of [1]) was prepared. Concentrations of elements from the Comondale komatiite [13] were used for minor elements such as Mn (these minor elements have not yet been detected on Mercury by XRS [1]), due to the similarity between the (Fe+Mg)/Si ratio of this komatiite and the shallow regolith. Sulfur was added as elemental sulfur. The composition was packed in a graphite capsule and sealed in a platinum envelope. This charge was held at 1200°C for 2 hours in an internally-heated pressure vessel (at ~500 bar pressure in order to prevent evolved sulfur gas from popping the platinum envelope), then cooled 100°C/hour to 900°C. The oxygen fugacity was buffered at ~IW-1 by the graphite capsule. The run product was analyzed and mapped using a Cameca SX-100 electron microprobe.

The run product (Figure 1) comprises nearly pure forsterite and diopside set in sulfur-rich glass (containing up to 3 wt. % S) studded with abundant sulfides (several vol. %). These sulfides include CaS, FeS (containing minor MnS and NiS), MnS, and NaCrS<sub>2</sub>. Not a single grain of MgS is observed in the run product (Figure 1).

**Implications of abundant CaS for Mercury:** Thermochemical and experimental evidence indicates that CaS is the major lithophile sulfide on Mercury. Sulfides in the shallow regolith probably include major FeS and CaS with minor MnS and NaCrS<sub>2</sub>. Our prediction agrees with orbital observations: correlations between Fe, Ca, and S abundances (as well as largely uncorrelated Mg and S abundances) in XRS data [1-2] have been taken to mean that FeS and CaS, but not MgS, are present in Mercury's regolith.

We conclude by considering some implications of this sulfide assemblage for Mercury.

**Sulfide mineralogy.** Even at high temperatures, limited solid solution (<10 wt.%) exists between CaS and FeS [14] due to the very different ionic radii of Ca<sup>2+</sup> and Fe<sup>2+</sup>. Also, high daytime surface temperatures [7] could promote exsolution on long timescales. Therefore, major sulfides on Mercury are likely present as separate, nearly pure phases, although there may be substantial solid solution of MnS in FeS [14].

**UV-vis spectroscopy.** Normative calculations suggest that the major mercurian silicates are enstatite, labradorite, and albite [10]. These silicates are likely to be almost FeO-free [5] and are almost featureless at UV-vis wavelengths. The lithophile sulfides CaS and MnS, which have prominent spectral features at visible wavelengths [15-16], are likely the most featureful mercurian minerals in the UV-vis. However, lithophile sulfide spectral features have not been definitively detected on Mercury (though see [17]). This could be due to low lithophile sulfide abundances (several vol. %) or high surface temperatures: thermal processing at 500°C has been shown to decrease the contrast of lithophile sulfide spectral features [18].

**Sodium-rich plagioclase.** The sulfidation of CaO and the sequestration of Ca in CaS lowers the activity of CaO in mercurian magmas. Crystallizing plagioclase will therefore be relatively sodium-rich, as normative models predict [10]. Lithophile sulfides link sulfide and silicate equilibria on Mercury.

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