

**SPECTRAL REFLECTANCE MEASUREMENTS OF SULFIDES AT THE PLANETARY EMISSIVITY LABORATORY – ANALOGS FOR HOLLOW-FORMING MATERIAL ON MERCURY?** Jörn Helbert<sup>1</sup>, Alessandro Maturilli<sup>1</sup>, Mario D'Amore<sup>1</sup>, William M. Vaughan<sup>2</sup>, James W. Head<sup>2</sup>, Rachel L. Klima<sup>3</sup>, David T. Blewett<sup>3</sup>, Timothy J. McCoy<sup>4</sup>. <sup>1</sup>Institute for Planetary Research, DLR, 12489 Berlin, Germany (joern.helbert@dlr.de); <sup>2</sup>Department of Geological Sciences, Brown University, Providence, RI 02912, USA; <sup>3</sup>The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723, USA; <sup>4</sup> Smithsonian Institution, Washington, DC 20560, USA.

**Introduction:** MESSENGER orbital observations at Mercury show that unusually bright and spectrally relatively blue deposits within large craters first observed during Mariner 10 and MESSENGER flybys of Mercury [1-4], are marked by irregular, shallow, fresh-appearing rimless depressions (hollows) that are associated with impact crater floors, central peaks, and wall terraces [5].

There is an ongoing debate about the nature of the deposits in which the hollows form. Sulfides have been proposed as a possible candidate [5,6]. Observations with MESSENGER's Mercury Dual Imaging System (MDIS) and X-Ray Spectrometer (XRS) indicate a generally volcanic surface with high abundances of magnesium and calcium. The XRS analysis has also shown surprisingly high abundances of up to 4 wt. % sulfur [7].

So far there are only limited spectral reflectance measurements of sulfides (e.g., oldhamite [8]) available in the wavelength ranges spanned by MDIS or the Mercury Atmospheric and Surface Composition Spectrometer (MASCS). Furthermore, there are no measurements available of sulfides that have been exposed to Mercury's high dayside temperatures.

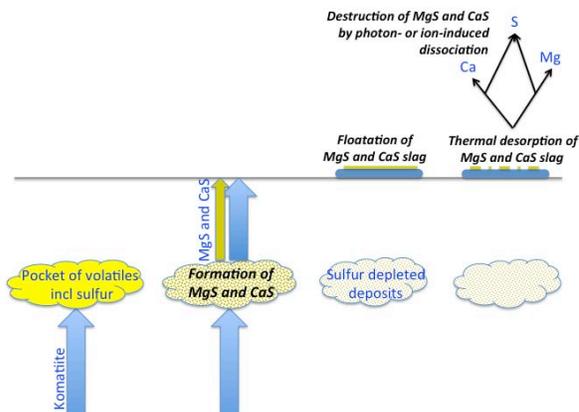
We present spectral reflectance measurements at visible and near-infrared wavelengths of fresh and heated samples of manganese sulfide (MnS), calcium sulfide (CaS), and magnesium sulfide (MgS), as well as elemental sulfur (S). From these new measurements, we infer that sulfides display a diagnostic feature at or near 0.6  $\mu\text{m}$ , a result consistent with the few available spectra in the literature [8].

**The slag scenario:** Blewett et al. discussed several mechanisms for formation of the hollows [5]. Vaughn et al. [6] recently suggested that impact melt differentiation provides a mechanism to form a sulfide-rich deposit that is partially removed to form the hollows.

We propose a slightly different mechanism, which connects the presence of highly magnesian volcanic deposits, the need for volatiles at depth to drive pyroclastic volcanic eruptions, and the observed volcanic flooding of most large craters on Mercury.

In industrial steel production, MgS and CaS are typical slag deposits. They are formed when Mg- or Ca-bearing materials are introduced into the molten ore. The Mg and Ca binds with the sulfur in the ore

and results in MgS or CaS, respectively [9]. Since the latter are less dense than the molten steel, they float and are removed from the top.



**Figure 1. Schematic of the slag scenario with komatiite as an example of a Mg-rich lava.**

If upwelling high-Mg (e.g., komatiitic) lava encounters a sulfur-rich (non-continuous) deposit in the subsurface, Mg and Ca would react with the sulfur, forming sulfides. The results for flooded craters would be MgS “slag” deposits at the top of lava infill. The slag deposit is then partially removed by space weathering and thermal desorption and the compounds destroyed by photo- or ion-dissociation. Little is known about the sublimation of MgS, CaS, or MnS under Mercury surface conditions, so for now thermal desorption is only a working hypothesis. Mg and Ca are persistent constituents of Mercury's exosphere [10].

**Sulfide samples:** Although a very simple idea, the slag scenario fits most observed characteristics of the hollows. However, an important observation is still missing. There has been so far no reliable detection of a spectral signature of sulfides in the MDIS or MASCS observations of surfaces containing hollows [11].

A possible reason for this situation is a lack of applicable laboratory spectral reflectance data for comparison. The minerals MgS (ninningerite) and CaS (oldhamite) are typically extracted from meteorites. It is challenging to assemble sufficient quantities (>5 g) of sample necessary to conduct high-temperature reflectance measurements.

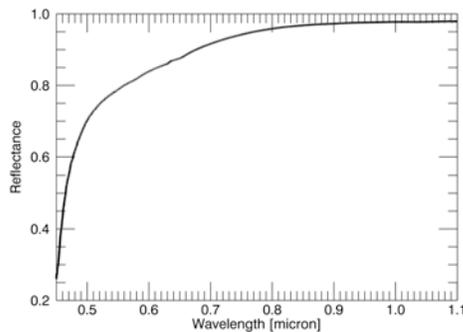
We have procured synthetic samples of MnS, CaS, and MgS. Although we could obtain large amounts of

the first two chemicals, we could obtain only 5 g of MgS. In addition, we measured elemental sulfur, for which a sample was already in our collection.

**PEL:** The Planetary Emission Laboratory (PEL) [12] operates two Bruker Fourier transform infrared (FTIR) spectrometers located on an optical table and connected to external chambers. The high-temperature chamber is connected to the Vertex 80V FTIR and can be evacuated to  $\sim 0.1$  mbar. The induction heating system heats the samples to temperatures of up to 700 K.

With the Bruker A513 accessory on the Vertex 80V, we measure the bidirectional reflectance of minerals, with incidence and emission angles varying between  $13^\circ$  and  $85^\circ$ . We measure at room temperature, under purge or vacuum conditions, covering the 1 to  $100 \mu\text{m}$  wavelength range. A Harrick Seagull<sup>TM</sup> variable-angle reflection accessory on the Bruker IFS 88 allows bidirectional reflectance measurement of minerals under purged conditions in the extended wavelength range from 0.4 to  $16 \mu\text{m}$  for angles between  $5^\circ$  and  $85^\circ$ .

**Spectral characteristics:** Example reflectance spectra of elemental sulfur, MgS, and MnS under ambient conditions are shown in Figs. 2-4. In progress are



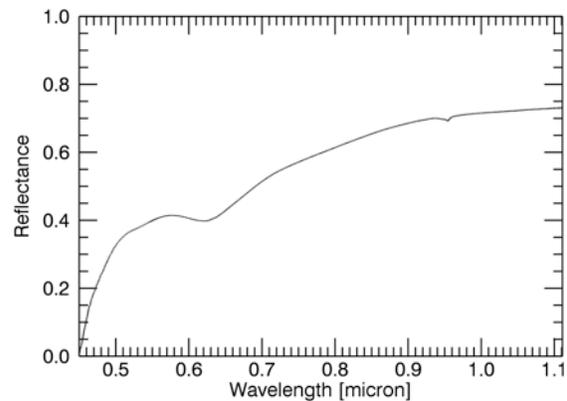
**Figure 2. Biconical reflectance spectrum of sulfur (0-25  $\mu\text{m}$  grain size). The spectrum was obtained on the Bruker IFS88 under purging at a biconical geometry with incidence and emission angles of  $15^\circ$ .**

low-temperature and high-temperature emissivity spectra for all samples. We are obtaining measurements at several temperature steps between room temperature and  $500^\circ\text{C}$ . We are also monitoring the sample surface using the camera built into the sample chamber.

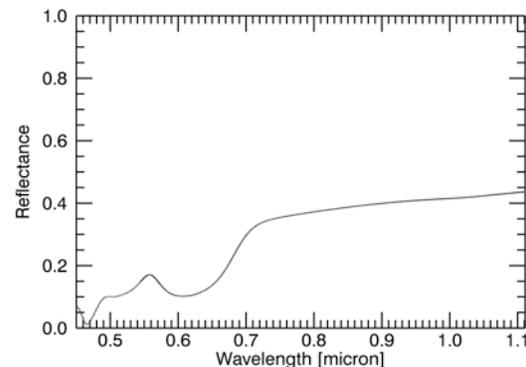
Finally, we are obtaining reflectance measurements of the heated samples (after cooling to room temperature) and comparing them to the spectra obtained before heating. This comparison provides important clues on changes in spectral characteristics resulting from exposure to Mercury dayside temperatures.

Reflectance spectra of MgS and MnS obtained under the same conditions as the sulfur are shown in Figs. 3 and 4, respectively. It is interesting to note how much brighter the sulfur is under the same geometry.

This difference might support the idea that decomposition of sulfides could lead to a temporary increase of surface brightness.



**Figure 3. Reflectance spectrum of MgS (0-25  $\mu\text{m}$  grain size) obtained under the same configuration as the sulfur in Fig. 2.**



**Figure 4. Reflectance spectrum of MnS (0-25  $\mu\text{m}$  grain size) obtained in the same configuration as the sulfur in Fig. 2.**

**Outlook:** From spectral reflectance measurements on sulfides currently underway at the PEL and from the available spectra in the literature [7], sulfides typically display a diagnostic absorption feature at or near  $0.6 \mu\text{m}$ . Such a feature could be used to locate sulfide deposits on the surface of Mercury. In combination with ongoing orbital measurements [e.g., 13], this spectral characterization of sulfides should help identify the material in which hollows form.

**References:** [1] Blewett D. T. et al. (2009) *EPSL*, 285, 272-282. [2] Blewett D. T. et al. (2010) *Icarus*, 209, 239-246. [3] Dzurisin D. (1977) *GRL*, 4, 383-386. [4] Robinson M. S. et al. (2008) *Science*, 321, 66-69. [5] Blewett D. T. et al. (2011) *Science*, 333, 1856-1859. [6] Vaughan W. M. et al. (2012) *LPS*, this mtg. [7] Nittler L. R. et al. (2011) *Science*, 333, 1847-1850. [8] Burbine T. H. et al. (2002) *MPS*, 37, 1233-1244. [9] Sarge T. W. (1944) U.S. patent 2358661. [10] Vervack R. J., Jr., et al (2010) *Science*, 329, 672-675 [11] Blewett D. T. et al. (2012) *LPS*, this mtg. [12] Helbert J. (2010) *LPS*, 1502. [13] D'Amore M. et al. (2012) *LPS*, this mtg.