

High-temperature spectroscopy of sulfides and implications for hollows on Mercury. Jörn Helbert¹, Alessandro Maturilli¹, Mario D'Amore¹, William M. Vaughan², James W. Head², Rachel L. Klima³, David T. Blewett³, Sean C. Solomon⁴. ¹Institute for Planetary Research, DLR, 12489 Berlin, Germany (joern.helbert@dlr.de); ²Department of Geological Sciences, Brown University, Providence, RI 02912, USA; ³The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723, USA; ⁴Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964, USA.

Introduction: MESSENGER orbital observations at Mercury show unusually bright deposits with less steeply sloped reflectance from visible to near-infrared wavelengths compared with the average Mercury spectrum. Such deposits are generally located within large craters, were first observed during Mariner 10 and MESSENGER flybys of Mercury of Mercury [1-4], and are marked by irregular, shallow, fresh-appearing rimless depressions or hollows [5]. Hollows are found on impact crater floors, central peaks, and wall terraces [5].

The nature of the deposits in which hollows formed is uncertain. Sulfides have been proposed as possible candidates [5,6]. MESSENGER's Mercury Dual Imaging System (MDIS) and X-Ray Spectrometer (XRS) indicate a generally volcanic surface with a magnesian composition (up to 25 wt. % MgO) [7,8] and surprisingly high abundances (up to 4 wt. %) of sulfur [7,8]. The XRS instrument also found indications for a correlation of the Ca/Si and S/Si ratios, hinting at CaS on the surface of Mercury [8].

To date there have been only limited measurements of the spectral reflectance of sulfides (e.g., natural oldhamite [9] and synthetic MgS, MnS, and CaS [10]) 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 calcium and magnesium sulfide. From these new measurements, we infer that the diagnostic spectral features of sulfides at or near 0.6 μm [9,10] can be strongly sensitive to thermal processing.

Sulfide samples: There has been so far no reliable detection of a spectral signature of sulfides in the MDIS or MASCs observations of surfaces containing hollows [5]. A possible reason for this situation is a lack of applicable laboratory spectral reflectance data for comparison. The minerals MgS (niningerite) 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 the following we present spectra of MgS and CaS; work on MnS is in progress.

PEL: The Planetary Emission Laboratory (PEL) [10] operates two Bruker Fourier transform infrared (FTIR) spectrometers that are 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 ~ 0.1 mbar. The induction heating system heats the samples to temperatures of up to 1200 K.

A Harrick SeagullTM 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 μm for phase angles between 5° and 85°.

Measurements: For both samples we obtained reflectance measurements of the fresh material at a phase angle of 80° (40° incidence and 40° emission angle). This viewing geometry is representative of more than 90% of the MASCs observations during the orbital phase of the MESSENGER mission.

After the reflectance measurements the samples were thermally processed in our high-temperature chamber following our established procedures (Fig. 1). The chamber was slowly evacuated to a pressure of approximately 10 Pa. Only after the vacuum was established were the samples heated to a maximum temperature of 770 K. The temperature was increased in steps of 100 K to the maximum temperature over a period of an hour. The samples were kept at this temperature for an hour. After this period the heating system was disabled and the sample cooled down to room temperature over a period of more than an hour. Only after the samples cooled down to room temperature again was the cham-



Figure 1. Setup for the thermal processing of CaS. The temperature sensor used to control the induction system is visible on the left. The sample was covered to reduce contamination of the chamber.

ber vented. The samples are transferred from the cups used for heating to cups made of Teflon for the measurements. This transfer ensures a mixing of the material, so spectral effects reported here are bulk effects and not just caused by a coating.

Spectral characteristics: The spectra of calcium sulfide obtained before and after thermal processing are shown in Fig. 2. The material darkens slightly, and the diagnostic bands lose some spectral contrast.

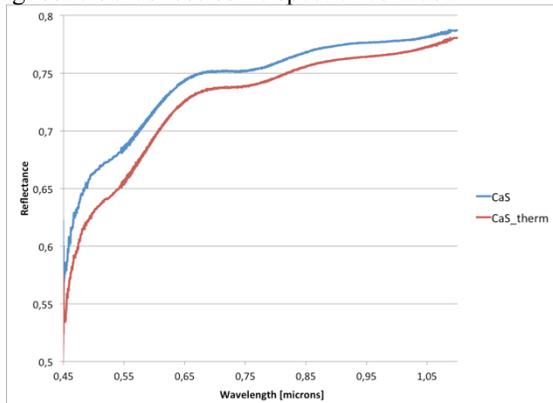


Figure 2. Biconical reflectance spectrum of calcium sulfide (0–25 μm grain size). The spectrum was obtained on the Bruker IFS88 under purging at a biconical geometry with incidence and emission angles of 40° before and after thermal processing.

The effect of thermal processing is even more pronounced for MgS, as shown in Fig. 3. The spectrum after thermal processing shows a substantial loss of spectral contrast in the diagnostic bands.

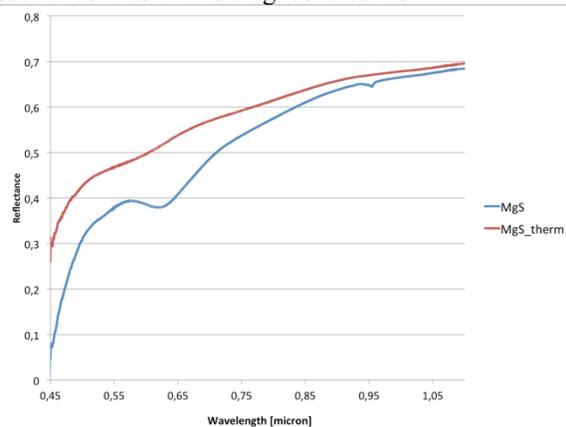


Figure 3. Reflectance spectrum of MgS (0–25 μm grain size) obtained under the same configuration as the CaS in Fig. 2.

Implications for MASCS: So far there has been no definitive detection of sulfides in observations of the hollows by either MDIS or MASCS [5]. Using our newly developed Berlin MASCS database [11] we investigated the statistical distribution of reflectance values at 650 nm, a wavelength near the center of one of the diagnostic bands for MgS. As a first-order photometric correction all spectra were first normalized at 700 nm [13].

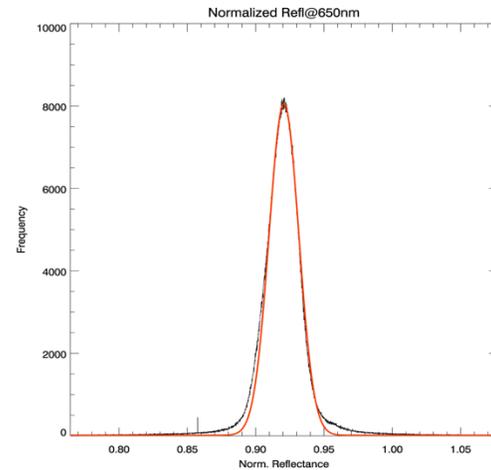


Figure 4. Statistical distribution of the normalized reflectance values at 650 nm (black) and a Gaussian fit (red).

The distribution on Mercury of reflectance values at 650 nm, shown in Fig. 4, is reasonably well fit by a Gaussian distribution. In other words, a substantial part of the data is indistinguishable from a random distribution. This distribution is most likely a combination of true variability on the surface, uncorrected illumination effects, and instrumental noise. There is a small but distinctive deviation from the Gaussian distribution for lower reflectance values. In general it seems, however, that the signal-to-noise ratio in this band is low, complicating the detection of MgS and CaS. Taking into account the effects of thermal processing only worsens the situation, because band depths are strongly diminished.

Outlook: The laboratory measurements currently underway at PEL in Berlin underline the need for high-temperature measurements to analyze the data returned by the MASCS and MDIS instruments. The fact that neither instrument has detected sulfides so far does not preclude their existence. The limited spectral resolution of MDIS makes the detection of sulfide bands challenging. MASCS has a much better spectral resolution, but the signal-to-noise ratio is most likely not sufficiently high, given the effects of high-temperatures on those bands demonstrated by the laboratory measurements reported here.

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