



Visible and near-infrared reflectance spectra of thermally processed synthetic sulfides as a potential analog for the hollow forming materials on Mercury



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ABSTRACT

We have obtained reflectance spectra in the visible spectral range of magnesium, calcium and manganese sulfides before and after thermal processing at Mercury dayside temperatures in vacuum conditions. All measurements were made at the Planetary Emissivity Laboratory (PEL) at DLR. These experiments are motivated by the recent findings of the MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) mission of hollows on Mercury and the notion that sulfides might be a candidate material for their formation. From these new measurements, we infer that all sulfides studied here display a diagnostic feature at or near 0.6 μm . The spectral contrast of this diagnostic feature can be strongly affected by heating of the samples to Mercury daytime temperatures of approximately 500 °C in a vacuum environment. Both the spectral slope and the color observed before and after thermal processing showed significant changes. The laboratory work also indicates that sulfides can be thermally decomposed at temperature below 500 °C, well below their melting point. Our results are consistent with models explaining hollows on Mercury's surface by the thermal decomposition of sulfides.

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1. Introduction

MESSENGER orbital observations with the Mercury Dual Imaging System (MDIS) at Mercury show that unusually bright and spectrally relatively blue deposits within large craters first observed during Mariner 10 and MESSENGER flybys of Mercury (Blewett et al., 2010, 2009; Dzurisin, 1977; Robinson et al., 2008), are marked by irregular, shallow, fresh appearing rimless depressions (hollows) that are associated with impact crater floors, central peaks, and wall terraces (Blewett et al., in press, 2011).

There is an ongoing debate about the nature of the deposits in which the hollows form. Sulfides have been proposed as a possible candidate (Blewett et al., in press, 2011; Vaughan et al., 2012). Observations with MESSENGER's 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 (Nittler et al., 2011). Recent global scale results from the XRS instrument (Weider et al., 2012) indicate a correlation between the calcium and sulfur abundance, hinting at the potential presence of calcium sulfides.

So far there are only limited spectral reflectance measurements of sulfides (e.g., oldhamite (Burbine et al., 2002)) 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 here spectral reflectance measurements at visible and near-infrared wavelengths of fresh and thermally processed samples of manganese sulfide (MnS), calcium sulfide (CaS), and magnesium sulfide (MgS). The measurements are obtained at a phase angle of 80° (40° incidence and 40° emission angle). This phase angle is comparable to the average phase angle under which the MASCS instrument on MESSENGER obtains data during the orbital phase of the mission. Therefore the laboratory measurements can be compared directly to the majority of MASCS spectral observations of Mercury's surface. From these new measurements, we infer that sulfides display a diagnostic feature at or near 0.6 μm , a result consistent with the few available spectra in the literature (Burbine et al., 2002). However the strength of this diagnostic feature is altered significantly when sulfides are exposed to Mercury daytime temperature of 500 °C in a vacuum environment.

In the following we introduce the setup at PEL and the materials used in this study. Then we describe the procedure used for thermally processing the samples and the acquisition of spectral measurements of the samples before and after heating. We discuss our findings and draw some conclusions for their applicability to analyzing recent data from the MESSENGER mission.

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2. Methods and materials

2.1. Planetary Emissivity Laboratory

The Planetary Emissivity Laboratory (PEL) has been operating in various configurations for more than 10 yr. High signal to noise and accurate spectra of a wide variety of silicate rocks and minerals have been published (e.g. Maturilli et al., 2006, 2008; Helbert and Maturilli, 2009; Sprague et al., 2009; Vernazza et al., 2010). The laboratory is located in an air-conditioned room at the Institute for Planetary Research in Berlin. PEL currently operates two Bruker Fourier transform infrared (FTIR) spectrometers both equipped with external chambers for emissivity measurements. Both spectrometers are located on an optical table. A purge gas generator (CMC PG 28L) provides purge air with a H₂O concentration of less than 1 ppm. This dry air purges the chambers and drives the air-bearings for the mirrors of both spectrometers. The whole setup is shown in Fig. 1.

The first spectrometer is a Bruker IFS 88, which operates completely under purged air. A Harrick Seagull™ variable-angle reflection accessory on this spectrometer allows bidirectional reflectance measurement of minerals under purged conditions in the extended wavelength range from 0.4 to 16 μm for angles between 5° and 85°. For the wavelength range from 0.4 to 1.1 μm a Si-diode in combination with a quartz beamsplitter is used. The range from 1.4 to 16 μm can be covered with a combination of a MCT detector and a KBr beamsplitter.

Motivated by the need for even better simulation of planetary regoliths in vacuum environments over a wide temperature range, PEL added a second spectrometer a Bruker Vertex 80 V which can be fully evacuated. The Bruker A513 accessory on this spectrometer permits the measurement of the bidirectional reflectance of minerals, with incidence and emission angles varying between 13° and 85°. Reflectance can be measured at room temperature, either under purge or vacuum conditions, from 1 to 100 μm. The wavelength coverage is achieved with a combination of a liquid nitrogen cooled MCT detector and KBr beamsplitter for the spectral range from 1 to 25 μm and a DTGS detector with a multilayer beamsplitter for the remaining spectral range.

The main feature of the PEL is a high-temperature chamber attached to the VERTEX 80 V that allows heating samples to temperatures of more than 700 K (426.85 °C) under vacuum conditions (medium vacuum—10–100 Pa). The unique feature of the setup is the heating system. Samples are placed in steel cups equipped with type K thermopiles as temperature sensors. A copper induction coil installed in the chamber and connected

to a Linntherm 1.5 kW induction system allows contactless heating of the ferromagnetic sample cups by induction. A high frequency alternating current in the coil system induces eddy currents in the stainless steel of the sample cups. These currents heat the steel, which by thermal conduction heats the sample material. Only the sample cup and the sample, but not the heating system reach high temperatures. Thermal losses to the rest of the chamber are minimized. Details of the heating system and its performance are discussed in Helbert and Maturilli (2009). The chamber is equipped with an automated sample transport system consisting of a high temperature resistant quartz glass sample carousel and a computer controlled stepper motor as driver. The automated system allows measuring a series of samples without breaking the vacuum.

The connection between the spectrometer and the chamber can be sealed with a hydraulic operated shutter. To maximize the signal throughput no window is installed between the spectrometer and the chamber. In typical operations the shutter is only opened during the measurement. This is a safety precaution to protect the spectrometer optics from potential outgassing of sample material in the chamber. A camera with switchable LED lights installed in the chamber allows monitoring the behavior of the sample. Using this camera we observed during preliminary testing of our heating experiments that the sulfides were thermally unstable. To avoid subjecting optical components in the spectrometer to thin deposits of decomposed material, no emissivity measurements of sulfides are included in this study.

2.2. Synthetic sulfides

Sulfides are common in terrestrial planetary regoliths and meteorites (Lodders and Fegley, 1992). The natural occurrence of sulfides in mineral form is niningerite for MgS, oldhamite for CaS and alabandite for MnS. These minerals are mainly found in meteoritic material. They are difficult to extract and therefore procuring large quantities as needed for this study is almost impossible. Furthermore there was good evidence to assume that the thermal processing would alter the samples, which prohibited performing the experiments on loaned samples. Synthesizing sulfides is a time-consuming and complex procedure that would go beyond the experimental capabilities available at the Planetary Emissivity Laboratory (PEL).

Our measurements were performed on synthetic sulfides procured from certified industrial suppliers. Each sample was guaranteed to be at least 99% pure by the provider and all data are given in Table 1.

3. Procedure

For the study here we follow a simple three-step procedure. First reflectance measurements are obtained on the fresh samples. The samples are then thermally processed at Mercury daytime temperatures under vacuum conditions in the PEL planetary simulation chamber. Finally for all thermally processed samples reflectance measurements are again obtained. Comparison of the reflectance spectra obtained before and after the thermal processing allows assessing permanent spectral changes induced by the exposure to Mercury daytime temperatures.

In the following we describe in detail the steps of the procedures.

3.1. Initial reflectance measurements

All samples are stored in a desiccator and are only removed immediately before the measurements. For reflectance measurements

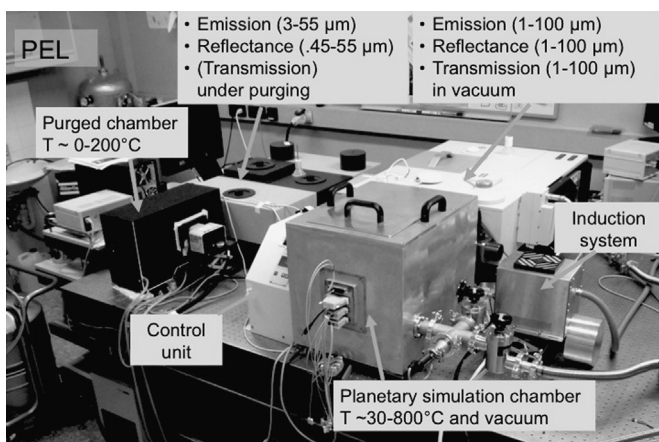


Fig. 1. Overview of the setup at the Planetary Emissivity Laboratory (PEL) for this study. The Bruker IFS88 spectrometer on the left was used in combination with the Planetary simulation chamber seen in front.

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