Self-cleaning Sulfides as Mercury Hollow Bright Material

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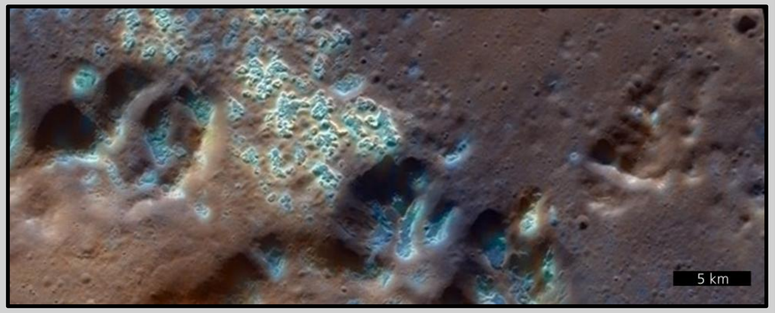
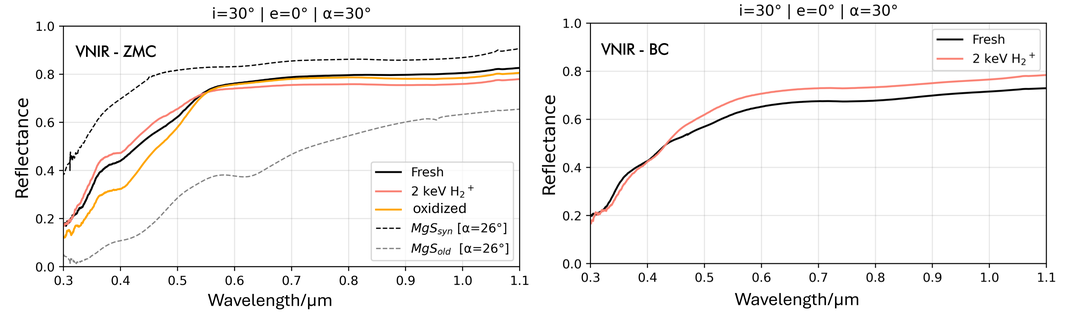
Hollows, Mercury's unique evaporation features and sulfides in their role as hollow darkening agents



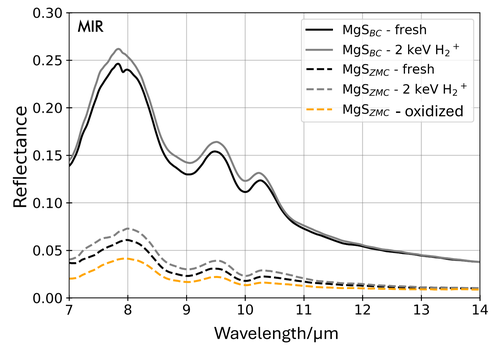
Planet Mercury is home to the unique features called hollows that are presumed to be created by evaporation processes. What distinguishes these features is their brightness in the visual to near infrared. **Sulfides were proposed as possible darkening agents that, when removed, would reveal the supposedly brighter material underneath.** This was motivated by the darkening and S-depletion of ion-sputtered FeS. Since then it was found that linear mixing of CaS, MgS, and Na_2S best reproduces the shape of the hollow spectra[1]. It is, however, unclear how said sulfides would react to irradiation. To test this, we irradiated CaS and MgS with H_2^+ ions at typical solar wind speeds.

The visual and infrared spectra of ion-irradiated MgS suggest **trends of increased and preserved reflectance**

Two different MgS samples were used, sourced from Zegem Metals&Chemicals Ltd. (ZMC) and Benchem (BC), respectively. **Unlike in FeS, a brightening was seen in all MgS spectra in both the VNIR and mid-infrared (MIR) range.** In the visual to near infrared (VNIR), significantly different spectral shapes were found for the ZMC and BC samples. Furthermore, the samples reflected slightly differently in the UV-VIS range of 0.1-0.8 µm under irradiation. At normal emission, the ZMC sample expressed brightening in the UV and lower VIS spectral range but a ~10% darkening in the upper VIS (> 500 nm), whereas the BC sample showed either no change or a darkening in the UV, with brightening in the VIS. **To understand if this behavior is a geometrical or a chemical effect, we reviewed the two samples' surface compositions and bond-chemistry data together with their grain size information.**



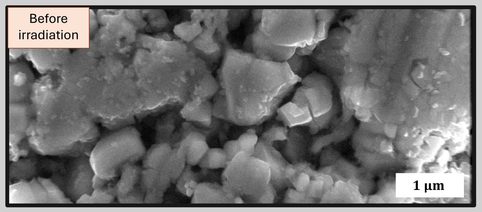
Visual-to-near infrared measurement of fresh MgS (black line) compared to 2 keV protons (salmon) and an old, oxidized sample (yellow). Two unirradiated reference samples are shown, whereas one is fresh (syn) and one is old and oxidized (old).



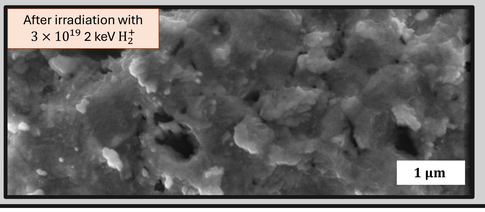
Mid infrared measurements of the two MgS samples BC (solid lines) and ZMC (dashed lines). **The irradiated samples (light gray) have a consistently higher reflectivity in the MIR than the unirradiated (fresh) samples.** The heavily oxidized sample (yellow) is the darkest, with a reflectance well below the fresh samples.

Morphology as cause of VNIR variability

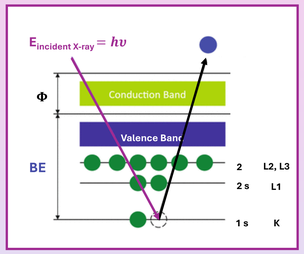
With the surface composition likely ruled out as the cause for the difference between the shapes of the VNIR reflectance spectra, we compared the grain-size distributions of the samples. We found MgS from BC to be made up of a slightly larger median grain size (1.0 ± 0.5 µm) than the ZMC one (0.7 ± 0.5 µm). Pressing the powder into a pellet overall preserved this discrepancy, although the flat surface area increased, and larger grains were broken down. **Because the resulting grain sizes lie within the VNIR range, we are confident that the different grain size distributions are the primary cause for the mismatch between the two spectral shapes.**



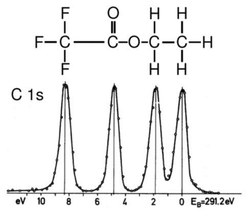
The presence of small surface features below the VNIR wavelength increases the chance of light absorption. With irradiation, we observed an overall smoothing of the surface, but also the introduction of hummocky features that are 10-100s of nm in size. **In the coarser BC sample (1.0 µm), the significant levels of brightening are confined to wavelengths >0.45 µm, whereas in the finer-grained ZMC sample (0.7 µm) the brightening occurs at lower wavelengths of 0.2-0.55 µm.** Knowing that the two surfaces are analogous in bond chemistry, we conclude that the **brightening occurs at wavelengths where the surface experiences an overall smoothing of the corresponding grain size.**

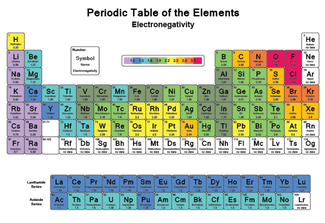


X-ray photoelectron spectroscopy (XPS): Compositional and chemical bond information



In X-ray photoelectron spectroscopy (XPS), an incident X-ray beam with known energy knocks an electron from its atomic shell. The measured kinetic energy of the ejected photoelectron – with a correction for the work function – is equal to the difference between the incident X-ray energy and the energy of the electron bound to its parent atom, known as the binding energy (BE). This binding energy is proportional to the number of protons, Z, composing the parent atom's nucleus. **The energy peaks in the BE distribution then represent the characteristic binding energies of their respective atomic shell.**



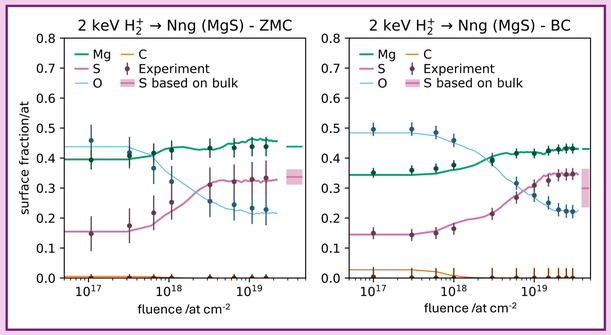


The key advantage of XPS in materials characterization lies in its ability to reveal chemical bonding through shifts in core-level photoelectron peak positions caused by changes in valence electron configuration.[2-4] Increased negative charge density (electronegativity) raises photoelectron kinetic energy, lowering binding energy. This shift, known as **the chemical shift,[5,6] reflects changes in the chemical environment and informs on the different bonds present at the sample surface.**

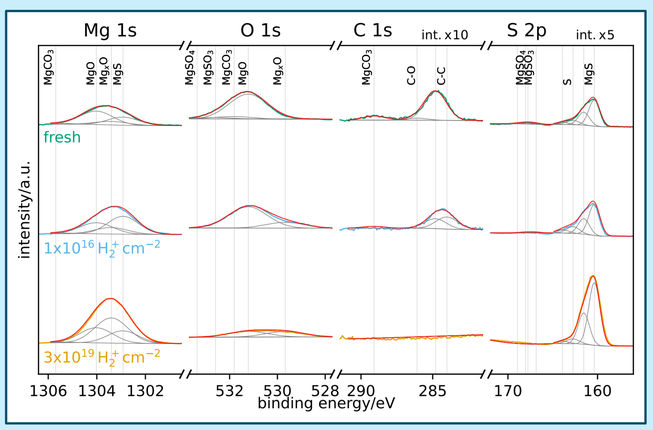
Composition variation is insufficient to explain VNIR discrepancy

During the irradiation experiment, XPS surface composition and chemistry measurements were acquired at logarithmically spaced fluence steps. Although the BC MgS sample expressed a larger Mg:S variability in the bulk (see line with shaded area), its upper surface composition is comparable to the ZMC bulk composition after irradiation, within uncertainty.

Based on the composition data of the surfaces in equilibrium with the irradiation ($\geq 1 \times 10^{19}$ ions cm^{-2}), **we can conclude that the two MgS sample surfaces are similar enough that they should only express negligible differences in VNIR reflectance and brightening.**



Radiation-hardness and no sulfur depletion preserves VNIR/MIR brightness



To understand what is happening on the surface in more detail, and to understand why the VNIR and MIR brighten under irradiation, the chemical bond information of the surface is analyzed. In the binding energy positions of the photoelectron peaks, we can identify the major chemical bonds present at the surface at prior to irradiation (fresh), after the first irradiation step (1×10^{16} ions cm^{-2}), and at the end of the irradiation (3×10^{19} ions cm^{-2}).

The S 2p feature is made up of a doublet ($2p_{3/2}$ and $2p_{1/2}$) assigned to MgS, a doublet attributed to elemental sulfur (7.8 % of S $2p_{3/2}$ peak), and one at higher binding energy corresponding to a minute contribution of sulfates (<0.2 % of S $2p_{3/2}$ peak). The elemental sulfur is attributed to residual reactant from the synthesis procedure. We are confident that after oxide removal, the surfaces exposed to ion irradiation are those of MgS. The lack of S depletion thus rejects the possibility of S mobilization in MgS, contrary to the observed mobilization in FeS. **Removal of the contaminants** (oxidation layer and adventitious carbon) **explains the overall brightening of the Mg-sulfides in the MIR and VNIR.** It does, however, not explain the difference in behavior and spectral shape between the two samples in VNIR.

References: [1] Barraud, O., Besse, S. & Doressoundiram, A. *Sci. Adv.* 9(12), (2023). [2] Wurz, P. et al. *Planet. Sci. J.* **6**, 24 (2025). [3] Sokolowski, E., Nordling, C. & Siegbahn, K. *Phys. Rev.* **110**, 776–776 (1958). [4] Hagström, S., Nordling, C. & Siegbahn, K. *Physics Letters* **9**, 235–236 (1964). [5] Greczynski, G. & Hultman, L. *Journal of Applied Physics* **132**, 011101 (2022). [6] Siegbahn, K. (Uppsala, Almqvist & Wiksells: 1967).

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