Sulfur enrichment on the surface of Mercury by sulfidation reactions. C.J. Renggli[1], A.N. Stojic[2], A. Morlok[2], J. Berndt[1], I. Weber[2], S. Klemme[1], H. Hiesinger[2], [1]University of Münster, Institute for Mineralogy, Corrensstr. 24, 48149 Münster, renggli@uni-muenster.de, [1]Univrsity of Münster, Institute for Planetology, Wilhelm-Klemm-Str. 10, 48149 Germany.

Introduction: The MESSENGER mission to Mercury determined unexpectedly high abundances of S on the planet's surface [1, 2]. The S is assumed to occur as magmatic sulfides, including CaS and MgS, requiring extremely reducing conditions, several logfO_2 units below the Iron-Wüstite buffer (IW), at IW-5 to IW-7 [3,4]. We have previously presented an alternative hypothesis for the high S abundance on the surface of Mercury, by sulfidation of silicates with hot S-rich volcanogenic gas [5]. For example, diopside is predicted to react with $CS_{2(g)}$ to form CaS, MgS, and quartz:

$$CaMgSi_2O_6 + CS_{2(g)} = CaS + MgS + 2SiO_2 + CO_{2(g)}$$

Here, we report mid-infrared spectral data on sulfidized glasses with Mercury compositions (low-Mg, high-Mg, high-Al), and the minerals anorthite, forsterite, and diopside. The Mercury Radiometer and Thermal Infrared Spectromenter (MERTIS) onboard ESA/JAXA BepiColombo mission to Mercury will map the planet's surface in the mid-IR [6]. The spectral data from our experimental analogues will be used as a reference for the observed Mercury surface spectra, allowing us to test the surface sulfidation hypothesis.

Experimental Setup: We used synthetic Mercury glasses (ID 155, 156, 174, 181) [5,7,8] and natural anorthite (ID1), diopside (ID134), and olivine (ID135, Fo90) as starting materials. The mineral grains had sizes of up to 250µm in diameter, and glasses were added as powders. The samples were placed in a graphite cup and loaded in a silica glass ampule (Fig. 1). Elemental S was loaded in a second graphite cup in the ampule. The ampules were sealed under a vacuum at 10^{-5} bar. The experiments were run at 800, 1000, and 1200 °C for 24 hours.

FTIR Measurements: The sulfidized materials were measured by micro FTIR with a Bruker Hyperion 3000 using a MCT detector. We report observations over the spectral range from 800-1300 cm^{-1} at a spectral resolution of 2 cm^{-1}. Prior to analysis the reacted samples were ground in an agate mortar to a powder. The bulk powder sample measurements were made over an area of 600x600 µm.

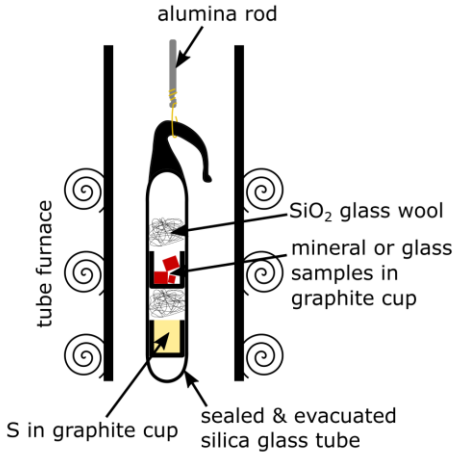

Figure 1: Experimental setup modified after [5]. Sample and S source were loaded in an evacuated and sealed silica glass ampule.

Results: The silicate glasses and minerals reacted with the reduced S-rich gas to form Ca- and Mg-rich sulfides, including oldhamite and niningerite, and quartz (Figure 2). These experimental observations agree with thermodynamic predictions [5] as described in the equation above. In this abstract we summarize results from sulfidation experiments with diopside and a low-Mg (ID 174) glass with a composition representative of the northern volcanic plains on Mercury [5,9].

Secondary electron images: The coating on the diopside reacted at 1000 °C (Fig. 2a) contains three different sulfides including (Ca,Mg)S, (Mg,Ca,Fe)S, and (Mg,Ca,Fe;Ti). In the coating on the low-Mg glass reacted at 1000 °C we identify the sulfides CaS (oldhamite) and (Fe,Ti,Ca)S (Fig. 2c). Quartz is not identified as a separate phase in the coatings of these two examples. Only at 1200 °C, where the degree of reaction was more extensive, could we identify quartz grains in the coatings.

FTIR spectra: The extent of sulfidation of diopside and the low-Mg glass strongly depends on reaction temperature, reflected in the mid-IR spectra (Fig. 2b & 2d). The spectra of the diopside reacted at 800 °C for 24 hours are very similar to the unreacted mineral in all primary spectral features. At 1000 and 1200 °C the sulfidation becomes evident in the mid-IR spectra of the altered diopside. The prominent diopside bands at 920 and 960 cm^{-1} disappear and the quartz bands appear at 1096, 1182, and 1212 cm^{-1} (Fig. 2b).

The low-Mg glass crystallized quartz during the sulfidation reactions [5]. We also observe a marked shift in the mid-IR spectra at 800-1200 °C (Fig. 2d). The main Reststrahlenband shifts from 1040 cm^{-1} for the unaltered glass to 1072 cm^{-1} at 1200 °C, and the Christiansen features shift to lower wavenumbers in the altered samples.

Discussion: We propose that reduced S-rich fumarolic and volcanic gases on Mercury rapidly react with silicate minerals and glasses to enrich the surface in S by forming sulfides and quartz. Quartz is not predicted to occur in most Mercury terranes based on MESSENGER data [10]. A detection of quartz by BepiColombo with the MERTIS instrument in regions with strong S enrichment would, therefore, support our hypothesis of surface sulfidation of silicates on Mercury. Importantly, if the sulfides are not magmatic phases, less reducing conditions would be required for the surface basalts. Oxidation from IW-7 to IW-3 from the mantle source of the magmas to the surface of the planet would result in extensive S degassing, followed by sulfidation of silicates at the surface. Possible oxidation mechanisms include assimilation of oxides [3] and smelting processes [11,12].

Acknowledgments: CJR acknowledges funding by the Deutsche Forschungsgemeinschaft (DFG) – project 442083018. A.M., A.N.S., and I.W. are supported by the DLR grants 50QW1701 and 50QW2201A.

References: [1] Nittler L. R. et al. (2011) *Science 333*, 1847-1850. [2] Weider S. et al. (2015) *Earth Planet. Sc. Lett. 416*, 109-120. [3] Zolotov M. (2011) *Icarus 212*, 24-41. [4] Namur O. et al. (2016) *Earth Planet. Sc. Lett. 448*, 102-114. [5] Renggli et al. (2022) *Earth Planet. Sc. Lett. 593*, 117647. [6] Hiesinger et al. (2022) *Space Sci. Rev. 216*, 110. [7] Morlok A. et al. (2021) *Icarus 361*, 114363. [8] MERTIS reference database: http://bc-mertis-pi.uni-muenster.de [9] Vander Kaaden K. E. et al. (2017) *Icarus 285*, 155-168. [10] Namur O. and Charlier B. (2017) *Nat. Geosci. 10*, 9-13. [11] McCubbin F. et al. (2017) *JGR Planets 122*, 2017JE005367. [12] Iacovino K. et al. (2023) *Earth Planet. Sc. Lett. 602*, 117908.

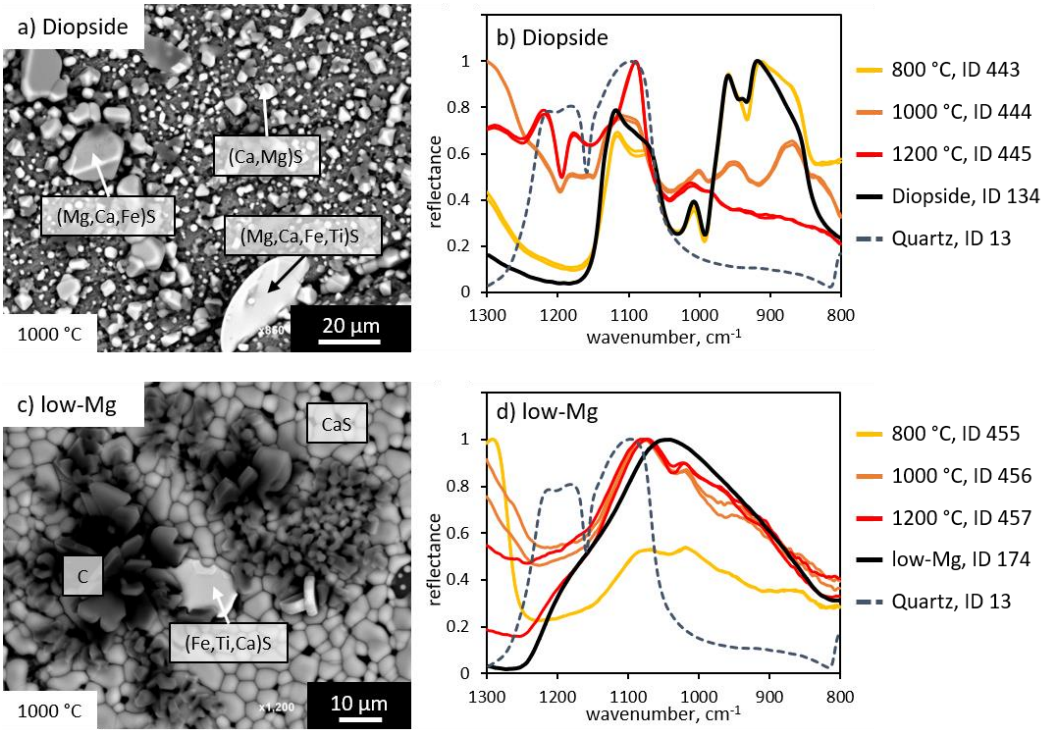

Figure 2: Experimental results from diopside and low-Mg glass sulfidation experiments. Panels a) and c) show back-scattered electron images of the reacted surfaces from the experiments at 1000 °C. Panels b) and d) show normalized mid-IR reflectance spectra of the bulk samples at 800 °C (yellow), 1000 °C (orange), and 1200 °C (red), the unreacted starting materials in black lines, and for reference a pure quartz spectrum as a stippled grey line. For sample ID numbers see [8].