Mid-infrared spectroscopy of sulfidation reaction products and implications for Sulfur on Mercury

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Abstract

We propose that the observed enrichment of sulfur at the surface of Mercury (up to 4 wt.%) is the product of silicate sulfidation reactions with a S-rich reduced volcanogenic gas phase. Here, we present new experiments on the sulfidation behavior of olivine, diopside, and anorthite. We investigate these reaction products, and those of sulfidized glasses with Mercury compositions previously reported, by mid-IR reflectance spectroscopy. We investigate both the reacted bulk materials as powders, as well as cross-sections of the reaction products by in-situ micro-IR spectroscopy. The mid-IR spectra confirm the presence of predicted reaction products including quartz. The mid-IR reflectance of sulfide reaction products, such as CaS (oldhamite) or MgS (niningerite), is insufficient to be observed in the complex run products. However, the ESA/JAXA BepiColombo mission to Mercury will be able to test our hypothesis by investigating correlated abundances of sulfides with other reaction products such as quartz.





















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15	Key points
16	• S-enrichment on the surface of Mercury by sulfidation of silicate minerals
17	• Mid-IR spectroscopy allows the identification of quartz as a main reaction product in
18	mineral and glass sulfidation.
19	• BepiColombo's MERTIS instrument will test the sulfidation hypothesis by mapping the surface
20	of Mercury in the mid-IR spectral range.

21 Abstract

22 We propose that the observed enrichment of sulfur at the surface of Mercury (up to 4 wt.%) is 23 the product of silicate sulfidation reactions with a S-rich reduced volcanogenic gas phase. Here, we 24 present new experiments on the sulfidation behavior of olivine, diopside, and anorthite. We investigate 25 these reaction products, and those of sulfidized glasses with Mercury compositions previously reported, 26 by mid-IR reflectance spectroscopy. We investigate both the reacted bulk materials as powders, as well 27 as cross-sections of the reaction products by in-situ micro-IR spectroscopy. The mid-IR spectra confirm 28 the presence of predicted reaction products including quartz. The mid-IR reflectance of sulfide reaction 29 products, such as CaS (oldhamite) or MgS (niningerite), is insufficient to be observed in the complex 30 run products. However, the ESA/JAXA BepiColombo mission to Mercury will be able to test our 31 hypothesis by investigating correlated abundances of sulfides with other reaction products such as 32 quartz.

33 Plain language summary

The surface of the planet Mercury is enriched in sulfur, with abundances of up to 4 wt.%. Sulfur on Mercury has previously been interpreted to occur in magmatic sulfide phases. We propose an alternative mechanism for the enrichment of S on Mercury, whereby reduced S-rich gases react with silicate minerals to form sulfides and quartz. We carried out sulfidation experiments on silicate minerals and glasses and used mid-infrared spectroscopy to characterize the products of these reactions. The upcoming ESA/JAXA BepiColombo mission to Mercury will allow us to test the sulfidation hypothesis and provide constraints on the origin of the S enrichment on the planet's surface.

41 Introduction

The surface of Mercury is distinctly enriched in S, with up to 4 wt. % as revealed by the NASA
MErcury Surface, Space ENvironment, GEochemistry and Ranging (MESSENGER) spacecraft
(McCoy et al., 2018; Larry R. Nittler et al., 2011; Larry R Nittler et al., 2018; Weider et al., 2015). The
processes that resulted in the enrichment of S on the surface of Mercury remain unresolved, however,

46 several processes have been proposed. At extremely reducing conditions several $\log fO_2$ units below the Iron-Wüstite buffer (IW), at IW-3 to IW-7, the solubility of S in basaltic melts is high and increases 47 48 with decreasing fO₂ (Anzures, Parman, Milliken, Lanzirotti, et al., 2020; Anzures, Parman, Milliken, Namur, et al., 2020; Cartier et al., 2014; Namur et al., 2016). Assuming that melts on Mercury 49 50 experience no oxidation from the highly reduced mantle source, sulfides in lavas on the surface of 51 Mercury may be of primary magmatic origin (Anzures, Parman, Milliken, Namur, et al., 2020; Namur 52 et al., 2016; Mikhail Y. Zolotov et al., 2013). However, if the magmas experienced even minor degrees 53 of oxidation from the mantle source to the surface, the solubility of S would have decreased from 54 approximately 7 wt.% at IW-7, to 3 wt.% at IW-5, and 1 wt.% at IW-3 (Namur et al., 2016), resulting 55 in the degassing of S. Processes that could have resulted in the oxidation of ascending magmas on 56 Mercury include assimilation of oxides into the melts (Mikhail Yu. Zolotov, 2011), decompression 57 oxidation (e.g. Foley, 2011), or smelting processes (Iacovino et al., 2023; McCubbin et al., 2017). 58 Previously, it was argued that such oxidation mechanisms have resulted in the formation of volcanic 59 gases that drive explosive volcanism on Mercury (Deutsch et al., 2021; Iacovino et al., 2023; Kerber et 60 al., 2011; L. R. Nittler et al., 2014; Weider et al., 2016), including the depletion of pyroclastic deposits 61 in the degassed volatiles, as observed in the S depleted Nathair Facula, NE of Rachmaninov crater 62 (Weider et al., 2016).

63 Sulfur species in hot volcanic gases are highly reactive with silicate minerals and glasses (King 64 et al., 2018). At oxidizing conditions a SO₂ disproportionation reaction forms sulfate coatings on glasses 65 (Renggli, Palm, et al., 2019; Christian J Renggli & King, 2018), whereas at reducing conditions gas species including S_2 , COS, and CS₂ react with glasses and minerals to form sulfides including troilite 66 (FeS), oldhamite (CaS), and niningerite (MgS) (C.J. Renggli et al., 2022). We have previously argued 67 68 that these sulfidation reactions may be responsible for the observed enrichment of S on the surface of 69 Mercury. For example, the sulfidation of the primary predicted silicate minerals anorthite, forsterite, 70 and diopside (Namur & Charlier, 2017) with CS₂ gas can be written as:

 $\begin{array}{ll} 71 & Mg_2SiO_4 + CaMgSi_2O_6 + 2CaSi_2Al_2O_8 + 3CS_{2(g)} \rightarrow \{7SiO_2 + 2Al_2O_3\}_{glass;\ melt;\ mineral} + 3CaS + 3MgS + \\ 72 & 6CO_{(g)} & Equation \ l \end{array}$

In addition to the sulfides, these reactions result in the formation of quartz and aluminosilicate phases (C.J. Renggli et al., 2022). Since quartz is not predicted to be present in most Mercury terranes, and as an accessory phase only in the low-Mg terrane and the Caloris interior plains (McCoy et al., 2018; Namur & Charlier, 2017), quartz presence on the surface of Mercury, together with sulfides such as oldhamite and niningerite, is evidence for sulfidation reactions.

78 Sulfidation results in a change of spectral properties due to the change in mineralogy. In this 79 study we use the experimental run products (low-Mg, high-Mg, and high-Al glasses) from Renggli et 80 al. (2022), and run additional sulfidation experiments at 800, 1000, and 1200 °C of olivine, diopside, 81 and anorthite, to determine the change in the mid-infrared spectra. We investigated the reaction products 82 using electron microscopy and micro-FTIR (Fourier Transform Infrared Spectroscopy), in the mid-IR from 2.5-16.7 µm (equivalent to 4000 to 666 cm⁻¹), to characterize their chemistry, mineralogy and 83 spectral properties. The spectral data of the sulfide coatings will be used as a reference for the MERTIS 84 85 spectrometer (Mercury Radiometer and Thermal Infrared Spectrometer) onboard the BepiColombo (ESA/JAXA) mission to Mercury (Hiesinger & Helbert, 2010). The observations from BepiColombo 86 87 will allow testing of our proposed mechanism for the formation of surface sulfides on Mercury by high-88 temperature gas-solid reactions with reduced S-rich gas. The ID-numbers of samples reported here refer 89 to the IRIS (Infrared and Raman for Interplanetary Spectroscopy) database hosted at the Institute for 90 Planetology, University of Münster (http://bc-mertis-pi.uni-muenster.de/), where the data is publicly 91 available.

92 Methods

93 Experiments

In this study we present mid-IR spectroscopic observations from silicate glass sulfidation
experiments that we previously reported (Renggli et al. 2022). We refer the reader to that publication
for details on the synthesis of the glasses with compositions based on observations from the NASA
MESSENGER mission. The glasses include a low-Mg sample (ID 174), based on the low-Mg Northern
Volcanic Plains, a high-Mg sample (ID 156), based on the similarly named high-Mg region, and a high-

- 99 Al sample (ID155) based on terrains southwest and southeast of the northern volcanic plains (Namur &
- 100 Charlier, 2017; Vander Kaaden et al., 2017). The mid-IR spectral properties of these pristine glasses
- 101 are described in Morlok et al. (2021).



103Figure 1: Experimental set-up of the silicate mineral and Mercury glass samples in an evacuated $(10^{-5}$ 104bar) and sealed silica glass ampule, suspended in a vertical tube furnace. This drawing is modified from Renggli105et al. 2022.

106 In addition to the synthetic Mercury glass samples, we conducted sulfidation experiments with 107 three natural rock-forming minerals. These mineral phases are included in the MERTIS sample 108 database, which is developed in context of the ESA/JAXA BepiColombo mission to Mercury, and were 109 previously characterized chemically by electron microprobe analyzer (EMPA) and mid-IR spectroscopy 110 (Hiesinger et al., 2020). The three mineral phases used in the sulfidation experiments are olivine (ID 111 135), diopside (ID 134), and anorthite (ID 1). The olivine (ID 135) has a forsterite content of 90.5% 112 (Table 1). The sample ID 135 contains two minor contaminants (<5 vol%.) that are not detectable in 113 the bulk FTIR spectrum of the unreacted material. However, in the SEM we were able to identify the 114 contaminants, which are a diopside and a Cr-Mg hercynite ("picotite", 33.4 wt.% Al₂O₃, 33.2 wt. Cr₂O₃, 115 17.2 wt. % MgO, 14.1 wt. FeO). The diopside (ID 134) was previously described and studied spectroscopically for its trace water contents (Kumamoto et al., 2017) and has a minor FeO content of 116 117 ~6.6 wt. % (Table 1). The anorthite contains minor impurities on a grain-scale including alkali feldspar

and a hydrous phase (see electron microprobe supplement). In Table 2 we list the ID numbers of the starting materials and the reaction products.

120 The sulfidation experiments were conducted in sealed and evacuated silica glass ampules 121 (Figure 1) which were short enough (~ 4 cm) to fit in the hot zone of the furnace with a length of ~ 6 cm 122 (C. J. Renggli & Klemme, 2020). The set-up consists of two graphite cups placed above each other in 123 the ampule (wall thickness of 1 mm), with the lower cup filled with elemental S (~0.0015g), and the 124 upper cup filled with the sample material. In previous experiments on the sulfidation of glasses with 125 Mercury compositions we used SiO_2 glass wool to separate the two cups (C.J. Renggli et al., 2022). 126 However, we determined that the addition of the glass wool separator was not necessary but a potential 127 source of sample contamination. Therefore, we did not use glass wool in the experimental set-up for the olivine, diopside, and anorthite sulfidation experiments (Figure 1). After loading the glass tubes, 128 they were sealed under a vacuum of 10⁻⁵ bar. At experimental temperatures the elemental S forms a gas 129 130 phase that reacts with the silicate sample. The fO_2 was controlled at the graphite-CO buffer due to the 131 presence of the graphite cups (C. J. Renggli & Klemme, 2021).

132 Table 1: Major oxide compositions (wt.%) of the three glasses lMgII A, hMgl, and hAl (Morlok et al., 133 2021; C.J. Renggli et al., 2022), and the minerals olivine, diopside (Kumamoto et al. 2017), and anorthite used

134 in the sulfidation experiments.

	IMgII A	hMgI	hAl	Olivine	Diopside	Anorthite
	ID174	ID156	ID155	ID135	ID134	ID1
	Morlok et al., 2021; Renggli et al.,			n=20	Kumamoto	n=20
		2022			et al. 2017	
SiO ₂	64.26(32)	56.01(38)	57.06(19)	41.04(34)	53.67(09)	43.09(16)
TiO ₂	0.46(02)	1.08(01)	1.39(08)	b.d.l.	0.08(01)	b.d.l.
Al ₂ O ₃	14.30(10)	10.80(14)	16.55(11)	-	0.21(06)	36.18(13)
FeO	0.05(08)	b.d.l.	0.07(03)	9.21(12)	6.62(04)	0.04(02)
MnO	0.16(02)	0.49(01)	0.70(04)	0.16(03)	0.55(18)	b.d.l.
MgO	8.97(12)	23.11(45)	14.78(15)	59.17(21)	14.06(24)	b.d.l.
CaO	6.81(08)	7.73(09)	6.05(10)	0.05(02)	25.35(18)	20.28(18)
Na ₂ O	4.81(12)	1.16(02)	3.15(08)	-	0.04(01)	b.d.l.
K ₂ O	0.19(03)	0.13(02)	0.24(02)	-	-	b.d.l.
Total	100.01	100.52	99.99	100.04	100.63	99.64

135

136 Table 2: ID numbers given to the starting materials and the experiments at 800, 1000, and 1200 °C.

137 These ID numbers refer to the IRIS MERTIS database where the corresponding bulk and in-situ FTIR spectra are 138

available (http://bc-mertis-pi.uni-muenster.de).

	ID of	ID	ID	ID
material	starting	experiment	experiment	experiment
name	material	800 °C	1000 °C	1200 °C
Olivine	135	440	441	442
Diopside	134	443	444	445
Anorthite	1	446	447	448
hMgI	156	449	450	451
hMgII	181	452	453	454
IMgII A	174	455	456	457
hAl	155	458	459	460

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140 **Analytical methods**

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The samples retrieved from the quenched silica glass ampules were split in two aliquots. The 142 first aliquot included larger grains that were first used to characterize the surfaces by Scanning Electron 143 Microscopy (SEM) and in-situ characterization by electron microprobe and FTIR microscopy of sample 144 cross-sections. The second aliquot was retained as a powder with unknown grain-size distribution and 145 used for FTIR bulk powder analysis.

146 Back-scattered electron (BSE) images were made on a JSM-6510 Series SEM in low-vacuum 147 mode at 50 Pa, which allowed imaging without carbon coating. The grains were then embedded in 148 epoxy resin and polished under anhydrous ethanol, with a final polish using 0.25 μ m diamond paste. 149 The chemistry of the reaction products was determined with a JEOL JXA 8530F electron microprobe 150 at 15 keV and 60 nA probe current. The spot size varied depending on grain-size from 1-10 μ m. For 151 details on standardization and reference materials we refer to the supplementary material in Renggli et 152 al. (2022).

The bulk and in-situ FTIR reflectance spectra were recorded with a Bruker Hyperion 3000 153 154 microscope using a liquid nitrogen cooled MCT detector over a spectral range of 4000 - 600 cm⁻¹ at a 155 spectral resolution of 4 cm⁻¹. In this study we discuss the features over the spectral range of 1300 -156 800 cm⁻¹ and the reported spectra are the averages of 64 or 128 scans. For the bulk measurements the 157 samples were ground dry for less than 30 seconds and placed in Al-metal sample cups. The bulk measurements were done on these powders with an aperture cross-section of 600x600 µm. For the in-158 159 situ measurements the microscope aperture was varied depending on the target sample, with the smallest 160 used aperture size of $15x15 \,\mu\text{m}$. The aperture sizes for all in-situ measurements are given with the full spectral data in the electronic supplement, and analysis locations are shown in the BSE images of the 161 162 respective samples. For bulk spectra we used a gold mirror standard and for the bulk measurements we 163 used an InfraGold diffuse scattering standard.

164 **Experimental results**

165 **Reacted surface**

The sulfidation of silicates is strongly temperature dependent, due to the diffusion-controlled 166 167 mobility of the sulfide forming cations (e.g. Fe, Ca, Mg, ±Mn, ±Ti, ±Na) (Renggli, King, et al., 2019; C.J. Renggli et al., 2022). Consequently, the coatings on the reacted samples vary in texture with time, 168 169 temperature, and silicate composition and structure. In Figure 2 we show BSE images of the surfaces of the 6 types of investigated samples, reacted for 24 h at 1000 °C. The reacted minerals (a-c) show a 170 less complete sulfide coating compared to the reacted glasses (d-f). The sulfide compositions labelled 171 172 on the BSE images were determined using qualitative EDS in the SEM low-vacuum mode. The detailed 173 sulfide compositions were analyzed by EPMA and are reported in Figure 3 and the supplement.

174 On the olivine grain sulfidized at 1000 °C we observe two sulfide compositions (Figure 2a), 175 including MgS (niningerite) with grain sizes of up to 8 µm, and (Fe,Mg)S, which appears white in the BSE image, and forms slightly larger grains. The sulfidized diopside is coated by three distinct sulfide 176 phases. First, (Mg,Ca,Fe)S forms the larges grains (<20 µm), second, a Ti-bearing sulfide forms platy 177 178 grains, and third, (Ca,Mg)S forms smaller grains with diameters $<10 \mu m$ (Figure 2b). The anorthite has 179 a very un-even coating with parts of the surface entirely coated by CaS, whereas other areas show no sulfide coatings. The CaS only occurs on the anorthite component of the grain, whereas the impurity, 180 181 an alkali feldspar, shows no sulfide coating. In addition, the textures reveal that the anorthite 182 experienced partial melting, apparent in the lower right corner of the BSE image (Figure 2c). The 183 textures in the coatings of the sulfidized glasses are reported in detail in Renggli et al. (2022). Here, we 184 show the BSE images (Figure 2d-e) to allow a comparison with the mineral experiments. Overall, the 185 sulfides on the glasses show a more diverse chemistry, including Mn, Fe, Na and Ti in predominantly 186 CaS and MgS phases, and the coatings are overall less patchy compared to the minerals. In addition, 187 we observe occasional graphite grains on these surfaces, which are contamination from the graphite 188 cups in which the samples were placed. Since we used SiO_2 glass wool as a spacer in the ampules for 189 the glass sulfidation experiments we looked for traces of this material but did not identify any 190 contamination.



Figure 2: Secondary backscattered electron microscopy images of mineral and glass grains sulfidized for 24 h at 1000 °C. a) olivine ID 441, b) diopside ID 444, c) anorthite ID 447, d) high-Mg glass ID 450, e) low-Mg glass ID 456, f) high-Al glass ID 459. The sulfide coatings are labeled on the images and include MgS, FeS, CaS, and mixed sulfide compositions. For a detailed description of sulfide reaction products in the glass sulfidation experiments we refer the reader to Renggli et al. 2022.

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Sulfide compositions

200 We observe exclusively CaS (oldhamite) on the sulfidized anorthite grains. In contrast, the compositions of the sulfides formed in olivine and diopside sulfidation experiments are compositionally 201 202 more diverse and vary with experimental temperature from 800 to 1200 °C. In Figure 3 we show the 203 compositional variations of the sulfides on the reacted olivines and diopsides. At 800 °C, the coating 204 on the olivine grains consists of Fe-depleted troilite (Fe_{1-x}S). This is compositionally removed from the 205 olivine composition (Mg_{1.83}Fe_{0.17}SiO₄, Table 1). However, the Mg/Fe ratio of the sulfide composition 206 (Mg,Fe)S approaches the Mg/Fe ratio of the educt olivine with increasing experimental temperature 207 and degree of sulfidation (Figure 3a). Similarly, the sulfide reaction products on the diopside grains 208 approach the Ca-Mg-(Fe+Ti) molar composition of the unreacted diopside. At 800 °C we observe 209 (Fe,Ti)_{1-x}S and CaS, whereas at higher temperatures (1000 and 1200 °) we also observe Mg-rich 210 (Mg,Ca)S in addition to a Ca-rich sulfide (Figure 3b). We reported the compositions of the sulfides in 211 the glass sulfidation experiments previously (Renggli et al., 2022). We observed similar variations in 212 the Ca-Mg-(Fe+Ti) compositional space in the glass experiments as in the sulfidation of the diopside 213 (Figure 3b). The sulfides in the high-Mg and high-Al glass experiments fell predominantly in the CaS-214 MgS compositional spaces, whereas we observed abundant Fe-rich and Mg-poor sulfides in the low-215 Mg glass experiment (Renggli et al., 2022).



Figure 3: Compositions of the sulfides formed in the reactions with a) olivine, and b) diopside. The yellow circles show the sulfide compositions of experiments at 800 °C, red diamonds at 1000 °C, and dark red squares at 1200 °C. The blue line in a) and the blue circle in b) indicate the compositions of the respective silicate starting material.



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Figure 4: Bulk mid-FTIR spectra of the reacted samples. a) olivine ID 135, b) diopside ID 134, c) anorthite ID 1, d) hMgI ID 156, e) lMgII A ID 174, f) hAl ID 155. The solid black line is the bulk spectrum of the unreacted starting material, the dashed grey line is the spectrum of quartz ID13, and the dashed green line in (d) the spectrum of olivine ID249.

228 We measured the mid-IR reflectance spectra of the experimental run products over a spectral 229 range of $800 - 1300 \text{ cm}^{-1}$ (12.5 - 7.7 µm) to test the effect of mineral and glass sulfidation on the spectral properties (Figure 4). The spectral positions of the reflectance minima (Christiansen Feature, 230 231 CF) and the reflectance maxima (e.g., Reststrahlenband, RB) of the starting materials are reported in 232 Table 3. Changes in the spectral features represent changes in the sample mineralogy and will be used 233 as a basis to test the sulfidation hypothesis for S-enrichment on the surface of Mercury with the MERTIS 234 instrument onboard BepiColombo. The degree of change in the spectra is strongly dependent on the 235 degree of sulfidation and change in mineralogy, which increases with temperature from 800 to 1200 °C. 236 The sulfidation reaction (Equation 1) predicts the formation of SiO_2 as a reaction product in addition to 237 sulfides. To test for the presence of quartz in the reaction products we show a quartz spectrum (ID 13) 238 in the panels of Figure 4. The three primary RBs are at 1096, 1181, and 1212 cm⁻¹.

Olivine has four RBs with decreasing reflectance at 946, 983, 1060, and 839 cm⁻¹. In the sulfidation experiment at 800 °C the relative intensities of these reflectance RBs largely remain unchanged (Figure 4a). At higher temperatures (1000, 1200 °C) the reflectance of the reacted sample decreases dramatically, and the reflectance maxima of the normalized spectra are at 1300 cm⁻¹. In addition, the high-temperature spectra are noisier compared to that of the 800 °C experiment, or the unreacted olivine. We observe no clear spectral features that we can attribute to quartz.

245 Diopside (ID 134) has four major RBs with decreasing reflectance at 918, 959, 1119, and 1008 cm⁻¹, a small RB, almost completely overlapped by the two main RBs, at 940 cm⁻¹, and a prominent 246 shoulder at ~ 1075 cm⁻¹ (Figure 4b). The more extensive sulfidation of diopside compared to olivine 247 248 observed in the SEM images (Figure 2) is also apparent in the bulk FTIR spectra of the diopside reaction 249 products. At 800 °C, where the degree of sulfidation is low, the spectrum retains the primary features 250 of the unreacted diopside. However, at 1000 and 1200 °C the overall reflectance amplitude decreases, 251 but we can also identify the appearance of RBs characteristic for quartz, most prominently at ~1090 cm⁻¹ 252 (Figure 4b). At this wavenumber a shoulder appears in the spectra of the experiment at 1000 °C, but becomes the main RB at 1200 °C. Similarly, shoulders and RBs attributable to quartz occur ~1220 cm⁻¹ 253 254 and 1178 cm⁻¹. These RB wavenumbers are within 8 cm⁻¹ of the quartz ID 13 reference spectrum, but are not perfect matches. However, vibrational modes are defined by crystallographic structure and record variations in crystal orientation, defect populations, impurities in the reference quartz, or the high-temperature formation conditions in the sulfidation experiments.

258 Anorthite (ID 1) has a complex mid-IR reflectance spectrum, with reflectance maxima at 948, 259 1021, 1036, 985, 914, 1099, 1081, and 1139 cm⁻¹ in order of decreasing reflectance. The reflectance minimum CF of anorthite is located at ~1230 cm⁻¹, at higher wavenumbers compared to olivine or 260 261 diopside (Figure 4c). The presence of RBs at high wavenumbers, in the range of the main quartz RB at \sim 1100 cm⁻¹ may pose a challenge to the identification of sulfidation reaction products in the mid-IR 262 263 spectra. A further challenge is the mineralogical heterogeneity of the anorthite sample (ID 1) used for 264 this study (see above). The experimental run products are much darker in appearance compared to the 265 starting material. Similarly, the overall reflectance of all experiments has decreased compared to ID 1 266 (Figure 4c). We observe no other spectral signatures of sulfidation in the mid-IR of the anorthite 267 sulfidation experiments.

268 The mid-IR spectra of the synthetic Mercury glasses hMgI (ID 156, Figure 4d), hMgII (ID 181, 269 only in supplement), lMgII A (ID 174, Figure 4e), and hAl (ID 155, Figure 4f) were previously 270 described in Morlok et al. (2021). The glass spectra are characterized by a reflectance minimum (CF) 271 at low wavenumbers, and a broad reflectance maximum (Table 3). The mid-IR spectra of the sulfidized 272 glasses show clear evidence for alteration, and crystallization (Figure 4d-f). In our previous study we 273 have shown that the glasses partially crystallized in the experiments. The hMgI glass formed forsterite 274 and enstatite, the lMgII A glass formed forsterite, and the hAl glass formed plagioclase and Mg-rich 275 clinopyroxene (Renggli et al. 2022). The sulfidation removed Ca and Mg from the glass and enriched 276 the altered substrate glass in SiO₂. The main band position shifts to higher wavenumbers with increasing 277 SiO₂ content (Dufresne et al., 2015; Morlok et al., 2021, 2023), which is apparent in the shift of the 278 main reflectance peak of the most strongly altered experiments at 1200 °C (Figure 4d,e). As in the case 279 of the sulfidized minerals, the overall reflectance is lower in the experiments compared to the unaltered 280 glasses, resulting in noisy mid-IR spectra (e.g. Figure 4f).

Table 3: Christiansen Feature (CF) and Reststrahlenband (RB) spectral positions in wavenumber and
 wavelength for the starting materials. The RBs are ordered by decreasing reflectance. For glasses we only report
 the spectral position of the reflectance maximum. For more details on the spectral features of the glasses see
 Morlok et al. (2021).

		Olivine ID 135	Diopside ID 134	Anorthite ID 1	Quartz ID 13	hMg I ID 156	hMg II ID 181	lMg IIA ID 174	hAl ID 155
CF		1163 cm ⁻¹ 8.60 μm	1184 cm ⁻¹ 8.44 μm	1229 cm ⁻¹ 8. <i>13 μm</i>	1354 cm ⁻¹ 7.39 μm	1229 cm ⁻¹ 8.13 μm	1242 cm ⁻¹ 8.05 μm	1268 cm ⁻¹ 7.89 μm	1242 cm ⁻¹ 8.05 μm
RB	1	946 cm ⁻¹ 10.57 μm	918 cm ⁻¹ 10.89 μm	948 cm ⁻¹ 10.54 μm	1096 cm ⁻¹ 9.12 μm	1005 cm ⁻¹ 9.95 μm	1021 cm ⁻¹ 9.79 μm	1045 cm ⁻¹ 9.57 μm	1019 cm ⁻¹ 9.81 μm
	2	983 cm ⁻¹ 10.18 μm	959 cm ⁻¹ 10.43 μm	1021 cm ⁻¹ 9.79 μm	1181 cm ⁻¹ 8.47 μm				
	3	1060 cm ⁻¹ 9.43 μm	940 cm ⁻¹ 10.64 μm	1036 cm ⁻¹ 9.65 μm	1212 cm ⁻¹ 8.25 μm				
	4	839 cm ⁻¹ 11.92 μm	1119 cm ⁻¹ 8.94 μm	985 cm ⁻¹ 10.15 μm					
	5		1075 cm ⁻¹ 9.30 μm	914 cm ⁻¹ 10.94 μm					
	6		1008 cm ⁻¹ 9.92 μm	1099 cm ⁻¹ 9.10 μm					
	7			1081 cm ⁻¹ 9.25 μm					
	8			1139 cm ⁻¹ 8.78 μm					

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287 In-Situ investigations

We report observations of cross-sectioned experimental samples, including SEM images and in-situ micro-FTIR spectra (Figures 5-10). Sulfidation is not limited to the surface of the mineral grains, but also occurs in cracks. These cracks were likely present in the grains prior to the experiments. The BSE images show changes in the silicate substrates and micro-FTIR measurement areas are indicated as blue rectangles. The dimensions of these measurement areas are approximate and reported in detail in the supplement with the micro-FTIR spectral data. Here, we describe the spectral features of the sulfidized mineral and glass grains.

The in-situ observations of the sulfidized olivine (ID 135) reacted at 1000 °C (ID 441) and 1200 °C (ID 442) are shown in Figure 5. The grain in Figure 5b was only polished superficially and not to the core of the grain. The spectra on the sample reacted at 1000 °C (Figure 5a), therefore represent those of the altered near-surface area. Nevertheless, these spectra are very similar to the unaltered olivine. An additional strong RB is apparent in the spectrum of area 2 at 1082 cm⁻¹. Similarly, the sulfidation of olivine at 1200 °C has not progressed sufficiently to result in a change in mineralogy (e.g. formation of quartz), and the mid-IR spectra remain characteristic for olivine (Figure 5c). Notably, sulfidation has occurred in thin cracks within the olivine grain, and the BSE image shows a gray-scale
 gradient towards the grain surface, indicative for diffusional loss of Fe to the sulfide (Figure 5d).

304 The surface SEM observations suggest a higher rate of sulfidation for diopside, compared to 305 olivine (Figure 2). This observation is also supported by the in-situ investigations. At 1000 °C little 306 alteration can be observed (Figure 6b) and the micro-FTIR spectra show no change from diopside 307 (Figure 6a). However, at 1200 °C strong sulfidation is evident in the BSE image of the sample cross-308 section (Figure 6d). The sulfidation reaction has extended into cracks by up to $200 \,\mu\text{m}$. The cracks are 309 widened and filled by (Ca,Mg)S and quartz (darker gray compared to diopside in Figure 6d). The spectra 310 recorded over the cracks (1-4), however, show limited changes compared to the unreacted diopside. 311 The overall reflectance of these spectra is low and they appear noisy. Despite the presence of quartz, 312 observed by SEM, no clear quartz RBs are evident. Instead, the spectral signature of the diopside 313 dominates the spectra (Figure 6c).

In-situ observations of sulfidized anorthite are limited to the experiment at 1200 °C (Figure 7), due to the heterogeneity of the starting material. The BSE image shows pervasive sulfidation, even in the interior of the sample (Figure 7b). The sample has partially molten and quench crystals can be observed. The partially glassy nature of the sample is apparent in the micro-FTIR spectrum of the area labelled "altered", as a broad band, reminiscent of the FTIR spectra of the unaltered glasses (Figure 4).

319 The high-Mg glass (hMgI, ID 156) has crystallized forsterite in the substrate at 800 °C (Figure 320 8b). Additionally, we observe Fe metal nuggets in the substrate which formed in the synthesis of the 321 glass used in the sulfidation experiments, because the FeO-content was too high for the imposed fO_2 322 (Morlok et al., 2021). The forsterite is clearly identified in the micro-FTIR spectra of the sample interior 323 (dotted lines, Figure 8a). At 1200 °C the only phase that crystallized in the substrate during the 324 experiment was enstatite, due to the loss of Mg to (Mg,Ca)S in the coating (Renggli et al., 2022). However, even though the enstatite was identified in the sample by electron microprobe analysis, the 325 mid-IR spectrum of the enstatite-rich sample interior remains ambiguous. The enstatite reference 326 327 material ID 53 (Weber et al., 2020), a bulk powder sample in the grain-size range of 63-125 µm, has two RBs at high wavenumbers (1099 cm⁻¹ & 1060 cm⁻¹), where the experimental spectrum has only one 328

(1084 cm⁻¹), and similarly three RBs at lower wavenumbers in ID 53 (978 cm⁻¹, 957 cm⁻¹, 929 cm⁻¹), where the experimental sample has a very broad RB at 949 cm⁻¹. This difference is likely due to differences in crystal grain orientation (Tappert et al., 2013). At the surface the sample is strongly Mg-depleted (Renggli et al., 2022). Surface spectrum 1 (Figure 8d) shows an enstatite band at 1005 cm⁻¹, whereas the surface spectra 2 and 3 show now enstatite and the main reflectance maxima are shifted to higher wavenumbers. Despite the abundant presence of (Mg,Ca)S in the sample area recorded by surface spectrum 2 (Figure 8e), there is no evidence for a spectral signature of the sulfide.

336 In Figure 9, we show the in-situ observations of the experiments with the low-Mg glass (lMgII 337 A, ID 174) at 1000 °C (Figure 9a, b) and 1200 °C (Figure 9c, d). At 1000 °C, the sulfide coating, 338 consisting primarily of CaS (Renggli et al., 2022), was thick enough to allow a micro-IR measurement of the sulfide only, shown as #2 in Figure 9a. The CaS spectrum is very noisy and the reflectance 339 maximum was normalized to 1. The reflectance maximum of "surf. 2" is at ~1082 cm⁻¹, which is in the 340 341 same spectral range as the surface areas including the substrate ("surf. 1" at 1070 and "surf. 3" at 1072 cm⁻¹). However, the absolute reflectance maximum of the CaS spectrum ("surf. 2") is at 0.03, compared 342 to 0.14 for "surf. 3", and 0.18 for "surf. 4", measured with the same aperture size of 20x20 µm. 343 344 Similarly, the reflectance spectra measured on the large (Ca,Mg)S grains in the experiment at 1200 °C 345 (Figure 9d) have very low absolute mid-IR reflectance values and are only reported in the supplement. 346 Figure 9c shows the clear identification of quartz, crystallizing from the sulfidized glass, in the mid-IR.

The high-Al glass (hAl, ID 155) did not crystallize at 800 °C (Figure 10d). Sulfidation extends into thin cracks. However, we observe no change in the mid-IR reflectance spectra measured along the cracks (Figure 10a), except for a decrease in overall reflectance and increase in spectral noise. At 1200 °C the sulfidation formed a thick coating of (Mg,Ca)S, and the interior of the sample crystallized plagioclase and Mg-rich Cpx (Renggli et al., 2022, Figure 10d). The mid-IR reflectance spectra recorded at the sulfidized sample surface show now sulfide signal, but a shift of the reflectance maximum to higher wavenumbers (Figure 10c).



Figure 5: In-situ micro-FTIR observations of the reacted olivine (ID 135) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1000 °C, ID 441; (c & d) experiment at 1200 °C, ID 442. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.



Figure 6: In-situ micro-FTIR observations of the reacted diopside (ID 134) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1000 °C, ID 444; (c & d) experiment at 1200 °C, ID 445. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.





Figure 7: In-situ micro-FTIR observations of the reacted anorthite (ID 1) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1200 °C, ID 448. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue box indicates the area where the in-situ spectrum was recorded.



Figure 8: In-situ micro-FTIR observations of the reacted high-Mg I glass (ID 156) and BSE images of the sample cross-sections and measurement locations. (a - c) experiment at 800 °C, ID 449; (d & e) experiment at 1200 °C, ID 451. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.



Figure 9: In-situ micro-FTIR observations of the reacted low-Mg II A glass (ID 174) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1000 °C, ID 456; (c & d) experiment at 1200 °C, ID 457. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.



Figure 10: In-situ micro-FTIR observations of the reacted high-Al glass (ID 155) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 800 °C, ID 458; (c & d) experiment at 1200 °C, ID 460. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.

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400 Discussion

401 We presented experimental results on sulfidation of minerals and glasses, and the effect of the sulfidation reactions on bulk and in-situ mid-IR spectra. The experiments show a strong temperature 402 403 dependence of silicate sulfidation, which is controlled by the mobility of sulfide-forming cations. The 404 sulfide coatings on the reacted samples exhibit varying textures depending on temperature, silicate 405 composition and structure (e.g. minerals vs. glasses), and time. The sulfide compositions also vary with 406 temperature and range from troilite and CaS to more diverse compositions containing Mg, Ca, Fe, Ti, 407 Mn, and Na (see also Renggli et al., 2022). The mid-IR reflectance spectra of the experimental run 408 products show changes in their spectral features, in particular, we can identify quartz as a reaction 409 product (e.g. equation 1) spectroscopically. The results of our experiments provide important insights 410 into sulfidation reactions and have implications for understanding the geochemistry of planetary 411 surfaces. We argue that S-rich fumarolic and volcanic gases on Mercury reacted at the planet's surface 412 with silicates in volcanic and regolith materials, and led to the observed (Evans et al., 2012; Larry R. 413 Nittler et al., 2011) S-enrichment on the surface of the planets.

414 At low fO₂ values elements that normally behave lithophile (Ca, Mg, Ti, Na, and K), bond to S^{2-} , in a pseudo-equilibrium in which S^{2-} replaces O^{2-} in the case of glasses and melts (Fincham & 415 416 Richardson, 1954; O'Neill & Mavrogenes, 2002). In crystalline phases this change of behavior is 417 expressed in the formation of sulfides such as oldhamite (CaS), niningerite (MgS), or daubréelite 418 $(FeCr_2S_4)$ amongst others, which have been predicted to occur on the surface of Mercury (Larry R. 419 Nittler et al., 2011; Weider et al., 2012), and are abundantly observed in enstatite chondrites (Keil, 420 1968). The high abundance of S on the surface of Mercury measured by MESSENGER, at 421 concentrations of up to 4 wt.% (Evans et al., 2012; Larry R. Nittler et al., 2011), was therefore 422 interpreted to be hosted in magmatic phases at highly reducing conditions (Anzures, Parman, Milliken, Namur, et al., 2020; Namur et al., 2016; Mikhail Y. Zolotov et al., 2013). For example, at 1350-1500 423 424 °C, 4 wt.% of S could be dissolved in silicate melts at very reducing conditions of ~IW-6 (Anzures, Parman, Milliken, Namur, et al., 2020; Namur et al., 2016). Yet, the FeO content in surface silicates on 425 426 Mercury was determined 0.2 to 4.5 wt% (Evans et al., 2012; McClintock et al., 2008; McCoy et al., 427 2018), which would be too high for such highly reducing conditions, if the FeO was dissolved in a silicate melt, requiring the presence of Fe in sulfides or a metal phase (Mikhail Y. Zolotov et al., 2013). 428 429 Further evidence for low fO_2 at the surface of Mercury is the low O/Si (1.2 ± 0.1) ratio measured by 430 Gamma-Ray Spectrometry (Larry R Nittler et al., 2018). However, this low O/Si ratio, observed at the 431 very surface of the planet, may be due to space weathering and graphite-induced smelting reactions 432 (Iacovino et al., 2023; McCubbin et al., 2017). Magmas and gases interacting with graphite would be 433 buffered at the graphite-CO buffer for fO_2 at the low pressure conditions on the surface of Mercury 434 (Keppler & Golabek, 2019). However, since the slope of the graphite-CO buffer in fO_2 vs. temperature 435 is not the same as that of mineral redox buffers, such as IW, it may be more useful fO_2 reference for the 436 surface of Mercury, in particular when referring to gas-solid reactions such as sulfidation or smelting.

437 Considering these observations and their caveats regarding the surface chemistry of Mercury, 438 it is important to consider alternative mechanisms that may explain the observations. As we have argued 439 previously (Renggli et al., 2022), the sulfidation of silicate minerals and glasses forms quartz as a 440 reaction product in association with sulfides including oldhamite, niningerite, troilite, and solid 441 solutions of sulfides. In the experiments that we present in this study, the formation of quartz is most 442 evident in the rapidly sulfidizing diopside together with (Ca,Mg)S. In the reflectance spectra of the bulk 443 powder samples (Figure 4) we observe the spectral signature of quartz in the diopside sample sulfidized 444 at 1200 °C. In the experiments with glasses we observe a shift of the mid-IR reflectance maximum to 445 higher wavenumbers, due to a relative increase of SiO₂ in the altered material (Figure 4d-f). In contrast, 446 we observe no spectral signature in mid-IR reflectance mode of the sulfides that formed in the 447 experiments, including a spectrum recorded on CaS alone (spectrum "surf. 2" in Figure 9a). The overall 448 mid-IR reflectance of the sulfides targeted in-situ is very low, suggesting a low albedo of the material, 449 perhaps due to the experimental setup in graphite crucibles. This observation is in opposition to a 450 previous study that observed spectral features in mid-IR reflectance and emission for CaS, and a high 451 albedo for a synthetic CaS material (Varatharajan et al., 2019).

In summary, we suggest that the effect of sulfidation and S enrichment on the surface of Mercury by gas-solid reactions will be testable by BepiColombo, using the MERTIS instrument that
454 observes the planet in the mid-IR spectral range. We expect the identification of quartz to correlate with 455 the surface abundance of sulfides, including oldhamite, niningerite, and troilite. The rates of sulfidation 456 reactions for different mineral phases remain poorly constrained and require further work. We also aim 457 to better constrain the changes in spectral properties of materials as a function of the degree of 458 sulfidation, as a function of time and S abundance, for reflectance and emission spectroscopy.

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464 **Open Research**

The spectral data will become available on the Infrared and Raman for Interplanetary Spectroscopy (IRIS) database at <u>http://bc-mertis-pi.uni-muenster.de/</u> upon acceptance of the manuscript for publication.

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607

608

Figure 1.



Figure 2.



Figure 3.





60 70 80 90 100

- 0

100

0

10 20 30 40

Figure 4.





Figure 5.



Figure 6.



Figure 7.



Figure 8.



Figure 9.



Figure 10.



1	Mid-infrared spectroscopy of sulfidation reaction products and						
2	implications for Sulfur on Mercury						
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15	Key points						
16	• S-enrichment on the surface of Mercury by sulfidation of silicate minerals						
17	• Mid-IR spectroscopy allows the identification of quartz as a main reaction product in						
18	mineral and glass sulfidation.						
19	• BepiColombo's MERTIS instrument will test the sulfidation hypothesis by mapping the surface						
20	of Mercury in the mid-IR spectral range.						

21 Abstract

22 We propose that the observed enrichment of sulfur at the surface of Mercury (up to 4 wt.%) is 23 the product of silicate sulfidation reactions with a S-rich reduced volcanogenic gas phase. Here, we 24 present new experiments on the sulfidation behavior of olivine, diopside, and anorthite. We investigate 25 these reaction products, and those of sulfidized glasses with Mercury compositions previously reported, 26 by mid-IR reflectance spectroscopy. We investigate both the reacted bulk materials as powders, as well 27 as cross-sections of the reaction products by in-situ micro-IR spectroscopy. The mid-IR spectra confirm 28 the presence of predicted reaction products including quartz. The mid-IR reflectance of sulfide reaction 29 products, such as CaS (oldhamite) or MgS (niningerite), is insufficient to be observed in the complex 30 run products. However, the ESA/JAXA BepiColombo mission to Mercury will be able to test our 31 hypothesis by investigating correlated abundances of sulfides with other reaction products such as 32 quartz.

33 Plain language summary

The surface of the planet Mercury is enriched in sulfur, with abundances of up to 4 wt.%. Sulfur on Mercury has previously been interpreted to occur in magmatic sulfide phases. We propose an alternative mechanism for the enrichment of S on Mercury, whereby reduced S-rich gases react with silicate minerals to form sulfides and quartz. We carried out sulfidation experiments on silicate minerals and glasses and used mid-infrared spectroscopy to characterize the products of these reactions. The upcoming ESA/JAXA BepiColombo mission to Mercury will allow us to test the sulfidation hypothesis and provide constraints on the origin of the S enrichment on the planet's surface.

41 Introduction

The surface of Mercury is distinctly enriched in S, with up to 4 wt. % as revealed by the NASA
MErcury Surface, Space ENvironment, GEochemistry and Ranging (MESSENGER) spacecraft
(McCoy et al., 2018; Larry R. Nittler et al., 2011; Larry R Nittler et al., 2018; Weider et al., 2015). The
processes that resulted in the enrichment of S on the surface of Mercury remain unresolved, however,

46 several processes have been proposed. At extremely reducing conditions several $\log fO_2$ units below the Iron-Wüstite buffer (IW), at IW-3 to IW-7, the solubility of S in basaltic melts is high and increases 47 48 with decreasing fO₂ (Anzures, Parman, Milliken, Lanzirotti, et al., 2020; Anzures, Parman, Milliken, Namur, et al., 2020; Cartier et al., 2014; Namur et al., 2016). Assuming that melts on Mercury 49 50 experience no oxidation from the highly reduced mantle source, sulfides in lavas on the surface of 51 Mercury may be of primary magmatic origin (Anzures, Parman, Milliken, Namur, et al., 2020; Namur 52 et al., 2016; Mikhail Y. Zolotov et al., 2013). However, if the magmas experienced even minor degrees 53 of oxidation from the mantle source to the surface, the solubility of S would have decreased from 54 approximately 7 wt.% at IW-7, to 3 wt.% at IW-5, and 1 wt.% at IW-3 (Namur et al., 2016), resulting 55 in the degassing of S. Processes that could have resulted in the oxidation of ascending magmas on 56 Mercury include assimilation of oxides into the melts (Mikhail Yu. Zolotov, 2011), decompression 57 oxidation (e.g. Foley, 2011), or smelting processes (Iacovino et al., 2023; McCubbin et al., 2017). 58 Previously, it was argued that such oxidation mechanisms have resulted in the formation of volcanic 59 gases that drive explosive volcanism on Mercury (Deutsch et al., 2021; Iacovino et al., 2023; Kerber et 60 al., 2011; L. R. Nittler et al., 2014; Weider et al., 2016), including the depletion of pyroclastic deposits 61 in the degassed volatiles, as observed in the S depleted Nathair Facula, NE of Rachmaninov crater 62 (Weider et al., 2016).

63 Sulfur species in hot volcanic gases are highly reactive with silicate minerals and glasses (King 64 et al., 2018). At oxidizing conditions a SO₂ disproportionation reaction forms sulfate coatings on glasses 65 (Renggli, Palm, et al., 2019; Christian J Renggli & King, 2018), whereas at reducing conditions gas species including S_2 , COS, and CS₂ react with glasses and minerals to form sulfides including troilite 66 (FeS), oldhamite (CaS), and niningerite (MgS) (C.J. Renggli et al., 2022). We have previously argued 67 68 that these sulfidation reactions may be responsible for the observed enrichment of S on the surface of 69 Mercury. For example, the sulfidation of the primary predicted silicate minerals anorthite, forsterite, 70 and diopside (Namur & Charlier, 2017) with CS₂ gas can be written as:

 $\begin{array}{ll} 71 & Mg_2SiO_4 + CaMgSi_2O_6 + 2CaSi_2Al_2O_8 + 3CS_{2(g)} \rightarrow \{7SiO_2 + 2Al_2O_3\}_{glass;\ melt;\ mineral} + 3CaS + 3MgS + \\ 72 & 6CO_{(g)} & Equation \ l \end{array}$

In addition to the sulfides, these reactions result in the formation of quartz and aluminosilicate phases (C.J. Renggli et al., 2022). Since quartz is not predicted to be present in most Mercury terranes, and as an accessory phase only in the low-Mg terrane and the Caloris interior plains (McCoy et al., 2018; Namur & Charlier, 2017), quartz presence on the surface of Mercury, together with sulfides such as oldhamite and niningerite, is evidence for sulfidation reactions.

78 Sulfidation results in a change of spectral properties due to the change in mineralogy. In this 79 study we use the experimental run products (low-Mg, high-Mg, and high-Al glasses) from Renggli et 80 al. (2022), and run additional sulfidation experiments at 800, 1000, and 1200 °C of olivine, diopside, 81 and anorthite, to determine the change in the mid-infrared spectra. We investigated the reaction products 82 using electron microscopy and micro-FTIR (Fourier Transform Infrared Spectroscopy), in the mid-IR from 2.5-16.7 µm (equivalent to 4000 to 666 cm⁻¹), to characterize their chemistry, mineralogy and 83 spectral properties. The spectral data of the sulfide coatings will be used as a reference for the MERTIS 84 85 spectrometer (Mercury Radiometer and Thermal Infrared Spectrometer) onboard the BepiColombo (ESA/JAXA) mission to Mercury (Hiesinger & Helbert, 2010). The observations from BepiColombo 86 87 will allow testing of our proposed mechanism for the formation of surface sulfides on Mercury by high-88 temperature gas-solid reactions with reduced S-rich gas. The ID-numbers of samples reported here refer 89 to the IRIS (Infrared and Raman for Interplanetary Spectroscopy) database hosted at the Institute for 90 Planetology, University of Münster (http://bc-mertis-pi.uni-muenster.de/), where the data is publicly 91 available.

92 Methods

93 Experiments

In this study we present mid-IR spectroscopic observations from silicate glass sulfidation
experiments that we previously reported (Renggli et al. 2022). We refer the reader to that publication
for details on the synthesis of the glasses with compositions based on observations from the NASA
MESSENGER mission. The glasses include a low-Mg sample (ID 174), based on the low-Mg Northern
Volcanic Plains, a high-Mg sample (ID 156), based on the similarly named high-Mg region, and a high-

- 99 Al sample (ID155) based on terrains southwest and southeast of the northern volcanic plains (Namur &
- 100 Charlier, 2017; Vander Kaaden et al., 2017). The mid-IR spectral properties of these pristine glasses
- 101 are described in Morlok et al. (2021).



102

103Figure 1: Experimental set-up of the silicate mineral and Mercury glass samples in an evacuated $(10^{-5}$ 104bar) and sealed silica glass ampule, suspended in a vertical tube furnace. This drawing is modified from Renggli105et al. 2022.

106 In addition to the synthetic Mercury glass samples, we conducted sulfidation experiments with 107 three natural rock-forming minerals. These mineral phases are included in the MERTIS sample 108 database, which is developed in context of the ESA/JAXA BepiColombo mission to Mercury, and were 109 previously characterized chemically by electron microprobe analyzer (EMPA) and mid-IR spectroscopy 110 (Hiesinger et al., 2020). The three mineral phases used in the sulfidation experiments are olivine (ID 111 135), diopside (ID 134), and anorthite (ID 1). The olivine (ID 135) has a forsterite content of 90.5% 112 (Table 1). The sample ID 135 contains two minor contaminants (<5 vol%.) that are not detectable in 113 the bulk FTIR spectrum of the unreacted material. However, in the SEM we were able to identify the 114 contaminants, which are a diopside and a Cr-Mg hercynite ("picotite", 33.4 wt.% Al₂O₃, 33.2 wt. Cr₂O₃, 115 17.2 wt. % MgO, 14.1 wt. FeO). The diopside (ID 134) was previously described and studied spectroscopically for its trace water contents (Kumamoto et al., 2017) and has a minor FeO content of 116 117 ~6.6 wt. % (Table 1). The anorthite contains minor impurities on a grain-scale including alkali feldspar

and a hydrous phase (see electron microprobe supplement). In Table 2 we list the ID numbers of the starting materials and the reaction products.

120 The sulfidation experiments were conducted in sealed and evacuated silica glass ampules 121 (Figure 1) which were short enough (~ 4 cm) to fit in the hot zone of the furnace with a length of ~ 6 cm 122 (C. J. Renggli & Klemme, 2020). The set-up consists of two graphite cups placed above each other in 123 the ampule (wall thickness of 1 mm), with the lower cup filled with elemental S (~0.0015g), and the 124 upper cup filled with the sample material. In previous experiments on the sulfidation of glasses with 125 Mercury compositions we used SiO_2 glass wool to separate the two cups (C.J. Renggli et al., 2022). 126 However, we determined that the addition of the glass wool separator was not necessary but a potential 127 source of sample contamination. Therefore, we did not use glass wool in the experimental set-up for the olivine, diopside, and anorthite sulfidation experiments (Figure 1). After loading the glass tubes, 128 they were sealed under a vacuum of 10⁻⁵ bar. At experimental temperatures the elemental S forms a gas 129 130 phase that reacts with the silicate sample. The fO_2 was controlled at the graphite-CO buffer due to the 131 presence of the graphite cups (C. J. Renggli & Klemme, 2021).

132 Table 1: Major oxide compositions (wt.%) of the three glasses lMgII A, hMgl, and hAl (Morlok et al., 133 2021; C.J. Renggli et al., 2022), and the minerals olivine, diopside (Kumamoto et al. 2017), and anorthite used

134 in the sulfidation experiments.

	IMgII A	hMgI	hAl	Olivine	Diopside	Anorthite
	ID174	ID156	ID155	ID135	ID134	ID1
	Morlok et al., 2021; Renggli et al.,		n=20	Kumamoto	n=20	
		2022			et al. 2017	
SiO ₂	64.26(32)	56.01(38)	57.06(19)	41.04(34)	53.67(09)	43.09(16)
TiO ₂	0.46(02)	1.08(01)	1.39(08)	b.d.l.	0.08(01)	b.d.l.
Al ₂ O ₃	14.30(10)	10.80(14)	16.55(11)	-	0.21(06)	36.18(13)
FeO	0.05(08)	b.d.l.	0.07(03)	9.21(12)	6.62(04)	0.04(02)
MnO	0.16(02)	0.49(01)	0.70(04)	0.16(03)	0.55(18)	b.d.l.
MgO	8.97(12)	23.11(45)	14.78(15)	59.17(21)	14.06(24)	b.d.l.
CaO	6.81(08)	7.73(09)	6.05(10)	0.05(02)	25.35(18)	20.28(18)
Na ₂ O	4.81(12)	1.16(02)	3.15(08)	-	0.04(01)	b.d.l.
K ₂ O	0.19(03)	0.13(02)	0.24(02)	-	-	b.d.l.
Total	100.01	100.52	99.99	100.04	100.63	99.64

135

136 Table 2: ID numbers given to the starting materials and the experiments at 800, 1000, and 1200 °C.

137 These ID numbers refer to the IRIS MERTIS database where the corresponding bulk and in-situ FTIR spectra are 138

available (http://bc-mertis-pi.uni-muenster.de).

	ID of	ID	ID	ID
material	starting	experiment	experiment	experiment
name	material	800 °C	1000 °C	1200 °C
Olivine	135	440	441	442
Diopside	134	443	444	445
Anorthite	1	446	447	448
hMgI	156	449	450	451
hMgII	181	452	453	454
IMgII A	174	455	456	457
hAl	155	458	459	460

139

140 **Analytical methods**

141

The samples retrieved from the quenched silica glass ampules were split in two aliquots. The 142 first aliquot included larger grains that were first used to characterize the surfaces by Scanning Electron 143 Microscopy (SEM) and in-situ characterization by electron microprobe and FTIR microscopy of sample 144 cross-sections. The second aliquot was retained as a powder with unknown grain-size distribution and 145 used for FTIR bulk powder analysis.

146 Back-scattered electron (BSE) images were made on a JSM-6510 Series SEM in low-vacuum 147 mode at 50 Pa, which allowed imaging without carbon coating. The grains were then embedded in 148 epoxy resin and polished under anhydrous ethanol, with a final polish using 0.25 μ m diamond paste. 149 The chemistry of the reaction products was determined with a JEOL JXA 8530F electron microprobe 150 at 15 keV and 60 nA probe current. The spot size varied depending on grain-size from 1-10 μ m. For 151 details on standardization and reference materials we refer to the supplementary material in Renggli et 152 al. (2022).

The bulk and in-situ FTIR reflectance spectra were recorded with a Bruker Hyperion 3000 153 154 microscope using a liquid nitrogen cooled MCT detector over a spectral range of 4000 - 600 cm⁻¹ at a 155 spectral resolution of 4 cm⁻¹. In this study we discuss the features over the spectral range of 1300 -156 800 cm⁻¹ and the reported spectra are the averages of 64 or 128 scans. For the bulk measurements the 157 samples were ground dry for less than 30 seconds and placed in Al-metal sample cups. The bulk measurements were done on these powders with an aperture cross-section of 600x600 µm. For the in-158 159 situ measurements the microscope aperture was varied depending on the target sample, with the smallest 160 used aperture size of $15x15 \,\mu\text{m}$. The aperture sizes for all in-situ measurements are given with the full spectral data in the electronic supplement, and analysis locations are shown in the BSE images of the 161 162 respective samples. For bulk spectra we used a gold mirror standard and for the bulk measurements we 163 used an InfraGold diffuse scattering standard.

164 **Experimental results**

165 **Reacted surface**

The sulfidation of silicates is strongly temperature dependent, due to the diffusion-controlled 166 167 mobility of the sulfide forming cations (e.g. Fe, Ca, Mg, ±Mn, ±Ti, ±Na) (Renggli, King, et al., 2019; C.J. Renggli et al., 2022). Consequently, the coatings on the reacted samples vary in texture with time, 168 169 temperature, and silicate composition and structure. In Figure 2 we show BSE images of the surfaces of the 6 types of investigated samples, reacted for 24 h at 1000 °C. The reacted minerals (a-c) show a 170 less complete sulfide coating compared to the reacted glasses (d-f). The sulfide compositions labelled 171 172 on the BSE images were determined using qualitative EDS in the SEM low-vacuum mode. The detailed 173 sulfide compositions were analyzed by EPMA and are reported in Figure 3 and the supplement.

174 On the olivine grain sulfidized at 1000 °C we observe two sulfide compositions (Figure 2a), 175 including MgS (niningerite) with grain sizes of up to 8 µm, and (Fe,Mg)S, which appears white in the BSE image, and forms slightly larger grains. The sulfidized diopside is coated by three distinct sulfide 176 phases. First, (Mg,Ca,Fe)S forms the larges grains (<20 µm), second, a Ti-bearing sulfide forms platy 177 178 grains, and third, (Ca,Mg)S forms smaller grains with diameters $<10 \mu m$ (Figure 2b). The anorthite has 179 a very un-even coating with parts of the surface entirely coated by CaS, whereas other areas show no sulfide coatings. The CaS only occurs on the anorthite component of the grain, whereas the impurity, 180 181 an alkali feldspar, shows no sulfide coating. In addition, the textures reveal that the anorthite 182 experienced partial melting, apparent in the lower right corner of the BSE image (Figure 2c). The 183 textures in the coatings of the sulfidized glasses are reported in detail in Renggli et al. (2022). Here, we 184 show the BSE images (Figure 2d-e) to allow a comparison with the mineral experiments. Overall, the 185 sulfides on the glasses show a more diverse chemistry, including Mn, Fe, Na and Ti in predominantly 186 CaS and MgS phases, and the coatings are overall less patchy compared to the minerals. In addition, 187 we observe occasional graphite grains on these surfaces, which are contamination from the graphite 188 cups in which the samples were placed. Since we used SiO_2 glass wool as a spacer in the ampules for 189 the glass sulfidation experiments we looked for traces of this material but did not identify any 190 contamination.



191

Figure 2: Secondary backscattered electron microscopy images of mineral and glass grains sulfidized for 24 h at 1000 °C. a) olivine ID 441, b) diopside ID 444, c) anorthite ID 447, d) high-Mg glass ID 450, e) low-Mg glass ID 456, f) high-Al glass ID 459. The sulfide coatings are labeled on the images and include MgS, FeS, CaS, and mixed sulfide compositions. For a detailed description of sulfide reaction products in the glass sulfidation experiments we refer the reader to Renggli et al. 2022.

197

198
Sulfide compositions

200 We observe exclusively CaS (oldhamite) on the sulfidized anorthite grains. In contrast, the compositions of the sulfides formed in olivine and diopside sulfidation experiments are compositionally 201 202 more diverse and vary with experimental temperature from 800 to 1200 °C. In Figure 3 we show the 203 compositional variations of the sulfides on the reacted olivines and diopsides. At 800 °C, the coating 204 on the olivine grains consists of Fe-depleted troilite (Fe_{1-x}S). This is compositionally removed from the 205 olivine composition (Mg_{1.83}Fe_{0.17}SiO₄, Table 1). However, the Mg/Fe ratio of the sulfide composition 206 (Mg,Fe)S approaches the Mg/Fe ratio of the educt olivine with increasing experimental temperature 207 and degree of sulfidation (Figure 3a). Similarly, the sulfide reaction products on the diopside grains 208 approach the Ca-Mg-(Fe+Ti) molar composition of the unreacted diopside. At 800 °C we observe 209 (Fe,Ti)_{1-x}S and CaS, whereas at higher temperatures (1000 and 1200 °) we also observe Mg-rich 210 (Mg,Ca)S in addition to a Ca-rich sulfide (Figure 3b). We reported the compositions of the sulfides in 211 the glass sulfidation experiments previously (Renggli et al., 2022). We observed similar variations in 212 the Ca-Mg-(Fe+Ti) compositional space in the glass experiments as in the sulfidation of the diopside 213 (Figure 3b). The sulfides in the high-Mg and high-Al glass experiments fell predominantly in the CaS-214 MgS compositional spaces, whereas we observed abundant Fe-rich and Mg-poor sulfides in the low-215 Mg glass experiment (Renggli et al., 2022).



Figure 3: Compositions of the sulfides formed in the reactions with a) olivine, and b) diopside. The yellow circles show the sulfide compositions of experiments at 800 °C, red diamonds at 1000 °C, and dark red squares at 1200 °C. The blue line in a) and the blue circle in b) indicate the compositions of the respective silicate starting material.



223

Figure 4: Bulk mid-FTIR spectra of the reacted samples. a) olivine ID 135, b) diopside ID 134, c) anorthite ID 1, d) hMgI ID 156, e) lMgII A ID 174, f) hAl ID 155. The solid black line is the bulk spectrum of the unreacted starting material, the dashed grey line is the spectrum of quartz ID13, and the dashed green line in (d) the spectrum of olivine ID249.

228 We measured the mid-IR reflectance spectra of the experimental run products over a spectral 229 range of $800 - 1300 \text{ cm}^{-1}$ (12.5 - 7.7 µm) to test the effect of mineral and glass sulfidation on the spectral properties (Figure 4). The spectral positions of the reflectance minima (Christiansen Feature, 230 231 CF) and the reflectance maxima (e.g., Reststrahlenband, RB) of the starting materials are reported in 232 Table 3. Changes in the spectral features represent changes in the sample mineralogy and will be used 233 as a basis to test the sulfidation hypothesis for S-enrichment on the surface of Mercury with the MERTIS 234 instrument onboard BepiColombo. The degree of change in the spectra is strongly dependent on the 235 degree of sulfidation and change in mineralogy, which increases with temperature from 800 to 1200 °C. 236 The sulfidation reaction (Equation 1) predicts the formation of SiO_2 as a reaction product in addition to 237 sulfides. To test for the presence of quartz in the reaction products we show a quartz spectrum (ID 13) 238 in the panels of Figure 4. The three primary RBs are at 1096, 1181, and 1212 cm⁻¹.

Olivine has four RBs with decreasing reflectance at 946, 983, 1060, and 839 cm⁻¹. In the sulfidation experiment at 800 °C the relative intensities of these reflectance RBs largely remain unchanged (Figure 4a). At higher temperatures (1000, 1200 °C) the reflectance of the reacted sample decreases dramatically, and the reflectance maxima of the normalized spectra are at 1300 cm⁻¹. In addition, the high-temperature spectra are noisier compared to that of the 800 °C experiment, or the unreacted olivine. We observe no clear spectral features that we can attribute to quartz.

245 Diopside (ID 134) has four major RBs with decreasing reflectance at 918, 959, 1119, and 1008 cm⁻¹, a small RB, almost completely overlapped by the two main RBs, at 940 cm⁻¹, and a prominent 246 shoulder at ~ 1075 cm⁻¹ (Figure 4b). The more extensive sulfidation of diopside compared to olivine 247 248 observed in the SEM images (Figure 2) is also apparent in the bulk FTIR spectra of the diopside reaction 249 products. At 800 °C, where the degree of sulfidation is low, the spectrum retains the primary features 250 of the unreacted diopside. However, at 1000 and 1200 °C the overall reflectance amplitude decreases, 251 but we can also identify the appearance of RBs characteristic for quartz, most prominently at ~1090 cm⁻¹ 252 (Figure 4b). At this wavenumber a shoulder appears in the spectra of the experiment at 1000 °C, but becomes the main RB at 1200 °C. Similarly, shoulders and RBs attributable to quartz occur ~1220 cm⁻¹ 253 254 and 1178 cm⁻¹. These RB wavenumbers are within 8 cm⁻¹ of the quartz ID 13 reference spectrum, but are not perfect matches. However, vibrational modes are defined by crystallographic structure and record variations in crystal orientation, defect populations, impurities in the reference quartz, or the high-temperature formation conditions in the sulfidation experiments.

258 Anorthite (ID 1) has a complex mid-IR reflectance spectrum, with reflectance maxima at 948, 259 1021, 1036, 985, 914, 1099, 1081, and 1139 cm⁻¹ in order of decreasing reflectance. The reflectance minimum CF of anorthite is located at ~1230 cm⁻¹, at higher wavenumbers compared to olivine or 260 261 diopside (Figure 4c). The presence of RBs at high wavenumbers, in the range of the main quartz RB at \sim 1100 cm⁻¹ may pose a challenge to the identification of sulfidation reaction products in the mid-IR 262 263 spectra. A further challenge is the mineralogical heterogeneity of the anorthite sample (ID 1) used for 264 this study (see above). The experimental run products are much darker in appearance compared to the 265 starting material. Similarly, the overall reflectance of all experiments has decreased compared to ID 1 266 (Figure 4c). We observe no other spectral signatures of sulfidation in the mid-IR of the anorthite 267 sulfidation experiments.

268 The mid-IR spectra of the synthetic Mercury glasses hMgI (ID 156, Figure 4d), hMgII (ID 181, 269 only in supplement), lMgII A (ID 174, Figure 4e), and hAl (ID 155, Figure 4f) were previously 270 described in Morlok et al. (2021). The glass spectra are characterized by a reflectance minimum (CF) 271 at low wavenumbers, and a broad reflectance maximum (Table 3). The mid-IR spectra of the sulfidized 272 glasses show clear evidence for alteration, and crystallization (Figure 4d-f). In our previous study we 273 have shown that the glasses partially crystallized in the experiments. The hMgI glass formed forsterite 274 and enstatite, the lMgII A glass formed forsterite, and the hAl glass formed plagioclase and Mg-rich 275 clinopyroxene (Renggli et al. 2022). The sulfidation removed Ca and Mg from the glass and enriched 276 the altered substrate glass in SiO₂. The main band position shifts to higher wavenumbers with increasing 277 SiO₂ content (Dufresne et al., 2015; Morlok et al., 2021, 2023), which is apparent in the shift of the 278 main reflectance peak of the most strongly altered experiments at 1200 °C (Figure 4d,e). As in the case 279 of the sulfidized minerals, the overall reflectance is lower in the experiments compared to the unaltered 280 glasses, resulting in noisy mid-IR spectra (e.g. Figure 4f).

Table 3: Christiansen Feature (CF) and Reststrahlenband (RB) spectral positions in wavenumber and
 wavelength for the starting materials. The RBs are ordered by decreasing reflectance. For glasses we only report
 the spectral position of the reflectance maximum. For more details on the spectral features of the glasses see
 Morlok et al. (2021).

		Olivine ID 135	Diopside ID 134	Anorthite ID 1	Quartz ID 13	hMg I ID 156	hMg II ID 181	lMg IIA ID 174	hAl ID 155
CF		1163 cm ⁻¹ 8.60 μm	1184 cm ⁻¹ 8.44 μm	1229 cm ⁻¹ 8. <i>13 μm</i>	1354 cm ⁻¹ 7.39 μm	1229 cm ⁻¹ 8.13 μm	1242 cm ⁻¹ 8.05 μm	1268 cm ⁻¹ 7.89 μm	1242 cm ⁻¹ 8.05 μm
RB	1	946 cm ⁻¹ 10.57 μm	918 cm ⁻¹ 10.89 μm	948 cm ⁻¹ 10.54 μm	1096 cm ⁻¹ 9.12 μm	1005 cm ⁻¹ 9.95 μm	1021 cm ⁻¹ 9.79 μm	1045 cm ⁻¹ 9.57 μm	1019 cm ⁻¹ 9.81 μm
	2	983 cm ⁻¹ 10.18 μm	959 cm ⁻¹ 10.43 μm	1021 cm ⁻¹ 9.79 μm	1181 cm ⁻¹ 8.47 μm				
	3	1060 cm ⁻¹ 9.43 μm	940 cm ⁻¹ 10.64 μm	1036 cm ⁻¹ 9.65 μm	1212 cm ⁻¹ 8.25 μm				
	4	839 cm ⁻¹ 11.92 μm	1119 cm ⁻¹ 8.94 μm	985 cm ⁻¹ 10.15 μm					
	5		1075 cm ⁻¹ 9.30 μm	914 cm ⁻¹ 10.94 μm					
	6		1008 cm ⁻¹ 9.92 μm	1099 cm ⁻¹ 9.10 μm					
	7			1081 cm ⁻¹ 9.25 μm					
	8			1139 cm ⁻¹ 8.78 μm					

286

287 In-Situ investigations

We report observations of cross-sectioned experimental samples, including SEM images and in-situ micro-FTIR spectra (Figures 5-10). Sulfidation is not limited to the surface of the mineral grains, but also occurs in cracks. These cracks were likely present in the grains prior to the experiments. The BSE images show changes in the silicate substrates and micro-FTIR measurement areas are indicated as blue rectangles. The dimensions of these measurement areas are approximate and reported in detail in the supplement with the micro-FTIR spectral data. Here, we describe the spectral features of the sulfidized mineral and glass grains.

The in-situ observations of the sulfidized olivine (ID 135) reacted at 1000 °C (ID 441) and 1200 °C (ID 442) are shown in Figure 5. The grain in Figure 5b was only polished superficially and not to the core of the grain. The spectra on the sample reacted at 1000 °C (Figure 5a), therefore represent those of the altered near-surface area. Nevertheless, these spectra are very similar to the unaltered olivine. An additional strong RB is apparent in the spectrum of area 2 at 1082 cm⁻¹. Similarly, the sulfidation of olivine at 1200 °C has not progressed sufficiently to result in a change in mineralogy (e.g. formation of quartz), and the mid-IR spectra remain characteristic for olivine (Figure 5c). Notably, sulfidation has occurred in thin cracks within the olivine grain, and the BSE image shows a gray-scale
 gradient towards the grain surface, indicative for diffusional loss of Fe to the sulfide (Figure 5d).

304 The surface SEM observations suggest a higher rate of sulfidation for diopside, compared to 305 olivine (Figure 2). This observation is also supported by the in-situ investigations. At 1000 °C little 306 alteration can be observed (Figure 6b) and the micro-FTIR spectra show no change from diopside 307 (Figure 6a). However, at 1200 °C strong sulfidation is evident in the BSE image of the sample cross-308 section (Figure 6d). The sulfidation reaction has extended into cracks by up to $200 \,\mu\text{m}$. The cracks are 309 widened and filled by (Ca,Mg)S and quartz (darker gray compared to diopside in Figure 6d). The spectra 310 recorded over the cracks (1-4), however, show limited changes compared to the unreacted diopside. 311 The overall reflectance of these spectra is low and they appear noisy. Despite the presence of quartz, 312 observed by SEM, no clear quartz RBs are evident. Instead, the spectral signature of the diopside 313 dominates the spectra (Figure 6c).

In-situ observations of sulfidized anorthite are limited to the experiment at 1200 °C (Figure 7), due to the heterogeneity of the starting material. The BSE image shows pervasive sulfidation, even in the interior of the sample (Figure 7b). The sample has partially molten and quench crystals can be observed. The partially glassy nature of the sample is apparent in the micro-FTIR spectrum of the area labelled "altered", as a broad band, reminiscent of the FTIR spectra of the unaltered glasses (Figure 4).

319 The high-Mg glass (hMgI, ID 156) has crystallized forsterite in the substrate at 800 °C (Figure 320 8b). Additionally, we observe Fe metal nuggets in the substrate which formed in the synthesis of the 321 glass used in the sulfidation experiments, because the FeO-content was too high for the imposed fO_2 322 (Morlok et al., 2021). The forsterite is clearly identified in the micro-FTIR spectra of the sample interior 323 (dotted lines, Figure 8a). At 1200 °C the only phase that crystallized in the substrate during the 324 experiment was enstatite, due to the loss of Mg to (Mg,Ca)S in the coating (Renggli et al., 2022). However, even though the enstatite was identified in the sample by electron microprobe analysis, the 325 mid-IR spectrum of the enstatite-rich sample interior remains ambiguous. The enstatite reference 326 327 material ID 53 (Weber et al., 2020), a bulk powder sample in the grain-size range of 63-125 µm, has two RBs at high wavenumbers (1099 cm⁻¹ & 1060 cm⁻¹), where the experimental spectrum has only one 328

(1084 cm⁻¹), and similarly three RBs at lower wavenumbers in ID 53 (978 cm⁻¹, 957 cm⁻¹, 929 cm⁻¹), where the experimental sample has a very broad RB at 949 cm⁻¹. This difference is likely due to differences in crystal grain orientation (Tappert et al., 2013). At the surface the sample is strongly Mg-depleted (Renggli et al., 2022). Surface spectrum 1 (Figure 8d) shows an enstatite band at 1005 cm⁻¹, whereas the surface spectra 2 and 3 show now enstatite and the main reflectance maxima are shifted to higher wavenumbers. Despite the abundant presence of (Mg,Ca)S in the sample area recorded by surface spectrum 2 (Figure 8e), there is no evidence for a spectral signature of the sulfide.

336 In Figure 9, we show the in-situ observations of the experiments with the low-Mg glass (lMgII 337 A, ID 174) at 1000 °C (Figure 9a, b) and 1200 °C (Figure 9c, d). At 1000 °C, the sulfide coating, 338 consisting primarily of CaS (Renggli et al., 2022), was thick enough to allow a micro-IR measurement of the sulfide only, shown as #2 in Figure 9a. The CaS spectrum is very noisy and the reflectance 339 maximum was normalized to 1. The reflectance maximum of "surf. 2" is at ~1082 cm⁻¹, which is in the 340 341 same spectral range as the surface areas including the substrate ("surf. 1" at 1070 and "surf. 3" at 1072 cm⁻¹). However, the absolute reflectance maximum of the CaS spectrum ("surf. 2") is at 0.03, compared 342 to 0.14 for "surf. 3", and 0.18 for "surf. 4", measured with the same aperture size of 20x20 µm. 343 344 Similarly, the reflectance spectra measured on the large (Ca,Mg)S grains in the experiment at 1200 °C 345 (Figure 9d) have very low absolute mid-IR reflectance values and are only reported in the supplement. 346 Figure 9c shows the clear identification of quartz, crystallizing from the sulfidized glass, in the mid-IR.

The high-Al glass (hAl, ID 155) did not crystallize at 800 °C (Figure 10d). Sulfidation extends into thin cracks. However, we observe no change in the mid-IR reflectance spectra measured along the cracks (Figure 10a), except for a decrease in overall reflectance and increase in spectral noise. At 1200 °C the sulfidation formed a thick coating of (Mg,Ca)S, and the interior of the sample crystallized plagioclase and Mg-rich Cpx (Renggli et al., 2022, Figure 10d). The mid-IR reflectance spectra recorded at the sulfidized sample surface show now sulfide signal, but a shift of the reflectance maximum to higher wavenumbers (Figure 10c).



Figure 5: In-situ micro-FTIR observations of the reacted olivine (ID 135) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1000 °C, ID 441; (c & d) experiment at 1200 °C, ID 442. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.



Figure 6: In-situ micro-FTIR observations of the reacted diopside (ID 134) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1000 °C, ID 444; (c & d) experiment at 1200 °C, ID 445. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.





Figure 7: In-situ micro-FTIR observations of the reacted anorthite (ID 1) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1200 °C, ID 448. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue box indicates the area where the in-situ spectrum was recorded.



Figure 8: In-situ micro-FTIR observations of the reacted high-Mg I glass (ID 156) and BSE images of the sample cross-sections and measurement locations. (a - c) experiment at 800 °C, ID 449; (d & e) experiment at 1200 °C, ID 451. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.



Figure 9: In-situ micro-FTIR observations of the reacted low-Mg II A glass (ID 174) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 1000 °C, ID 456; (c & d) experiment at 1200 °C, ID 457. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.



Figure 10: In-situ micro-FTIR observations of the reacted high-Al glass (ID 155) and BSE images of the sample cross-sections and measurement locations. (a & b) experiment at 800 °C, ID 458; (c & d) experiment at 1200 °C, ID 460. Solid lines indicate spectra recorded at or near the altered surface of the grain, dotted lines are spectra of the unaltered interiors of the samples, dashed lines are the bulk spectra of reference phases. The blue boxes indicate the areas where the in-situ spectra were recorded.

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400 Discussion

401 We presented experimental results on sulfidation of minerals and glasses, and the effect of the sulfidation reactions on bulk and in-situ mid-IR spectra. The experiments show a strong temperature 402 403 dependence of silicate sulfidation, which is controlled by the mobility of sulfide-forming cations. The 404 sulfide coatings on the reacted samples exhibit varying textures depending on temperature, silicate 405 composition and structure (e.g. minerals vs. glasses), and time. The sulfide compositions also vary with 406 temperature and range from troilite and CaS to more diverse compositions containing Mg, Ca, Fe, Ti, 407 Mn, and Na (see also Renggli et al., 2022). The mid-IR reflectance spectra of the experimental run 408 products show changes in their spectral features, in particular, we can identify quartz as a reaction 409 product (e.g. equation 1) spectroscopically. The results of our experiments provide important insights 410 into sulfidation reactions and have implications for understanding the geochemistry of planetary 411 surfaces. We argue that S-rich fumarolic and volcanic gases on Mercury reacted at the planet's surface 412 with silicates in volcanic and regolith materials, and led to the observed (Evans et al., 2012; Larry R. 413 Nittler et al., 2011) S-enrichment on the surface of the planets.

414 At low fO₂ values elements that normally behave lithophile (Ca, Mg, Ti, Na, and K), bond to S^{2-} , in a pseudo-equilibrium in which S^{2-} replaces O^{2-} in the case of glasses and melts (Fincham & 415 416 Richardson, 1954; O'Neill & Mavrogenes, 2002). In crystalline phases this change of behavior is 417 expressed in the formation of sulfides such as oldhamite (CaS), niningerite (MgS), or daubréelite 418 $(FeCr_2S_4)$ amongst others, which have been predicted to occur on the surface of Mercury (Larry R. 419 Nittler et al., 2011; Weider et al., 2012), and are abundantly observed in enstatite chondrites (Keil, 420 1968). The high abundance of S on the surface of Mercury measured by MESSENGER, at 421 concentrations of up to 4 wt.% (Evans et al., 2012; Larry R. Nittler et al., 2011), was therefore 422 interpreted to be hosted in magmatic phases at highly reducing conditions (Anzures, Parman, Milliken, Namur, et al., 2020; Namur et al., 2016; Mikhail Y. Zolotov et al., 2013). For example, at 1350-1500 423 424 °C, 4 wt.% of S could be dissolved in silicate melts at very reducing conditions of ~IW-6 (Anzures, Parman, Milliken, Namur, et al., 2020; Namur et al., 2016). Yet, the FeO content in surface silicates on 425 426 Mercury was determined 0.2 to 4.5 wt% (Evans et al., 2012; McClintock et al., 2008; McCoy et al., 427 2018), which would be too high for such highly reducing conditions, if the FeO was dissolved in a silicate melt, requiring the presence of Fe in sulfides or a metal phase (Mikhail Y. Zolotov et al., 2013). 428 429 Further evidence for low fO_2 at the surface of Mercury is the low O/Si (1.2 ± 0.1) ratio measured by 430 Gamma-Ray Spectrometry (Larry R Nittler et al., 2018). However, this low O/Si ratio, observed at the 431 very surface of the planet, may be due to space weathering and graphite-induced smelting reactions 432 (Iacovino et al., 2023; McCubbin et al., 2017). Magmas and gases interacting with graphite would be 433 buffered at the graphite-CO buffer for fO_2 at the low pressure conditions on the surface of Mercury 434 (Keppler & Golabek, 2019). However, since the slope of the graphite-CO buffer in fO_2 vs. temperature 435 is not the same as that of mineral redox buffers, such as IW, it may be more useful fO_2 reference for the 436 surface of Mercury, in particular when referring to gas-solid reactions such as sulfidation or smelting.

437 Considering these observations and their caveats regarding the surface chemistry of Mercury, 438 it is important to consider alternative mechanisms that may explain the observations. As we have argued 439 previously (Renggli et al., 2022), the sulfidation of silicate minerals and glasses forms quartz as a 440 reaction product in association with sulfides including oldhamite, niningerite, troilite, and solid 441 solutions of sulfides. In the experiments that we present in this study, the formation of quartz is most 442 evident in the rapidly sulfidizing diopside together with (Ca,Mg)S. In the reflectance spectra of the bulk 443 powder samples (Figure 4) we observe the spectral signature of quartz in the diopside sample sulfidized 444 at 1200 °C. In the experiments with glasses we observe a shift of the mid-IR reflectance maximum to 445 higher wavenumbers, due to a relative increase of SiO₂ in the altered material (Figure 4d-f). In contrast, 446 we observe no spectral signature in mid-IR reflectance mode of the sulfides that formed in the 447 experiments, including a spectrum recorded on CaS alone (spectrum "surf. 2" in Figure 9a). The overall 448 mid-IR reflectance of the sulfides targeted in-situ is very low, suggesting a low albedo of the material, 449 perhaps due to the experimental setup in graphite crucibles. This observation is in opposition to a 450 previous study that observed spectral features in mid-IR reflectance and emission for CaS, and a high 451 albedo for a synthetic CaS material (Varatharajan et al., 2019).

In summary, we suggest that the effect of sulfidation and S enrichment on the surface of Mercury by gas-solid reactions will be testable by BepiColombo, using the MERTIS instrument that 454 observes the planet in the mid-IR spectral range. We expect the identification of quartz to correlate with 455 the surface abundance of sulfides, including oldhamite, niningerite, and troilite. The rates of sulfidation 456 reactions for different mineral phases remain poorly constrained and require further work. We also aim 457 to better constrain the changes in spectral properties of materials as a function of the degree of 458 sulfidation, as a function of time and S abundance, for reflectance and emission spectroscopy.

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464 **Open Research**

The spectral data will become available on the Infrared and Raman for Interplanetary Spectroscopy (IRIS) database at <u>http://bc-mertis-pi.uni-muenster.de/</u> upon acceptance of the manuscript for publication.

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