1   # Sulfur solubility in reduced mafic silicate melts: Implications for

2   # the speciation and distribution of sulfur on Mercury

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Abstract

Chemical data from the MESSENGER spacecraft revealed that surface rocks on Mercury are unusually enriched in sulfur compared to samples from other terrestrial planets. In order to understand the speciation and distribution of sulfur on Mercury, we performed high temperature (1200-1750 °C), low- to high-pressure (1 bar to 4 GPa) experiments on compositions representative of Mercurian lavas and on the silicate composition of an enstatite chondrite. We equilibrated silicate melts with sulfide and metallic melts under highly reducing conditions (IW-1.5 to IW-9.4; IW = iron-wüstite oxygen fugacity buffer). Under these oxygen fugacity conditions, sulfur dissolves in the silicate melt as S^{2-} and forms complexes with Fe^{2+}, Mg^{2+} and Ca^{2+}. The sulfur concentration in silicate melts at sulfide saturation (SCSS) increases with increasing reducing conditions (from < 1 wt.% S at IW-2 to >10 wt.% S at IW-8) and with increasing temperature. Metallic melts have a low sulfur content which decreases from 3 wt.% at IW-2 to 0 wt.% at IW-9. We developed a parameterization to predict SCSS in Mercurian magmas as a function of melt composition, temperature, pressure and oxygen fugacity. Sulfide saturation from silicate melts depends on the melt FeO content and is not a redox reaction. The oxygen fugacity term in our expression of SCSS therefore imposes this expression is strictly valid for magmatic systems containing a metal phase. Using physical constraints of the Mercurian mantle and magmas as well as our experimental results, we suggest that basalts on Mercury were free of sulfide globules when they erupted. The high sulfur contents revealed by MESSENGER result from the high sulfur solubility in silicate melt at reducing conditions. We make the realistic assumption that the oxygen fugacity of mantle rocks was set during equilibration of the magma ocean with the core and/or that the mantle contains a minor metal phase and combine our parameterization of SCSS with chemical data from MESSENGER to constrain the oxygen fugacity of Mercury's interior to IW-5.4±0.4. We also calculate that the mantle of Mercury contains 7-11 wt.% S and that the metallic core of the planet has little sulfur (< 1.5 wt.% S). The external part of the Mercurian core is likely to be made up of a thin (< 90 km) FeS layer.

1. Introduction

Mercury is the innermost planet of our Solar system. It is made of a very large core (~65 wt.% of the planet; Hauck et al., 2013) and a thin mantle (420±30 km; Hauck et al., 2013, Padovan et al., 2015) dominated by olivine, orthopyroxene, clinopyroxene, ± spinel and feldspar (Stockstill-Cahill et al., 2012; Charlier et al., 2013; Namur et al., 2016, Vander Kaaden and McCubbin 2016). Building blocks of Mercury could be compositionally close to enstatite chondrite or bencubbinite chondrite meteorites (Brown and Elkins-Tanton, 2009; Malavergne et al., 2010, 2014; Chabot et al., 2014). The surface of Mercury is a secondary crust produced during volcanic eruptions (Weider et al., 2012; Byrne et al., 2013). Based on crater densities and chemical compositions, several provinces were described (Denevi et al., 2013; Weider et al., 2015): (1) the Northern Volcanic Plains (NVP) with calculated model ages ranging from 3.7 to 2.5 Ga (Neukum et al., 2001; Marchi et al., 2009; Le Feuvre and Wieczorek, 2011; Ostrach et al., 2015); (2) the 4.0-3.7 Ga Smooth Plains (SP) and (3) the 4.2-4.0 Ga Inter-crater Plains and Heavily Cratered Terrains (IcP-HCT), which also contain a High-Mg Terrane (HMg).

Chemical data from the MESSENGER spacecraft show that Mercurian lavas are MgO-rich and have a low Fe content (< 2wt.%; Weider et al., 2014). They are also unusually enriched in sulfur (Weider et al., 2015), with the highest sulfur concentrations (~ 3 wt.% S) observed in HMg lavas (Peplowski et al., 2015). The sulfur content of Mercurian lavas is much higher than that observed in mantle rocks and lavas from the Earth, Mars and the Moon (< 1 wt.% S) and is as high as the bulk S content of chondrites (1-5 wt.% S; Fig. 1). High sulfur concentrations in Mercurian lavas may result either from high sulfur solubility in magmas (Zolotov et al., 2013) and/or from transport of sulfide droplets from the mantle source regions to the surface of the planet (Malavergne et al., 2014). The first hypothesis is consistent with the absence of spectral evidence for sulfide minerals in surface rocks (McClintock et al., 2008; Izenberg et al., 2014) while the second could explain the

82 correlations between S and Ca-Mg observed in Mercurian lavas (Weider et al., 2012).

83 Understanding the origin of high sulfur concentrations at the surface of Mercury is important

84 to better constrain the structure of the planet and the distribution of sulfur amongst the

85 different reservoirs (mantle, core and crust), the mechanisms of explosive volcanism (Kerber

86 et al., 2009; Thomas et al., 2014a; Weider et al., 2016), and the formation of the hollows (sub-

87 kilometer scale, shallow depressions surrounded by bright deposits) which may have formed

88 during sublimation of volatiles (Blewett et al., 2013; Thomas et al., 2014b).

89   The high sulfur concentrations in lavas, together with their low Fe contents and the

90 large metal/silicate ratio of Mercury are strong evidence for accretion and differentiation of

91 the planet under highly reducing conditions (< IW-3; IW = iron-wüstite oxygen fugacity

92 buffer; Malavergne et al., 2010; McCubbin et al., 2012; Zolotov et al., 2013). However, any

93 interpretation of magmatic processes on Mercury and, in particular, the behavior of sulfur in

94 magmas are presently very difficult because of the very limited number of experimental

95 studies performed under oxygen fugacity conditions relevant to Mercury (McCoy et al., 1999;

96 Berthet et al., 2009; Chabot et al., 2014; Malavergne et al., 2014; Vander Kaaden and

97 McCubbin, 2016). In this study, we present the results of 100 new, high-temperature, low- to

98 high-pressure (1 bar to 4 GPa), experiments performed under highly reducing conditions (IW-

99 1.5 to IW-9). Experiments were performed on compositions representative of the basalts and

100 the mantle of Mercury. We investigate sulfur distribution in coexisting silicate melt, sulfide

101 melt and metallic melt and use our experimental data to build a predictive model of sulfur

102 solubility in silicate melt as a function of intensive parameters (temperature, pressure, oxygen

103 fugacity). We then discuss sulfur transport from the mantle to the surface of Mercury, the

104 redox conditions of the mantle and sulfur partitioning between the metallic core and the

105 silicate mantle, with implications for the formation of a FeS layer at the mantle-core

106 boundary.

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108 **2. Experimental and analytical procedures**

109 2.1. Choice and preparation of starting compositions

110   Experiments were performed on three silicate compositions (Table 1) that were equilibrated

111   with a Fe-bearing metallic phase and a sulfide phase. Silicate compositions were chosen to

112   match (1) lavas of the Northern Volcanic Plains (NVP), (2) the high-Mg terrane (HMg) of the

113   IcP-HCT and (3) a composition representative of the silicate fraction of an enstatite chondrite

114   (EH). NVP and HMg compositions are based on geochemical data presented by Weider et al.

115   (2012). For NVP, we used 34 X-Ray Spectroscopy (XRS) measurements and calculated

116   median values for the Mg/Si, Al/Si and Ca/Si ratios and re-calculated the compositions on an

117   oxide basis. For minor elements (TiO_2, MnO and K_2O), we used data from Nittler et al.

118   (2011) and Peplowski et al. (2012). We considered a Na/Si ratio of 0.20 (Peplowski et al.,

119   2014), leading to ~7 wt.% Na_2O in the NVP composition. For some experiments, we also

120   used a Na-free NVP composition. For HMg, we prepared a starting composition

121   corresponding to the median composition of the High-Mg terrane (HMg) of the Inter-crater

122   Plains and Heavily Cratered Terrains (IcP-HCT). We used 49 XRS measurements with a

123   Mg/Si ratio greater than 0.6. We considered a Na/Si ratio of 0.06 (~2.7 wt.% Na_2O) and 0.1

124   wt.% K_2O. For the EH starting material, we used the silicate composition of the Indarch

125   meteorite (McCoy et al., 1999; Berthet et al., 2009).

126   Silicate compositions were produced from high-purity oxides and carbonates.

127   Mixtures were decarbonated at 900 °C for 10 hours. The reagents were then mixed under

128   ethanol. Silicate compositions were mixed with metallic and sulfide materials produced with

129   FeS, S and Fe in different proportions (Table 1). For the sulfur source, we used FeS, FeS + S

130   or S because CaS was not stable during preparation of the starting materials. We used several

131   combinations of the silicate/metal/sulfide mixture (Table 1; Supplementary Dataset 1). The

132   total Fe content in our experiments ranges from 15-25 wt.%, which is lower than the bulk Fe

133   content of the planet (~ 65 wt.%; Hauck et al., 2013) and higher than the Fe content of

134   Mercurian lavas (0-2 wt.%; Weider et al., 2014).

135   The intrinsic oxygen fugacity (fO_2) of the samples was reduced by adding Si metal

136   powder to the silicate starting material (Berthet et al., 2009; Cartier et al., 2014a; Malavergne

137   et al., 2014). In most experiments, we varied the Si/SiO_2 ratio (0-0.5) in order to control fO_2

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138 without affecting cation ratios of the starting compositions. In other experiments, we added

139 additional Si (total of 20 and 50 wt.% Si) to reach highly reducing conditions.

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141 2.2. Experiments, analytical methods and oxygen fugacity

142 Low- pressure (1 bar) experiments were performed in a Gero gas-mixing furnace in evacuated

143 silica tubes at the University of Hannover. Medium-pressure experiments (0.1−0.3 GPa) were

144 performed in large volume internally heated pressure vessels (IHPV) at the University of

145 Hannover (Germany). Argon was used as the pressure medium. High-pressure experiments (1

146 to 4 GPa) were performed at the Bayerisches Geoinstitut (BGI; Germany) in 0.5" piston

147 cylinder apparatuses. A comprehensive description of the experimental methods and

148 conditions with details of temperature and pressure calibration and run procedures is included

149 in the Experimental Methods Online (Appendix and Supplementary Dataset 1). Experiments

150 were run for 4-8 hours, which was shown to be ideal to reach equilibrium and to avoid

151 significant oxidation of metal Si (Vander Kaaden and McCubbin, 2016).

152 Quantitative analyses were performed using a CAMECA SX100 electron microprobe

153 analyser (EMPA) at the University of Hannover (see details in Appendix). Repeated analyses

154 of international standards and standard deviations of measurements for our experimental

155 products indicate errors of less than 5 % for major elements and 10 % for minor elements.

156 Errors on sulfur concentrations in silicate melts are more difficult to estimate because no glass

157 standard with high S content exists. Accurate calibrations on pyrite and the high

158 reproducibility of our measurements suggest errors of less than 10 %. Raman spectroscopy

159 was performed with a confocal Bruker Senterra micro-Raman spectrometer equipped with an

160 Olympus BX 51 microscope and an Andor DU420-OE CCD camera. The spot size for

161 analyses was ~1 μm.

162 The presence of silicate melt (*Sil*) and Fe-rich metallic melt (*Met*) in most of our

163 experiments constrain the intrinsic fO_2 of the experiment by the equilibrium:

164 $Fe^{Met} + 1/2O_2 = FeO^{Sil}$ (Eq. 1)

165   For most experiments, the FeO content of the silicate melt is too low (< 0.1 wt.%) to be

166   accurately measured by EMPA and the activity coefficient of FeO in the silicate melt is

167   poorly estimated in FeO-poor magmas (Wykes et al., 2015). We have therefore calculated the

168   fO_2 of the experiments using the following equilibrium (Cartier et al., 2014a):

169   $Si^{Met} + O_2 = SiO_2^{Sil}$ (Eq. 2)

170   A comprehensive description of the method of calculation is given in Appendix. Errors on

171   calculated oxygen fugacity (Fig. 2) take into account the 1σ standard deviation of repeated

172   measurements (silicate melt and metal melt). Absolute errors are estimated using

173   thermodynamic properties of the elements and oxides involved in Eq. 2 (Robie and

174   Hemingway, 1995) and are lower than 0.5 log unit.

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176   **3. Experimental results**

177   3.1. Phase assemblages and microstructures

178   All experiments show a multi-component assemblage dominated by quenched silicate melt

179   (X_{Sil}: 0.51−0.88), sulfide melt (X_{Sul}: 0.01−0.42) and metallic melt (X_{Met}: 0−0.26; Fig. 2a;

180   Supplementary Dataset 1), where X_{Sil}, X_{Sul} and X_{Met} are the weight fractions of the different

181   melts. Subliquidus experiments also show silicate minerals. In most experiments, forsterite is

182   the liquidus phase (Fig. 2b) while enstatite is observed in some high-pressure experiments ($\geq$

183   2 GPa; Fig. 2a) and in medium-pressure (0.1−0.3 GPa) experiments performed on the Na-free

184   NVP composition (Fig. 2c). In the silicate fraction of the experiments, the proportion of

185   silicate melt ranges from 0.78 to 1.00 wt.%, while the forsterite and enstatite proportions

186   range from 0−0.22 wt.% and 0−0.14 wt.%, respectively. Except in some high-pressure

187   experiments, no quench microstructure is observed in the silicate melt.

188   Enstatite and forsterite form homogeneous, unzoned, euhedral crystals with sizes

189   ranging from 5 to 500 μm (Figs 2a and b). They are homogeneously distributed in the low- to

190   medium-pressure experimental charges while they are usually observed along the edges of the

191   capsule in piston cylinder experiments. Quenched metal and sulfide melts generally form

192   large (50 to 500 μm), sub-spherical globules attesting that they represent quenched melt

193   droplets formed at high temperature. They are very often distributed along the sides of the

194   experimental capsule although abundant sulfide and metal droplets are also observed in the

195   central part of the samples. In many experiments, we observe large-size (> 100 μm)

196   composite globules with a core made of metallic melt and a rim dominated by sulfide melt

197   (Fig. 2a), which coexist with smaller globules of sulfide or metal melt. In highly reducing

198   experiments (e.g. IW-6 to IW-9), we also observe the presence of Mg- and Ca-rich sulfide

199   melts forming large pools (Fig. 2d). In contrast to silicate melts, sulfide melts usually show

200   μm-scale tablet- or lamella-shaped quench microstructures which appear to be Fe-, Mn-, Cr-

201   bearing monosulfide crystals. Submicrometric globules of metallic melt, and possibly sulfide

202   melts, are also commonly observed. In addition to the presence of large metal and sulfide

203   globules, some experiments (especially in IHPV) show abundant submicrometric globules of

204   metallic melt homogeneously distributed in the silicate melt. We interpret these small

205   globules as the result of inefficient coarsening of the metal globules (Ertel et al., 2006;

206   Malavergne et al., 2016).

207

208   3.2. Major element compositions of the experiments and sulfur concentration in silicate melts

209   In the following, we present the compositions of the phases obtained in the experimental runs.

210   We express the chemical analyses of silicate melts as cations (wt.%) rather than as oxides

211   because under highly reducing conditions sulfur replaces oxygen in the silicate melt structure

212   (O'Neill and Mavrogenes, 2002). In the less reduced super-liquidus or near-liquidus

213   experiments, the major element compositions of the silicate melts (Supplementary Dataset 2;

214   Supplementary Fig. S1) are relatively similar to those of starting silicate compositions (Table

215   1). Under more reduced conditions, the presence of abundant sulfur in the silicate melt dilutes

216   all major elements compared to the starting compositions but cation ratios remain relatively

217   constant. In sub-liquidus experiments, the crystallization of forsterite or enstatite changes the

218   composition of the residual silicate melts by decreasing the Mg content (e.g. 7 to 3 wt.% from

219   1310 to 1200 °C for the NVP composition) and increasing the Si content (26 to 30 wt.% from

220   1310 to 1200 °C). In the most reducing experiments (IW-6 to IW-9), the formation of

221   (Mg,Ca,Fe)S sulfide melt globules (see below) also affects the Ca and Mg contents of the

222   silicate melts. With increasing reducing conditions, Fe decreases from 6.57 wt.% to 0.01 wt.%

223   in the silicate melt, with most experiments having Fe contents below 0.5 wt.%. Calculated

224   oxygen contents decrease from 50 to 39 wt.% in the silicate liquid. Three experiments show

225   silicate melts with remarkably high Si contents (> 35 wt.%) and correspond to the

226   experiments in which the highest amounts of Si metal were added to the starting materials.

227   This indicates partial oxidation of metal Si during some experiments (Vander Kaaden and

228   McCubbin, 2016). Mineral compositions match forsterite and enstatite endmembers.

229   The sulfur content at sulfide saturation (SCSS) in silicate melts is shown and

230   compared with relevant literature data in Fig. 3a. Depending on fO_2 conditions, pressure and

231   temperature, S in silicate melts ranges from < 0.5 wt.% to ~ 18 wt.%. There is an obvious

232   increase of SCSS with decreasing fO_2. For experiments performed in a restricted range of

233   temperature (e.g. 1350−1500 °C), SCSS increases from < 0.5 wt.% to 13 wt.% from IW-1.5

234   to IW-8.5. An identical effect is observed by Chabot et al. (2014) in experiments performed at

235   1500 °C and a pressure of 1 bar. At any given oxygen fugacity, SCSS also increases with

236   temperature. This effect becomes stronger with decreasing fO_2. At fO_2 conditions < IW-6,

237   SCSS increases by a factor of 3 between experiments < 1350 °C and experiments > 1500 °C.

238   This magnitude is identical to that observed in previous experiments (Vander Kaaden and

239   McCubbin, 2015a). The effect of pressure on SCSS is more difficult to assess because high-

240   pressure experiments also correspond to the experiments performed at the highest

241   temperatures, which makes it difficult to isolate the individual effect of these two parameters.

242   The effect of the silicate melt composition (Fig. S1) is more subtle and will be discussed and

243   modeled below. Overall, our new experiments reproduce data from previous studies (McCoy

244   et al., 1999; Berthet et al., 2009; Malavergne et al., 2014), but they significantly expand the

245   investigated range of fO_2, temperature, pressure and melt compositions. Unlike previous

246   studies, we produced silicate melts with > 10 wt.% S. Such high S concentrations have not

247   been described yet in complex, multi-component, silicate melts but were experimentally

248   produced in simplified systems (e.g. diopside melt; Vander Kaaden and McCubbin, 2015a).

249   The metallic phase in equilibrium with the silicate melt is dominated by Fe (69−100

250   wt.%), Si (0−29 wt.%), with minor Cr (0−3 wt.%) and Ni (0−8 wt.%; Fig. 3b). Although

251   compositional variability was observed in some experiments, a single, homogeneous, metallic

252   melt is observed in most experiments. The sulfur content of the metal melt is low and

253   decreases continuously with fO_2 from ~ 2.2 wt.% at IW-3.5 to 0 wt.% at IW-9, leading to a

254   decrease of $D_S^{Met/Sil}$ from ~ 2.5 to 0.01. In the most oxidized experiments (> IW-2.5), we

255   observe higher $D_S^{Met/Sil}$ values (5−20). The totals in the metallic phase increase from 94 to

256   100 % with increasing Si content (and decreasing S content) suggesting a lower concentration

257   of dissolved carbon (Li et al., 2015). The sulfide phase observed in the majority of our

258   experiments is dominated by Fe (54−69 wt.%) and S (27−39 wt.%), with minor Ti (0.0−4.5

259   wt.%), Mn (0.0−2.3 wt.%), Mg (0.0−4.1 wt.%), Ca (0.0−2.8 wt.%), Cr (0.1−3.2 wt.%) and

260   Ni (0.0−3.0 wt.%), and has a Fe/S ratio close to 1 ($Fe_{0.91}S_{1.09}$ to $Fe_{1.13}S_{0.87}$; average $Fe_{1.0}S_{1.0}$).

261   Part of this compositional variability is attributed to the formation of quench phases and

262   formation of monosulfide crystals. Some experiments show a second sulfide melt with lower

263   Fe content (10−33 wt.%) but higher Mg (7−30 wt.%), Mn (0−10 wt.%), Ca (2−35 wt.%) and

264   S (38−49 wt.%) concentrations and an average composition of $(Fe_{0.25}Mn_{0.03}Mg_{0.60}Ca_{0.14})S_{0.98}$.

265

266   3.3. Sulfur speciation in silicate melts

267   Raman spectra (see analytical details in Appendix) in quenched FeS sulfide melts show very

268   low intensity with dominant peaks at 310 and 360 cm^{-1} (Fe-S vibration). Spectra in

269   (Fe,Mg,Ca)S sulfide globules are significantly more intense with higher signal-to-noise ratios

270   (Fig. 4a). They display a major peak at 285 cm^{-1} and a prominent shoulder at 350 cm^{-1}. With

271   increasing (Mg+Ca)/Fe ratio, a peak at 210 cm^{-1} progressively appears. Similar peak positions

272 were identified in oldhamite (CaS) and niningerite ((Mg,Fe)S; Avril et al., 2013). Raman

273 spectra in silicate melts were acquired with a 1 μm spot and care was taken to avoid

274 contamination from micro-nuggets of sulfide and metal melts or crystals. Raman spectra show

275 a major peak at ~480 cm^{-1} and broad peaks at ~750 cm^{-1} and ~1050 cm^{-1} which are assigned

276 to symmetric stretching vibrations of Si-O-Si (McMillan and Wolf, 1995). Sulfur in silicate

277 melt generally forms complexes with Fe^{2+} (O'Neill and Mavrogenes, 2002) which is shown

278 by Raman vibration peaks occurring at ~ 360 cm^{-1}. However, with increasing sulfur content in

279 the silicate glass, we observe the appearance of increasingly intense peaks at 285 cm^{-1} and

280 350 cm^{-1} (Fig. 4b). The positions of these two peaks are identical to those observed in

281 (Fe,Mg,Ca)S sulfide globules. In our experiments where the sulfur content of the glasses

282 significantly exceeds the total amount of Fe^{2+}, we interpret these peaks as an evidence for the

283 formation of MgS and CaS complexes in reducing silicate melts. This is in agreement with

284 previous studies on S-bearing melts at reducing conditions (Fogel, 2005; Métrich et al., 2009).

285

286 **4. Modeling sulfur solubility in silicate melts**

287 Several predictive models of SCSS in silicate melts have been previously published and allow

288 prediction of SCSS in magmas relevant to the Earth or Mars (Holzheid and Grove, 2002; Li

289 and Ripley, 2005; Righter et al., 2009; Ding et al., 2014). These models do not reproduce our

290 experimental results (Supplementary Fig. S2) because they were calibrated on the basis of

291 oxidized experiments only. The new model of Malavergne et al. (2014) was designed to

292 estimate SCSS in reducing magmas. It was, however, calibrated on a very limited number of

293 experiments and is not accurate enough to reproduce our data, possibly due to the smaller

294 ranges of composition, temperature and pressure used in their calibration dataset. The recent

295 thermodynamic expression of Wykes et al. (2015) captures extremely well the important

296 effect of FeO (controlled by fO_2 during silicate-metal equilibration; Gaillard and Scaillet,

297 2009) on SCSS and therefore predicts the high SCSS observed for most of our experiments. A

298 robust application of this model is unfortunately hampered by its extreme sensitivity to minor

299 changes of the melt FeO content which are unconstrained for Mercurian magmas (Weider et

300   al., 2014). There is therefore a need for a new, accurate, predictive model of SCSS, calibrated

301   over a large range of pressure, temperature, melt compositions and fO_2, which can be used to

302   model the sulfur behavior in Mercurian magmas.

303   At reducing conditions (< IW+3), sulfur (S^{2-}) replaces oxygen (O^{2-}) on the anion

304   sublattice of the silicate melt following the expression (O'Neill and Mavrogenes, 2002):

305     $O^{2-} + \frac{1}{2}S_2 = S^{2-} + \frac{1}{2}O_2$ (Eq. 3)

306   The equilibrium constant of Eq. 3 can be described as:

307     $lnK_{(3)} = lna_{S^{2-}}^{Sil} + \frac{1}{2}fO_2 - \frac{1}{2}fS_2 - lna_{SO^{2-}}^{Sil}$ (Eq. 4)

308   where a is the activity of O^{2-} or S^{2-}. The abundance of O^{2-} anions in silicate melts is high and

309   Eq. 4 can therefore be simplified as follows:

310     $ln[Swt.\%]_{SCSS} = lnC_S + \frac{1}{2}ln\left(\frac{fO_2}{fS_2}\right)$ (Eq. 5)

311   where S_{SCSS} is the sulfur content of the silicate melt at sulfide saturation and C_S is a

312   pseudoequilibrium constant (sulfide capacity) controlled by silicate liquid composition

313   (Haughton et al., 1974; O'Neill and Mavrogenes, 2002):

314     $lnC_S = A_o + \sum A_i X_i$ (Eq. 6)

315   where X is the mole fraction of cation i and A are regression coefficients. Combining Eq. 5

316   and Eq. 6 indicates that the sulfur content in the silicate melt at sulfide saturation (Eq. 5) is a

317   function of melt composition, fO_2 and fS_2, the last two parameters being partly controlled by

318   pressure and temperature.

319   The equilibrium between a silicate melt and a sulfide phase (solid or liquid) can be

320   described by:

321     $MO^{Sil} + \frac{1}{2}S_2 = MS^{Sul} + \frac{1}{2}O_2$ (Eq. 7)

322   Our experiments contain a silicate melt in equilibrium with a sulfide melt, which is either FeS

323   and/or (Fe,Mg,Ca)S. The cation M in Eq. 7 can therefore be Fe, Ca or Mg. The equilibrium

324   constant of Eq. 7 can be expressed as:

325     $\frac{-\Delta G^0(7)}{RT} = lna_{MS}^{Sul} - lna_{MO}^{Sil} + \frac{1}{2}lnfO_2 - \frac{1}{2}lnfS_2$ (Eq. 8)

326   for which ΔG^0 is the Gibbs free energy of reaction. Combining Eq. 5 and Eq. 8 allows

327   calculating SCSS:

328    $ln[S wt.\%]_{SCSS} = \frac{-\Delta G^0(7)}{RT} + lnC_S + lna_{MS}^{Sul} - lna_{MO}^{Sil}$ (Eq. 9)

329   Equation 9 cannot be readily applied to our experiments and to Mercurian magmas in general

330   for several reasons: (1) the relationship between C_S and melt composition (Eq. 6) was only

331   calibrated for simplified systems and FeO-rich terrestrial basalts (Haughton et al., 1974;

332   O'Neill and Mavrogenes, 2002); (2) a robust application of Eq. 9 not only requires an

333   accurate determination of silicate melt compositions but also expressions accounting for the

334   evolution of the activity coefficients (γ) of divalent cation under highly reducing conditions.

335   There is currently not enough information to predict the effect of melt composition and fO_2 on

336   these coefficients (O'Neill and Eggins, 2002; Toplis, 2005); (3) Eq. 9 requires an independent

337   knowledge of the composition of sulfide melts (lna_{MS}^{Sul}) in equilibrium with the magma.

338   Mercurian basalts show a correlation between S, Ca and Mg, possibly indicating the presence

339   of (Mg,Ca,Fe)S sulfide melts (Malavergne et al., 2014) for which activities of the various

340   components cannot be calculated.

341   Given the impossibility of using Eq. 9 to model the behavior of sulfur in Mercurian

342   magmas, we developed a new thermodynamically inspired empirical model to predict SCSS

343   in FeO-poor magmas. We used an equation with a form similar to that of recent models of

344   SCSS (Li and Ripley, 2005; Righter et al., 2009; Ding et al., 2015). We replaced the Gibbs

345   free energy term of Eq. 9 by two terms taking into account pressure and temperature. The C_S

346   term is replaced by several terms accounting for liquid composition. For these compositional

347   terms, we used molar fractions normalized to SiO_2. This takes into account the degree of

348   polymerization of the melt, which plays a role on SCSS (Holzheid and Grove, 2002), and also

349   reduces the errors when applying the model to Mercurian magmas for which elemental ratios

350   (normalized to Si) were measured by MESSENGER. In theory, SCSS could be adequately

351   modeled independently of fO_2 because S in both the silicate melt and the sulfide melt is

352   present as S^{2-}. In that case, SCSS is controlled by the FeO content of the silicate melt (Wykes

353   et al., 2015) and sulfide saturation is not a redox reaction. However in a reduced system,

354   estimating SCSS requires an accurate estimate of the melt FeO content and the activity

355   coefficients at very low FeO concentrations (O'Neill and Mavrogenes, 2002; Gaillard and

356   Scaillet, 2009; Wykes et al., 2015), which is problematic. We therefore replaced the term

357   lna_{FeO}^{Sil} (Eq. 9) by $logfO_2$, which controls the FeO content of a silicate melt in equilibrium

358   with metallic melt (Gaillard et al., 2009; Zolotov et al., 2013) and exerts a major control on

359   SCSS (Wykes et al., 2015). For our experiments which contain a metal phase in which sulfur

360   dissolves as S^0, the use of a fO_2 term is appropriate. However, care must be taken when

361   applying this model to natural, magmatic systems which may not contain a metal phase. By

362   stepwise multiple-linear regression, we obtained the following expression for SCSS:

363    $$ln[S wt.\%]_{SCSS} = a + \frac{b}{T} + \frac{cP}{T} + d logfO_2 + \sum e_i \frac{X_i}{X_{SiO_2}}$$ (Eq. 10)

364   where S is the sulfur content at sulfide saturation, T is temperature (K), P is pressure (bar),

365   fO_2 is the oxygen fugacity (bar) and X_i are the mole fractions of oxides in the melt

366   recalculated to a total of 100% on a sulfur-free basis. We ran several statistical tests and only

367   kept statistically significant terms (X_i) in the regression. Coefficients of regression and details

368   on uncertainties are described in Table 2. The individual effects of pressure, temperature, fO_2

369   and melt compositions cannot be easily determined from Eq. 10 because these parameters are

370   strongly correlated. However, it appears that fO_2 and temperature exert the main control on

371   SCSS. We also calculate a minor positive effect of pressure on SCSS. This is in agreement

372   with previous experimental studies (Malavergne et al., 2014) and confirms that the effect of

373   temperature on SCSS is slightly dependent on pressure (Vander Kaaden and McCubbin,

374   2015a).

375

376   **5. Discussion**

377   Our experiments and new parameterization of SCSS allow us to track the behavior of sulfur

378   during the magmatic history of Mercury. Assuming that Mercury differentiated through the

379   formation of a magma ocean (Brown and Elkins-Tanton, 2009; Charlier et al., 2013; Chabot

14

380   et al., 2014), early differentiation of the planet did set the sulfur content of the core and the

381   lherzolitic mantle. Partial melting of the mantle then produced the secondary crust (Weider et

382   al., 2015; Namur et al., 2016). In the following, we discuss the mechanism of sulfur migration

383   from the Mercurian mantle to the crust. We then consider that the oxygen fugacity conditions

384   during accretion and differentiation of the planet did set the activity of FeO content of the

385   mantle during mantle-core equilibration. We therefore used the sulfur content of Mercurian

386   lavas together with our expression of SCSS (Eq. 10) to calculate the oxygen fugacity

387   conditions of their mantle source regions. The use of Eq. 10 is appropriate because some

388   surface melts were produced at the mantle-core interface indicating that the mantle source

389   was metal saturated (Namur et al., 2016) and Mercurian lavas contain some Fe, possibly

390   included in Fe-silicides (Weider et al., 2014). We finally discuss the likely distribution of

391   sulfur between the core and mantle on Mercury.

392

393   5.1. Transport of sulfur from the mantle to the Mercurian surface

394   An important question about Mercurian lavas concerns the origin of their high sulfur

395   concentrations. Our experiments suggest that they could simply be explained by high SCSS

396   under reducing conditions. However, they could also result from accumulation of sulfides

397   transported as sulfide globules during flow of silicate melt from the mantle to the surface of

398   the planet (Malavergne et al., 2014). During mantle melting on Earth, it is commonly

399   assumed that sulfide melts (FeS) stay in the mantle restite. This is partly because they form

400   isolated droplets at four-grain junctions (Holzheid et al., 2000) but also because of the large

401   density contrast between silicate melts (2.75 g/cm^3; Sparks et al., 1980), mantle rocks (3.5

402   g/cm^3; Shorttle et al., 2014) and FeS melts (4.5 g/cm^3; Mungall and Su, 2005). Most of the

403   experiments presented in this study show equilibrium between a silicate melt and an

404   immiscible sulfide dominated by FeS. However, in our most reducing experiments, the sulfide

405   melt contains a significant proportion of Mg, Ca as well as a variable proportion of Fe (Fig.

406   3b). This is important for the magmatic history of Mercury because of the small density

407   contrast between (Mg,Ca)S melts (2.6 g/cm^3), the mantle rocks (3.0-3.2 g/cm^3;

408   Supplementary Fig. S3; Hauck et al., 2013) and the primary mantle-derived silicate melts (<

409   2.7 g/cm^3; Supplementary Fig. S3; Vander Kaaden and McCubbin, 2015b). However, even

410   for such a low density contrast, the capillary pressure imposed by reducing the radius of

411   curvature of a sulfide droplet (10^4 Pa) still strongly exceeds the buoyancy force for sulfide

412   melt migration (< 10 Pa; calculated using Mercurian gravity; Mungall and Su, 2005) in a

413   typical lherzolite. This makes segregation of sulfide droplets quantitatively impossible. With

414   increasing degree of mantle melting, the capillary pressure decreases and sulfide melt droplets

415   eventually become mobile. This however requires a degree of melting exceeding 40 vol.%

416   (Holzheid et al., 2000), which is higher than the melt fraction needed to produce the S-rich

417   lavas from NVP, SP and IcP-HCT (Namur et al., 2016). In addition, coalescence of sulfide

418   droplets through Ostwald ripening would require extremely low abundances of sulfides and a

419   mantle with unrealistically large (cm-scale) crystals before sulfide melts become effectively

420   mobile (Mungall and Su, 2005).

421   Our calculations and physical arguments presented above therefore suggest that

422   Mercurian lavas did not carry sulfide melts or sulfide minerals during their ascent from the

423   mantle source regions to the surface of the planet. This implies that their high sulfur content is

424   related to high sulfur solubility in the mafic magma, which probably explains the absence of

425   spectral evidence for a sulfide phase at the Mercurian surface (McClintock et al., 2008;

426   Izenberg et al., 2014).

427

428   5.2. Oxygen fugacity conditions during mantle melting and basaltic eruptions

429   It was suggested that Mercurian lavas were in equilibrium with a sulfide-bearing lherzolite

430   when they left their mantle source regions (Zolotov et al., 2013; Malavergne et al., 2014).

431   This implies that sulfide minerals were not entirely exhausted during the partial melting

432   process. This is in qualitative agreement with chemical data from MESSENGER (Weider et

433   al., 2015) which show that rocks from the HMg terrane, which require the highest degree of

434   mantle melting (> 40 %), are not depleted in sulfur compared to lavas from IcP-HCT (< 35 %

435   of melting), SP and NVP (< 30 % of melting; Namur et al., 2016; Vander Kaaden and

436 McCubbin, 2016). It is therefore reasonable to assume that Mercurian lavas were still at

437 sulfide saturation when they erupted at the surface of the planet. Their sulfur content can be

438 used to estimate the redox conditions of their mantle source regions using Eq. 10 assuming

439 that the mantle contain a metal phase (Weider et al., 2015). Even in the absence of metal in

440 the Mercurian mantle, this treatment is valid because the fO_2 conditions during mantle-core

441 equilibration did set the low FeO content of the mantle and therefore the high SCSS in mantle

442 melts (Gaillard and Scaillet, 2009; Wykes et al., 2015).

443 We calculated the compositions of Mercurian surface magmas using the most recent

444 maps produced from MESSENGER XRS data (Weider et al., 2015). We focused on the

445 northern hemisphere for which the spatial resolution of MESSENGER measurements is the

446 highest. We combined individual maps of Mg/Si, Ca/Si, Al/Si and S/Si and only worked on

447 pixels for which those 4 ratios were measured (Supplementary Fig. S4). This method allows

448 investigating only some parts of the northern hemisphere because the Ca/Si and S/Si maps are

449 incomplete. We produced > 49000 groups of 4 pixels (0.5° latitude x 0.5° longitude) that we

450 converted to chemical compositions (SiO_2, Al_2O_3, MgO, CaO and S). Each pixel group was

451 assigned to a geochemical terrane (NVP, SP, IcP-HCT and HMg; Peplowski et al., 2015). We

452 considered that NVP lavas have high Na_2O contents (Na/Si: 0.20; ~7 wt.% Na_2O), SP lavas

453 have intermediate Na_2O contents (Na/Si: 0.14; ~5 wt.% Na_2O) and IcP-HCT and HMg lavas

454 have lower Na_2O contents (Na/Si: 0.06; ~2 wt.%Na_2O; Peplowski et al., 2014). The

455 calculated sulfur content of Mercurian basalts is variable but generally high. It averages

456 2.54±0.41 wt.% in the High Mg terrane and 1.92±0.41 wt.% in IcP-HCT lavas, but is lower in

457 SP (1.71±0.33 wt.%) and NVP (1.64±0.43 wt.%) lavas (Fig. 6).

458 For each pixel group, we calculated a volatile-free composition (Supplementary Fig.

459 S4) and estimated the 1-bar liquidus temperature of each magma (Supplementary Fig. S5).

460 We then iteratively estimated SCSS for fO_2 conditions between IW and IW-8. Results were

461 finally compared to the actual sulfur content of each composition to extract the fO_2 conditions

462 during eruption of these basalts (Fig. 7). We estimate that Mercurian magmas were produced

463 at fO_2 conditions ranging from IW- 3.4 to IW-6.6 (error map in Supplementary Fig. S6). This

range is relatively similar to that obtained based on the Fe-content of Mercurian basalts

(McCubbin et al., 2012) but our new data show that a large majority of Mercurian magmas

were produced in a more restricted range of fO_2 conditions (IW-5.4±0.4). The average fO_2 is

furthermore relatively similar for the various geochemical provinces of Mercury.

Nevertheless, lavas from the NVP show a relatively large variability of fO_2. The region

between 180−290°E and 50−85°N shows the most reducing conditions of the northern

hemisphere, while the region between 15-70°E and 40−55°N shows the most oxidizing

conditions. Although this could be explained by melting mantle source regions which are

heterogeneous in terms of intrinsic fO_2 conditions, other explanations cannot be ruled out: (1)

highly reducing conditions could be an artifact due to high S concentrations originating from

thermal migration of sulfur from the equator to the poles of Mercury (Sprague et al., 1995);

(2) the oxidizing conditions could also be an artifact due to low S concentrations originating

from S volatilization during impacts (Nittler et al., 2001; Arai et al., 2008), sulfur degassing

during volcanic eruptions (Righter et al., 2009; Nittler et al., 2014; Weider et al., 2016) or

sulfur loss during thermal decomposition of sulfide phases (Helbert et al., 2013; Blewett et

al., 2013). However, we note that these regions with less sulfur do not show a higher than

average crater density (Weider et al., 2015) and sulfur degassing at reducing conditions is

minimal because sulfur is more stable in the melt phase than in the gas (Gaillard and Scaillet,

2009).

5.3. Sulfur content of the mantle and the core

Our new constraints on oxygen fugacity in Mercury's interior can be used to estimate the bulk

sulfur content of the Mercurian primordial mantle and the core. We made the assumption that

Mercury formed by accretion of metal-rich chondritic building blocks (enstatite chondrites

and/or bencubbinite chondrites; Malavergne et al., 2010, 2014; Zolotov et al., 2013). We used

average sulfide modes (10.0±2.50 wt.%; Jarosewich, 1990; Javoy et al., 2010) and

compositions (~ FeS with 37.0±1.5 wt.% S; Javoy et al., 2010) in EH and CB meteorites and

calculated that Mercury may contain 2.7−4.6 wt.% S with the highest probability lying in the

range of 3.8±0.5 wt.% S. The exact nature of Mercurian building blocks is however

unimportant for the following discussion because all chondritic materials have high S content

(∼ 2-5 wt.% S; Fig. 1). We considered that the bulk Fe content of the planet (mostly in the

core) is 65±5 wt.% (Hauck et al., 2013) and that the mantle is 420±30 km thick (mantle-core

boundary at 5 GPa; Padovan et al., 2015). We used a single-stage core formation model

(Rubie et al., 2003; Walter and Cottrell, 2013) in which the sulfur content of the various

reservoirs is set by metal-silicate equilibration at the bottom of the magma ocean (Corgne et

al., 2009; Chabot et al., 2014). We estimated that the liquidus temperature of the S-free

magma ocean was 1900±25 °C at 5 GPa (Namur et al., 2016). Using Eq. 10, we calculated the

maximum sulfur content that can be dissolved in the silicate magma ocean (SCSS) and

iteratively recalculated the liquidus temperature by considering a liquidus depression of 10

°C/wt.% S (Namur et al., 2016). We also used the experimental database from Boujibar et al.

(2014) and metal melt compositions in experiments at 5 GPa from Cartier et al. (2014a) to

estimate $D_S^{Met/Sil}$ (0.05-2.90) for the fO_2 range of Mercury's interior. These values are in

agreement with those reported by Gaillard et al. (2013).

Within the possible range of fO_2 for Mercury's interior (IW-3.5 to IW-6.5; Fig. 7), the

primordial Mercurian mantle may have contained 2−12 wt.% S (Fig. 8a). However, results

from Fig. 7 show that Mercury probably differentiated at IW-5.4±0.4. Within this more

restricted fO_2 range, the sulfur content of the Mercurian mantle must be between 7 and 11

wt.%. For a bulk sulfur concentration of ∼ 4 wt.% for the planet, the primordial mantle would

contain 8−9 wt.% S. For most of the fO_2 conditions investigated in Fig. 8a, a significant

amount of sulfur cannot be dissolved in the silicate magma ocean or in the equilibrium

metallic core. Given the presence of an immiscibility field in the Fe-Si-S system at low

pressure (< 15 GPa; Morard and Katsura, 2010), we considered that the excess sulfur formed

an immiscible FeS melt at the mantle-core boundary. The presence of 200 km-thick solid FeS

layer has been initially proposed by Smith et al. (2012) to account for the moment of inertia

518 parameters of Mercury. This interpretation has been revisited by Hauck et al. (2013) who

519 suggested that such a solid layer is not required to explain the geophysical properties of

520 Mercury. However, experimental constraints (Chabot et al., 2014; Malavergne et al., 2014)

521 indicate that sulfur not dissolving into the metallic core or the silicate mantle will form a FeS

522 layer at the mantle-core interface. We calculate that the thickness of this sulfide layer is likely

523 to be smaller than 90 km (Fig. 8b) or even lower than 40 km if Mercury's bulk S content is ~

524 4 wt.%. Our approach however does not bring any constraint on the present physical state

525 (solid or liquid) of the FeS layer. Future investigations of the physical properties of Mercury

526 using results from MESSENGER and BepiColombo will be useful to refine our new

527 calculations on core structure and composition.

528

529 **6. Conclusions**

530 Our new experiments on compositions relevant to Mercury allow us to draw a few key

531 conclusions:

532   1. Under reducing conditions, sulfur dissolves as S^{2-} in the silicate melt and forms

533   complexes with Fe^{2+}, Ca^{2+} and Mg^{2+}. The sulfur concentration at sulfide saturation

534   (SCSS) in the silicate melts strongly increases with reducing conditions and

535   increasing temperature.

536   2. The composition of a sulfide melt in equilibrium with the silicate melt is dominated

537   by a FeS component at fO_2 conditions from IW to IW-6. At more reducing conditions

538   (< IW-6), under which the FeO content of the silicate melts approaches 0, the

539   equilibrium sulfide melt is dominated by (Mg,Ca,Fe)S, ± FeS.

540   3. A new parameterization of SCSS in silicate melts relevant to Mercurian magmas is

541   proposed. SCSS can be adequately modeled with an expression taking into account

542   temperature and oxygen fugacity, which controls the melt FeO content.

543 We applied our experimental results to constrain the distribution of S in the different

544 reservoirs of Mercury and to decipher the oxygen fugacity of the Mercurian mantle. We

545 suggest that the S concentrations observed at the surface of Mercury were transported as

546   dissolved S^{2-} in silicate melts. We also estimated that Mercurian lavas were produced in

547   mantle source regions having intrinsic oxygen fugacity conditions ranging from IW-3.5 to

548   IW-6.5. However, a large majority of the chemical compositions (> 75%) can be explained by

549   a much narrower range of oxygen fugacity (IW-5.4±0.4). Using these new constraints, we

550   calculated that the primordial mantle of Mercury probably contains 7 to 11 wt.% S and that

551   the core is layered. We suggest that it is made up of a large S-poor (~ 1 wt.% S) internal

552   metallic (FeSi) core surrounded by a thin (< 90 km) FeS layer.

553

563

564   **8. References**

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784

Figure captions

786 Figure 1: Sulfur concentrations in the Mercurian crust, chondrites, achondrites, silicate

787   mantles and crusts of terrestrial planets and primary mantle derived melts. Symbols

788   show average concentrations and vertical bars show the 1σ standard deviations. The

789   data for the Mercurian crust were calculated using the MESSENGER data presented

790   by Weider et al. (2015). The complete list of references and number of analyses used

791   in the compilation are given in Appendix. C = Carbonaceous; Chond. = chondrite;

792   Cont. = continental.

793 Figure 2: Back-scattered electron images of experimental products. A. Run A707; 1560 °C; 2

794   GPa. Sulfide melt is observed around droplets of metallic melt. Note the presence of

795   quench crystals in the sulfide melts. Enstatite forms large crystals on the edges of the

796   experimental charge. B. RY-14-1; 1250 °C; 0.3 GPa. Forsterite forms small crystals

797   disseminated in the quenched silicate melt. Note the presence of micro globules

798   (nuggets) of metal (FeSi alloy) in this experiment performed in IHPV. C. RY-10;

799   1250 °C; 0.3 GPa. Enstatite forms small and large crystals disseminated in the silicate

800   melt. Note the presence of micro globules (nuggets) of metal (IHPV experiment). D.

801   Y030-1; 1420 °C; 0.1 GPa. Note the presence of (Mg,Ca,Fe)S globules in a matrix of

802   FeS melt. Sil = silicate; Sul = sulfide; Ens = enstatite; Fo = forsterite.

803 Figure 3: A. Sulfur concentration in experimental silicate melts at sulfide saturation (SCSS)

804   as a function of oxygen fugacity (ΔIW). Symbols are color-coded as a function of

805   temperature and dashed curves show the best fits for S (wt.%) vs. ΔIW for

806   temperatures below 1350 °C, between 1350 °C and 1500 °C and above 1500 °C.

807   Error bars for the sulfur content are 1σ standard deviations of electron microprobe

808   measurements. Error bars for ΔIW take into account 1σ standard deviations of metal

809   melt compositions and estimated errors on pressure and temperature during

810   experiments. Absolute errors on S are estimated to be lower than 10% relative and

811   absolute errors on ΔIW are estimated to be lower than 0.5 log unit. Literature data are

812 from Mavrogenes and O'Neill (1999), McCoy et al. (1999), O'Neill and Mavrogenes

813 (2002), Malavergne et al. (2007), Berthet et al. (2009), Boujibar et al. (2014), Cartier

814 et al. (2014a,b), Chabot et al. (2014) and Malavergne et al. (2014). fO_2 of literature

815 data were recalculated using the equations described in Supplementary Material. B.

816 Fe - Si+S - Ca+Mg ternary diagram showing the composition of the metal melts and

817 sulfide melts produced in this study. Symbols are color-coded as a function of oxygen

818 fugacity (ΔIW). Note that (Mg,Ca,Fe)S liquids are only observed in the most reducing

819 experiments.

820 Figure 4: A. Raman spectra of experimental (Mg,Ca,Fe)S metal melts. Spectra are color-

821 coded as a function of the Fe/(Mg+Ca) ratio. Experiments were performed at

822 temperatures between 1310 and 1560 °C, 0.1 GPa and fO_2 conditions between IW-7.0

823 and IW-8.4. The vertical dashed lines show the position of Raman peaks observed

824 and calculated in natural and synthetic MgS and CaS by Avril et al. (2013). B. Raman

825 spectra of experimental quenched silicate melts. Spectra are color-coded as a function

826 of the sulfur concentration of the melt (SCSS). Experiments were performed between

827 1200 and 1560 °C, 0.1 GPa and fO_2 conditions between IW-3.6 and IW-8.4. Note the

828 appearance of increasingly intense peaks at 285 and 350 cm^{-1} with increasing sulfur

829 content in the melt. This suggests that sulfur (S^{2-}) forms complexes with Mg^{2+} and

830 Ca^{2+} in the structure of the silicate melt (O'Neill and Mavrogenes, 2002).

831 Figure 5: Modeling of sulfur concentration at sulfide saturation in silicate melts. A.

832 Calculated vs observed $\ln[S]_{SCSS}$. The model was calibrated using the experiments of

833 this study (blue symbols) only. Grey symbols are literature data, not included in the

834 calibration database, that are plotted to test the reliability of our expression. The black

835 dashed line is the line of equality (1:1) while the red line shows the slope of the linear

836 regression. Dashed blue lines show the 90% confidence interval. The green area

837 represents the result of a Monte Carlo simulation showing the robustness of the fit

838 when 1σ standard errors on melt (silicate and metal) compositions, error on pressure

839   and temperature are taken into account. The quality of the regression is given in the

840   white box on the right side of the diagram. B. Same model calibrated using the

841   experiments performed in this study and published experiments performed under

842   similar experimental conditions. See coefficients in Table 2. n = number of

843   experiments, SEE = standard error of estimates.

844   Figure 6: Histograms of calculated sulfur content (wt.%) in lavas from the different

845   geochemical provinces of Mercury. Lava compositions were calculated using the

846   most recent maps of MESSENGER measurements presented by Weider et al. (2015).

847   Black curves show kernel density distributions. Numbers in each diagram show the

848   mean ± 1σ standard deviation.

849   Figure 7: A. Map of the northern hemisphere of Mercury showing calculated conditions of

850   fO_2 during mantle melting and eruption of Mercurian basalts. Calculations are based

851   on the bulk compositions of the lavas (Weider et al., 2015), an estimate of their

852   liquidus temperatures (Supplementary Fig. S4) and the assumption that Mercurian

853   lavas were sulfide saturated when they erupted (see text for details). The thin black

854   lines represent the limits of the smooth plains as mapped by Denevi et al. (2013). B.

855   Histograms showing the distribution of fO_2 conditions calculated for each

856   geochemical province.

857   Figure 8: A. Theoretical model showing the evolution of SCSS as a function of fO_2 (ΔIW) in

858   the Mercurian magma ocean (1900±25 °C at 5 GPa; cyan curve) and the sulfur

859   content of the equilibrium metallic core (orange curve). Vertical dashed lines show

860   the most likely fO_2 conditions for Mercury's accretion and differentiation (IW-

861   5.4±0.4). We considered three potential bulk sulfur contents for Mercury (3, 4 and 5

862   wt.%), a bulk Fe content of 65±5 wt.% (Hauck et al., 2013) and that the thickness of

863   the mantle is 420±30 km. Grey fields below the red, blue and green curves show the

864   result of iterative calculations of the amount of sulfur that does not dissolve in the

865   metallic core and contributes to the formation of a FeS external core. Dashed red,

866 blue and green curves show the effect of the uncertainty on the bulk Fe content (65±5

867 wt.%) of the planet and the mantle thickness. B. Results of a Monte Carlo simulation

868 showing the calculated thickness of the FeS layer as a function of fO_2. We used metal

869 and sulfide densities from Hauck et al. (2013). Red, blue and green curves correspond

870 to a Mercurian bulk S content of 5, 4 and 3 wt.%, respectively.