How Mercury can be the most reduced terrestrial planet and still store iron in its mantle

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A B S T R A C T

Mercury is notorious as the most reduced planet with the highest metal/silicate ratio, yet paradoxically data from the MESSENGER spacecraft show that its iron-poor crust is high in sulfur (up to ~6 wt%, ~80× Earth crust abundance) present mainly as Ca-rich sulfides on its surface. These particularities are simply impossible on the other terrestrial planets. In order to understand the role played by sulfur during the formation of Mercury, we investigated the phase relationships in Mercurian analogs of enstatite chondrite-like composition experimentally under conditions relevant to differentiation of Mercury (~1 GPa and 1300–2000 °C). Our results show that Mg-rich and Ca-rich sulfides, which both contain Fe, crystallize successively from reduced silicate melts upon cooling below 1550 °C. As the iron concentration in the reduced silicates stays very low (~<1 wt%), these sulfides represent new host phases for both iron and sulfur in the run products. Extrapolated to Mercury, these results show that Mg-rich sulfide crystallization provides the first viable and fundamental means for retaining iron as well as sulfur in the mantle during differentiation, while sulfides richer in Ca would crystallize at shallower levels. The distribution of iron in the differentiating mantle of Mercury was mainly determined by its partitioning between metal (or troilite) and Mg–Fe–Ca-rich sulfides rather than by its partitioning between metal (or troilite) and silicates. Moreover, the primitive mantle might also be boosted in Fe by a reaction at the core mantle boundary (CMB) between Mg-rich sulfides of the mantle and FeS-rich outer core materials to produce (Fe, Mg)S. The stability of Mg–Fe–Ca-rich sulfides over a large range of depths up to the surface of Mercury would be consistent with sulfur, calcium and iron abundances measured by MESSENGER.

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1. Introduction

The recent results obtained from the MErcury Surface, Space ENvironment GÉochemistry and Ranging (MESSENGER) spacecraft show that the surface of Mercury has a low iron (~3.3 wt%) and a high sulfur abundance (up to ca. 6–7 wt%) (Nittler et al., 2011; Weider et al., 2012; Starr et al., 2012; Evans et al., 2012) compared to the Earth’s surface. Correlation between major elements in the MESSENGER data thus suggested that sulfur cannot be present only as Fe-rich sulfide but more likely as oldhamite (Ca-rich sulfide, CaS) with possibly minor niningerite (Mg-rich sulfide, (Mg,Fe,Mn)S) (e.g. Nittler et al., 2011; Weider et al., 2012; Zolotov et al., 2013). Such Ca- and Mg-rich sulfides are commonly found in enstatite chondrites (EC), which also have low FeO abundances. Previous studies (e.g. Nittler et al., 2011; Weider et al., 2012) showed a globally good match of Mg/Si and Al/Si weight ratios for EC systems and MESSENGER data, suggesting that they share similar precursor materials and/or evolution (Fig. 1a). MESSENGER data
Fig. 1. Mg/Si (a), Al/Si and Ca/Si (b), Fe/Si and S/Si (c) mass ratios for Mercury obtained from the average MESSENGER data (Nittler et al., 2011; Weider et al., 2012; Starr et al., 2012; Evans et al., 2012) compared with enstatite chondrite Indarch (samples obtained at 1 GPa with $f_{O_2}$ ranging between 4 to 5 log units below IW (Berthet et al., 2009)); samples obtained at 1 atm with $f_{O_2}$ ranging between 4 to 6 log units below IW, with no S volatilization (McCoy et al., 1999) and the isothermal samples of this study.

Interpretation relative to EC becomes more challenging with the addition of S/Si, Fe/Si and Ca/Si weight ratios (Nittler et al., 2011; Weider et al., 2012; Starr et al., 2012; Evans et al., 2012). The Fe/Si ratios from MESSENGER data (Nittler et al., 2011; Weider et al., 2012; Starr et al., 2012; Evans et al., 2012) though low ($\sim 0.05 \leq (\text{Fe/Si})_{\text{MESSENGER}} \leq \sim 0.1$) are still much higher than those in the silicate melts produced experimentally as shown in Fig. 1 ($\langle \text{Fe/Si} \rangle_{\text{silicates of EC}} \sim 0.015$, from Berthet et al., 2009; McCoy et al., 1999 and the present study). This difference was already pointed out by Weider et al. (2012) and Zolotov et al. (2013). Since the very low oxygen fugacity ($f_{O_2}$) of Mercury precludes excess Fe to be located within indigenous silicates, Weider et al. (2012) proposed that Fe might have been implanted by meteoroid impacts. However, such an exogenous origin of Fe cannot explain the high abundance of sulfur on Mercury’s surface: S abundance is obviously not correlated to iron only (e.g. Nittler et al., 2011; Weider et al., 2012) and Zolotov et al. (2013) proposed this excess of Fe to be stored within sulfides in lavas. Our high pressure and high temperature experiments confirm that Fe has an indigenous origin and comes from Mg-Ca-Fe-bearing sulfides, which formed during the differentiation of Mercury.

Large impact melting events must have occurred on Mercury during accretion (Charlier et al., 2013; McCubbin et al., 2012; Brown and Elkins-Tanton, 2009) as for all the terrestrial planets (e.g. Wetherill, 1975; Righter and O’Brien, 2011), implying the formation of a possible large magma ocean during the formation of Mercury (e.g. Brown and Elkins-Tanton, 2009; Benz et al., 2007). Moreover, Schubert et al. (1988) have estimated that only 20% of the heat generated during its accretion (i.e. accretional heat, core-mantle differentiation, decay of short- and long-lived radioactive elements, minus the loss of heat to space) might melt all of Mercury. The reduced state of the surface of Mercury suggests EC, or reduced materials close to the mineralogy of ECs, to have been the building blocks of Mercury. Melting experiments with an EC (Indarch) at atmospheric pressure and up to 1500°C (McCoy et al., 1999) did suggest that oldhamite or ningerite could be totally dissolved in the silicate melt of the meteorite, and might crystallize back from the same silicate melt upon cooling (McCoy et al., 1999; Fogel, 2005). High pressure and high temperature experiments
Table 1
Experimental conditions and observed phases. All experiments were performed at ~1 GPa.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C) – duration</th>
<th>S (wt%) in the starting materials</th>
<th>Observed phases</th>
<th>ΔIW</th>
<th>Δff</th>
<th>Fe (wt%) in Mg-rich sulfide</th>
<th>S (wt%) in silicate melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>#H150</td>
<td>2000 – 3 mn</td>
<td>5.9 (A)</td>
<td>Met-SL-FeS</td>
<td>−5.9</td>
<td>0.3</td>
<td>−</td>
<td>5.82</td>
</tr>
<tr>
<td>#H161</td>
<td>1700 – 45 mn</td>
<td>7.6 (B)</td>
<td>SL-Met-FeS</td>
<td>−4.3</td>
<td>−</td>
<td>−</td>
<td>5.37</td>
</tr>
<tr>
<td>#H961</td>
<td>1665 – 25 mn</td>
<td>9 (C)</td>
<td>Fe5-SL</td>
<td>−2.1</td>
<td>−1.9</td>
<td>−</td>
<td>0.30</td>
</tr>
<tr>
<td>#H160</td>
<td>1500 – 1 h 50 mn</td>
<td>7.6 (B)</td>
<td>Met-SL-Fe6−qts-px-sulf</td>
<td>−4.85</td>
<td>0.2</td>
<td>40.3</td>
<td>7.81</td>
</tr>
<tr>
<td>#H151</td>
<td>1450 – 1 h 40 mn</td>
<td>5.9 (A)</td>
<td>Met-SL-px-qts-sulf</td>
<td>−5.8</td>
<td>0.2/0.15</td>
<td>2.08</td>
<td>9.74</td>
</tr>
<tr>
<td>#H162</td>
<td>1350 – 6 h 10 mn</td>
<td>7.6 (B)</td>
<td>Met-SL-qts-Fe5−p-sulf</td>
<td>−4.3</td>
<td>0.2/0.25</td>
<td>23.95</td>
<td>2.80</td>
</tr>
</tbody>
</table>

1 hr at 1700°C followed by slow cooling down to T and then quench

#H241  | 1500(1) – 68 mn   | 7.6 (B)                          | Met-SL-Fe6−sulf  | −5.9| 0.13| (4)                      | 4.77                   |
| #H170  | 1400(1) – 124 mn  | 7.6 (B)                          | Met-SL-sulf-px   | −6.2| −0.25| 14.42 | 7.40                   |
| #H242  | 1300(1) – 150 mn  | 7.6 (B)                          | Met-SL-sulf-px   | −5  | −0.70| 25.4  | 4.41                   |

(1) – 2.2 °C/min; (2) – 2 °C/min; (3) – 3.2 °C/min; (4) Mg–Fe–Ca–rich sulfide grains too small in the silicate matrix to be quantitatively analyzed with EPMA or EDS.

2.2. High-pressure and high-temperature experiments

The experiments were performed with a piston-cylinder apparatus (non-end loaded), at the NASA Johnson Space Center, Houston, Texas, USA. The samples were loaded in conventional high-pressure assemblies consisting of BaCO3 as pressure transmitting medium (e.g. McDade et al., 2002), MgO internal parts, graphite furnace and capsule. Temperatures were measured with a W5Re/W26Re thermocouple, isolated from the capsule by an alumina disc. More details about the experimental setups are given in Musselwhite et al. (2006), Filiberto et al. (2008) and Berthet et al. (2009). Several samples followed two different heat treatments; in a first set of experiments, called isothermal hereafter, the sample was re-acted at temperature above the solidus for several hours and then quenched. In a second set of dynamic crystallization experiments, called slowly cooled in the following, the sample was maintained for 1 hour at 1700°C, i.e. above the liquids temperature, and then cooled according to a controlled temperature ramp with cooling rates near 150°C/h down to a chosen temperature (Table 1), and finally quenched. The goal of a quench is to preserve as far as possible the composition, textures and mineralogy of the phase assemblage formed at high temperature in order, for example, to derive partition coefficients. On the other hand, a slower and controlled cooling may foster olivinite or ninningerite crystallization from a reduced silicate melt upon cooling as suggested by McCoy et al. (1999) and Fogel (2005), who never actually tested this hypothesis with controlled cooling rates experiments. Although this latter type of experiment does not necessarily provide equilibrium data, it potentially allows probing isobaric melting phase relations within a single experiment provided that textures are interpreted carefully. After decompression, all samples were mounted in epoxy, sectioned, and polished for characterization.

2.3. Analytical methods

Samples were first characterized with a Scanning Electron Microscope (SEM, ultra55, Zeiss) operating at 15 kV and a working distance of about 8 mm. Qualitative and quantitative chemical analyses were acquired using a Silicon Drift Drift Detector (SDD).
Ultrathin sections for Transmission Electron Microscope (TEM) observations were prepared using the triopid technique followed by ion thinning with a Precision Ion Polishing System (PIPS Gatan). A thin carbon layer was deposited to prevent charging under the electron beam. TEM investigations were performed in Lille (France) at a 200 kV accelerating voltage with a FEI Tecnai G2 20 microscope. Elemental distributions were obtained in the TEM by EDS X-ray intensity maps, using spectral imaging wherein each pixel of a spectrum image contains a full EDS spectrum mode. Spectrum images were acquired in the Scanning Transmission Electron Microscopy (STEM) mode.

CAMECA SX-50 and SX-100 electron probe microanalyzers (EPMA), equipped with wavelength dispersive X-ray spectrometer (WDS) were used to analyze the samples (at CAMPARIS, Jussieu, Paris, France). Four monochromators were used to detect the first order reflection of Kα (WDS) were used to analyze the samples (at CAMPARIS, Jussieu, Paris, France). Four monochromators were used to detect the first order reflection of Kα emission lines: TAP for Mg, Al, Si, or Mα lines: M for Ca, S, and LLIF for Fe. The counting times for the major elements were 10 s or 20 s and a typical beam current of 10 nA was used at 15 kV with a minimum spot size of 1 μm. The major elements were analyzed first under these conditions. The oxygen concentrations in the silicate were calculated based on standard valences for the measured major elements: 4+ for Si, 3+ for Al, 2+ for Fe, Mg, Ca. The trace elements were analyzed with EPMA with a counting time of 120 s with a current of 40 nA and an accelerating voltage of 15 kV with a spot size ranging from around 1 to 10 μm, depending on the analyzed phases (tiny crystals or large area of silicate melts). The standards used were Fe₂O₃ for Fe, clinopyroxene or diopside for Si, Ca and Mg, MnTiO₃ for Mn, orthoclase for K and Al, pyrite for S, NiO for Ni, Cr₂O₃ for Cr, albite for Na, V₂O₅ for V, pure metallic Mo for Mo, pure metallic Pd for Pd. The uncertainty is defined by the (σ/√N) where σ is the standard deviation of the measurements and N is the number of analyses. The uncertainty is less than 5% for major elements and less than 15% for minor elements. The compositions of each phase found in our samples are reported in Tables 2, 3 and 4. The analyzed total for metal obtained by EPMA ranges from 97.08 to 99.8 wt%, which shows a maximum weight deficit of 2.9 wt%. This is partly due to the dissolution of carbon from the capsule material as it is seen for 4 samples, in which the carbon concentrations were measured by Nuclear Reaction Analysis (NRA) (Table 2), performed at the nuclear microprobe of SIS2M, CEA Saclay (France).

A 1500 keV deuterium beam was used to measure the carbon contents of the metallic phases by means of the nuclear reaction 12C(d, p)13C. A 50 μm Mylar filter stopped backscattered deuterons (Khodja et al., 2001). Protons generated after incident 2H⁺ impact with sample were detected at 170° using an annular detector with a solid angle of 110 mSr. All measurements were performed by scanning the microbeam (spot size 4 × 4 μm²) on 26 × 26 μm² areas. Data analysis was performed using dedicated software (Daudin et al., 2003). The RISM IN program was used to build 2D elemental maps, allowing us to isolate the metallic phase contribution exactly (Mayer, 1997). Data processing was done using SIMNRA: each experimental spectrum was analyzed on the basis of the composition determined with EPMA measurements, except for the carbon content, which was adjusted using the experimental data.

Raman measurements were carried out on a T64000 Jobin–Yvon confocal microRaman spectrometer equipped with the CCD detector and with a Renishaw INVIA spectrometer based on an Ar laser source (514.5 nm), focused through a Leica ×50 magnification objective (École Normale Supérieure, Paris, France). The 514.5 nm of a coherent 70 Ar⁺ laser was used for sample excitation. This line operated between 0.2–0.02 W. The Rayleigh scattering component was removed by a notch filter, and the Raman-scattered light was dispersed by a holographic grating with 1800 lines/mm and detected by a CCD camera. The integration time was between 20

### Table 2
Average compositions (in wt%) of the metallic phases obtained by EPMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Si</th>
<th>S</th>
<th>Ni</th>
<th>Pd</th>
<th>Mo</th>
<th>Cr</th>
<th>V</th>
<th>C</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>#H150</td>
<td>73.46</td>
<td>23.66</td>
<td>0.021</td>
<td>0.08</td>
<td>0.43</td>
<td>0.47</td>
<td>0.06</td>
<td>0.50</td>
<td>0.10</td>
<td>98.78</td>
</tr>
<tr>
<td>#H161</td>
<td>85.1</td>
<td>7.9</td>
<td>0.34</td>
<td>2.3</td>
<td>0.66</td>
<td>0.85</td>
<td>0.01</td>
<td>0.06</td>
<td>nd</td>
<td>97.22</td>
</tr>
<tr>
<td>#H160</td>
<td>85.25</td>
<td>9.89</td>
<td>0.52</td>
<td>0.13</td>
<td>0.65</td>
<td>1.25</td>
<td>0.04</td>
<td>0.12</td>
<td>1.42</td>
<td>99.27</td>
</tr>
<tr>
<td>#H151</td>
<td>75.3</td>
<td>22.61</td>
<td>0.07</td>
<td>0.03</td>
<td>0.25</td>
<td>0.24</td>
<td>0.05</td>
<td>0.46</td>
<td>nd</td>
<td>99.01</td>
</tr>
<tr>
<td>#H162</td>
<td>85.13</td>
<td>10.30</td>
<td>0.33</td>
<td>0.04</td>
<td>0.51</td>
<td>0.70</td>
<td>0.01</td>
<td>0.06</td>
<td>nd</td>
<td>97.08</td>
</tr>
</tbody>
</table>

“Slowly” cooled

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Si</th>
<th>S</th>
<th>Ni</th>
<th>Pd</th>
<th>Mo</th>
<th>Cr</th>
<th>V</th>
<th>C</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>#H241</td>
<td>90.01</td>
<td>6.04</td>
<td>0.45</td>
<td>1.04</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
<td>0.19</td>
<td>2.80</td>
<td>100.7</td>
</tr>
<tr>
<td>#H170</td>
<td>85.5</td>
<td>8.22</td>
<td>0.53</td>
<td>1.57</td>
<td>1.02</td>
<td>0.74</td>
<td>0.05</td>
<td>0.27</td>
<td>2.29</td>
<td>100.2</td>
</tr>
<tr>
<td>#H242</td>
<td>87.30</td>
<td>8.90</td>
<td>0.57</td>
<td>2.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.22</td>
</tr>
</tbody>
</table>

- means below detection limit. No significant oxygen was detected in the metal; nd = not detected. However, the presence of small amount of oxygen (<0.5 wt%) in the metal cannot be ruled out. The presence of carbon is very likely but not measured with EPMA. For 4 samples, direct measurements of carbon have been performed with a nuclear microprobe (see text for details).

### Table 3
Average compositions (in wt%) of the sulfide phases obtained by EPMA and SEM-EDS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Si</th>
<th>S</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Mn</th>
<th>V</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>#H150</td>
<td>63.10</td>
<td>-</td>
<td>36.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.20</td>
</tr>
<tr>
<td>#H161</td>
<td>61.70</td>
<td>0.20</td>
<td>37.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100.1</td>
</tr>
<tr>
<td>#H160</td>
<td>61.61</td>
<td>0.36</td>
<td>36.10</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.12</td>
</tr>
<tr>
<td>#H160</td>
<td>40.30</td>
<td>0.24</td>
<td>41.83</td>
<td>11.80</td>
<td>2.88</td>
<td>-</td>
<td>1.20</td>
<td>1.04</td>
<td>99.29</td>
</tr>
<tr>
<td>#H151</td>
<td>2.08</td>
<td>-</td>
<td>59.80</td>
<td>35.07</td>
<td>2.89</td>
<td>0.10</td>
<td>0.20</td>
<td>0.25</td>
<td>100.19</td>
</tr>
<tr>
<td>#H162</td>
<td>23.95</td>
<td>0.14</td>
<td>49.30</td>
<td>19.50</td>
<td>5.90</td>
<td>0.06</td>
<td>0.06</td>
<td>0.48</td>
<td>99.27</td>
</tr>
<tr>
<td>#H162</td>
<td>61.34</td>
<td>0.19</td>
<td>36.95</td>
<td>0.92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99.65</td>
</tr>
<tr>
<td>#H961</td>
<td>61.75</td>
<td>0.37</td>
<td>36.82</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>0.03</td>
<td>0.52</td>
<td>99.52</td>
</tr>
</tbody>
</table>

“Slowly” cooled

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>Si</th>
<th>S</th>
<th>Mg</th>
<th>Ca</th>
<th>Cr</th>
<th>Mn</th>
<th>V</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>#H241</td>
<td>62.30</td>
<td>0.34</td>
<td>33.41</td>
<td>0.30</td>
<td>-</td>
<td>1.38</td>
<td>-</td>
<td>2.19</td>
<td>99.92</td>
</tr>
<tr>
<td>#H170</td>
<td>14.42</td>
<td>-</td>
<td>50.46</td>
<td>27.03</td>
<td>7.40</td>
<td>-</td>
<td>-</td>
<td>0.33</td>
<td>99.64</td>
</tr>
<tr>
<td>#H242</td>
<td>25.4</td>
<td>0.29</td>
<td>48.14</td>
<td>16.32</td>
<td>5.84</td>
<td>0.86</td>
<td>1.7</td>
<td>0.64</td>
<td>99.19</td>
</tr>
</tbody>
</table>

(1) phases too small and/or too close to metal to obtain minor elements concentrations. – means below detection limit. (2) (Mg,Fe,Ca)S grains are too small (<1 μm) in the silicate matrix to be quantitatively analyzed with EPMA or EDX.
and 60 s. The spectra of all phases were accumulated three times and were recorded between 70 and 1200 cm\(^{-1}\). It was impossible to collect good quality spectra for the metallic phases, and spectra of sulfides are given in Avril et al. (2013).

2.4. \(f_{O_2}\) and \(f_{S_2}\) calculations

The oxygen fugacity of the samples was determined relative to the iron-wüstite (IW) equilibrium, as in previous studies (e.g. Berthet et al., 2008; Rose-Weston et al., 2008; Siebert et al., 2004; Kilburn and Wood, 1997), according to the following equation:

\[
\Delta IW = \log f_{O_2,\text{experiment}} - \log f_{O_2,\text{IW}} = 2 \log (\gamma_{FeO}/a_{FeO}) \tag{1}
\]

with \(\gamma_{FeO} = \gamma_{\text{FeO}}/a_{\text{FeO}}\) (activity of FeO in the silicate melt), and \(a_{Fe} = \gamma_{Fe}(\text{activity of Fe in the Fe-rich metallic alloy})\). For Fe in iron-rich alloys, Raoult’s law applies (e.g. Hultgren et al., 1973). For FeO in the silicate melt, ideal behavior was assumed (\(\gamma_{\text{FeO}} = 1\)), when the concentration of FeO is very low (<0.5 wt%). For the most oxidized samples, previous studies (O’Neill and Eggins, 2002; Holzheid et al., 1997) showed that the activity coefficient \(\gamma_{FeO}\) is around 1.10. We found \(f_{O_2}\) for our samples ranging from around IW-2.2 (i.e. 2.2 log units below the IW buffer) up to IW-6.2 (i.e. 6.2 log units below the IW buffer) (Table 1). An uncertainty of 0.5 log units was estimated for these \(f_{O_2}\) calculations.

There is a Fe-rich sulfide but no metal in sample #H961. We could use the activity of Fe in Fe-S systems (Lee and Morita, 2002) and Eq. (1) to estimate the \(f_{O_2}\) of the run and found IW-2.2, but as Fe in sulfides does not have the same oxidation state as in metal, it is important to check the consistency of our estimate. We found a perfect experimental match with one sample performed at 1 GPa and 1700 °C by Berthet et al. (2009). This sample had about the same FeO content in its silicate liquid (10.17 wt%) as in #961 (9.33 wt%), contained Fe-rich sulfide (similar to that in #961) but also a metallic phase. They calculated the \(f_{O_2}\) with (1) and found \(\Delta IW - 2.1\). We therefore adopted this \(f_{O_2}\) value for #H961.

Sulfur fugacities \(f_{S_2}\) were determined relative to the iron-troilite (IT) buffer as for \(f_{O_2}\) from the IW buffer, according to the following equation:

\[
\Delta IT = \log f_{S_2,\text{experiment}} - \log f_{S_2,\text{IT}} = 2 \log (a_{FeS}/a_{Fe}) \tag{2}
\]

with \(a_{FeS} = 1\) when troilite is present in the sample and/or \(a_{FeS} = \gamma_{FeS}\) of (Fe,Mg,Ca)S, as the activity of FeS in (Mg,Fe,Ca)S sulfides is not known. The \(f_{S_2}\) of the samples ranges between 0.2 log units above IT to 1.9 log units below IT. These values confirm the fact that our experiments are close to the IT buffer since both troilite and Fe-rich alloys are often present in the samples, as in EC where troilite is present with iron-rich alloys and Mg- and/or Ca-rich sulfides.

3. Results

3.1. General features of isothermal and slowly cooled samples

Depending on the peak temperature in the isothermal runs or the quench temperature in the slowly cooled runs, the charges contained either a complex mineralogical assemblage of metal, troilite, (Mg,Fe,Ca)S sulfide, pyroxene, quenched silicate melts (and quartz only at 1350 °C, 1450 °C and 1500 °C in the isothermal runs), or simply quenched metal and silicate melts (Fig. 2). The silicate was totally molten above 1500 °C. The pure Si metal initially added to the starting material reacted fully with FeS and/or the silicates and was no longer observed in the run products; instead Si alloyed with Fe in the metallic liquids. The metallic phase within the silicate matrix often exhibited a quasi-spherical shape as a result of melting (Fig. 2). Sulfides in the isothermal runs were mainly in close association with metallic grains (Fig. 2), but sometimes isolated within the silicates (pyroxenes and/or silicate melts) (Fig. 2). Generally, the Fe content of the silicates was very low (from 0.09 wt% to 0.55 wt% FeO) showing that the silicate glass of the starting material (6.2 wt% FeO) has been reduced during the experiments. The main chemical (and even mineralogical) characteristics of a material close to an equilibrated EC (e.g. Berthet et al., 2009; McCoy et al., 1999) are therefore reproduced. Our results show that it is possible to reproduce mineralogical assemblages very similar to EC from a simplified volatile-free CI starting material, which was heated under reduced conditions, as already proposed by Ebel and Alexander (2011).

3.2. Characteristics of the isothermal samples

Quartz was observed only in the three isothermal samples heated at and below 1500 °C (Fig. 2). It was absent in all the slowly cooled samples. This difference can be ascribed to two different sulfide formation mechanisms. In the three low temperature isothermal samples, the only way to form Mg-rich sulfides from our starting materials was through the reaction:

\[
\text{Si} + 2[\text{MgSiO}_3]^{\text{pyroxene}} + 2\text{FeS} \leftrightarrow 2[\text{MgS}]^{\text{sulfide}} + 2[\text{Fe}]^{\text{metal}} + 3\text{SiO}_2. \tag{3}
\]
Fig. 2. Scanning Electron Microscopy (SEM) images showing the different textures and phases in isothermal (a–c) and slowly cooled (d) samples: (a) #H151 heated at 1450°C where the silicate was partly molten. Grains of quartz (qz), pyroxene (px), metal and grains of Mg–Fe–Ca-rich sulfide (sulf) are labeled. Quenched silicate liquid is also observed (QSL). The grains of sulfides are well defined, homogeneous and could be even longer than 10 μm; (b) #H161 heated at 1700°C, the charge was completely melted; we observed numerous tiny globules of troilite in the quenched silicate melt. (c) #H170, heated for 1 h at 1700°C, cooled over 110 min quench down to 1400°C. Part of the melt has crystallized into (Mg,Fe,Ca)S sulfide rods embedded in a pyroxene matrix. This microtexture is a typical pseudo-eutectic structure (e.g. Liu et al., 2011; Cheng and Chen, 2013). The remaining S-bearing liquid has been quenched to a glass. (d) Raman spectra of the different silicate phases encountered in the experiments: (A) orthopyroxene in #160 or #151, (B) quenched silicate liquid in #241, (C) quenched silicate liquid in #150, (D) quartz in #160 or #151.

This reaction thus accounted for the formation of quartz, iron-rich alloy and the Mg-rich sulfides shown in Fig. 1a. Moreover, formation of SiO2 is also promoted by the reduction of FeO present in pyroxene, due to the low fO2 of the runs (cf. Table 1). Reaction (3) also accounted for the absence of troilite in isothermal sample #H151, in which excess Si and MgSiO3 led to the consumption of all the starting FeS and the production of more Si-rich Fe–Si alloy. The highly reducing conditions allowed the dissolution, into the silicate melt, of most of the S present in the system following the reaction:

\[ \text{FeS} \leftrightarrow \text{[Fe]}_{\text{metal}} + \text{[S]}_{\text{silicate melt}} \]  

with troilite being the only source of S in our experiments (Table 1). When the sulfur saturation limit at the given fO2 and temperature of the run was reached in the silicate melt, excess troilite was still present, which could then stably coexist with both metal and silicate melt (Fig. 2b).

3.3. Characteristics of the slowly cooled samples

Reaction (3) did not proceed in the slowly cooled experiments most likely for kinetic reasons and hence quartz did not crystallize. As shown in Figs. 2c and 3, Mg–Fe–Ca rich sulfide intergrowths with pyroxene were produced from the silicate melt upon cooling. TEM observations revealed the presence of very small crystallites of Mg–Fe–Ca–Sulfide (with sizes \(\ll 1 \mu m\)) indicating that this process was still going on shortly before (Fig. 3b) or during (Fig. 3d&e) the quench. The formation of Mg–Fe–Ca–sulfides can be explained by the two successive reactions: (i) first, the formation of Mg–rich sulfide upon cooling of the silicate melt due to MgS solubility decrease with decreasing temperature:

\[ [\text{Mg}]_{\text{silicate melt}} + [\text{S}]_{\text{silicate melt}} \rightarrow [\text{Mgs}]_{\text{sulfide}}, \]

(ii) in a second step, MgS and excess FeS reacted to form (Mg,Fe)-sulfides:
Fig. 3. Sample #H170 and #H241, heated at 1700 °C and cooled at ~2°C/min down to 1550 °C (#H241) or to 1400 °C (#H170). (a) SEM image of a heterogeneous sulfide grain which formed during slow cooling from 1700 °C down to 1550 °C and then quenched (#H241). A small blob of initial troilite FeS was progressively enriched in Mn and then in Mg. (b) Scanning Transmission Electron Microscopy (STEM) bright field image of #241, a tiny (~250 nm in diameter) flower-shaped Mg-rich sulfide in the S-rich glass. (c) STEM bright field image of #H170 and its chemical maps (400 × 400 pixels) acquired in STEM with an 8 nm probe size and a 300 ms dwell time. The rods are made of a Mg-rich sulfide containing also Ca and Fe. The crystalline matrix exhibits an orthopyroxene composition (#H170). (d) TEM bright field image of the silicate glass showing a dispersed crystalline phase (#H170). (e) Chemical maps (400 × 400 pixels) acquired in STEM mode on the area delimited in (d) with an 8 nm probe size and a 200 ms dwell time. The crystalline phase is made of Mg and Fe–Ca-rich sulfides, which formed during the quench.

\[ x \text{MgS} + (1-x) \text{FeS} \leftrightarrow (\text{Mg}_x \text{Fe}_{1-x})_S \]  

(6)

as illustrated in Fig. 3a. Note that in contrast to reaction (3) no quartz formed along with Mg–Fe–Ca-rich sulfides during this two-step process. Fig. 2c shows that the pyroxene of charge #H170 contains rods of (Mg,Fe,Ca)S with a diameter ~1–3 μm and a length ranging between ~6 and 25 μm. Such microstructures are characteristic of a pseudo-eutectic solidification where a liquid phase transforms into two solid phases (e.g. Liu et al., 2011; Suzuki et al., 2005; Cheng and Chen, 2013). Upon cooling of the silicate melt from 1700 °C, nanocrystal seeds of (Mg,Fe,Ca)S formed in the melt (Fig. 3b&d). They kept growing continuously to yield quasi-regular rod-structures (Figs. 2c and 3c) while the temperature decreased to the temperature at which pyroxene crystallized. Run #H242, quenched after cooling down to 1300 °C, also showed evidence for a pseudo-eutectic decomposition of the silicate melt, but with coarser rod-microstructures consistent with the textural evolution already described and modeled in cooling alloys and ceramics (e.g. Trivedi et al., 1987; Fan et al., 2006). In the two runs in which a pseudo-eutectic texture was observed, an S-rich residual silicate glass was also present, in which nano-particles of (Mg,Fe,Ca)S started to nucleate above the glass transition temperature (around 700 °C) during the quench (Fig. 3d&e).

4. Discussion

4.1. Implications for the behavior of iron in the differentiating mantle of Mercury

Using the model from Zolotov et al. (2013) to estimate \( f_{O_2} \) from FeO contents of our Mercury silicate analogs, we find that the lowest FeO content (0.09 wt% in silicate melt #H150, cf. Table 1...
and Table 4) corresponds to an $f_{O_2}$ value of around 6.4 log units below IW (compared to 5.9 log units estimated from phase compositions) and the highest value corresponds to an $f_{O_2}$ of around 4.8 log units below IW (compared to 4.3 log units with 0.27 wt% FeO in silicate melt #H161, cf. Table 1 and Table 4). The agreement between our $f_{O_2}$ estimates and those obtained from Zolotov et al. (2013) demonstrates that our samples did undergo the low $f_{O_2}$ conditions that we targeted in order to reproduce those having prevailed during the formation of Mercury, EC and aubrites (e.g. Zolotov et al., 2013; Berthet et al., 2009; McCoy et al., 1999; Gaillard and Scaillet, 2009; Smith et al., 2012). The results illustrated in Figs. 2 and 3 unambiguously show that Mg–Ca–Fe-bearing sulfides can crystallize directly during the cooling of reduced chondritic melts such as those present in EC or in proto-Mercury. Moreover, because of the additional presence of troilite in the precursors, these sulfides can contain significant amount of iron (Table 1 and Table 3). These S-rich minerals are thus the likely host for Fe in the primitive mantle of Mercury during the segregation of the core, rather than the reduced sulficates, as already suggested in the model of Zolotov et al. (2013). This point is particularly important because Mg- and Ca-bearing sulfides in EC range from 1.2 to 12 vol.% and troilite from 7 to 15 vol.% (e.g. Berthet et al., 2009; Yanai et al., 1995; Gaillard and Scaillet, 2009). Moreover, the core of Mercury could be composed of a shell structure comprising an outer layer of Fe–S, poor in Si, and an inner layer of Fe–Si, poor in S (e.g. Hauck et al., 2013; Smith et al., 2012; Malavergne et al., 2010). The density of troilite (3.9 g/cm$^3$, e.g. Hauck et al., 2013) is always much lower than that of Fe–Si alloy (3.1–7.1 g/cm$^3$ or even higher depending on the exact Si content of the alloy, e.g. Hauck et al., 2013). This means that the FeS-rich layer of the core is likely to have segregated more slowly than the Fe–Si alloy, thus remaining longer in the primitive mantle, reinforcing again the interactions between the silicates and sulfides. In any case, whatever the exact difference of densities between troilite and highly reduced silicate melts (between 3.0 and 11 g/cm$^3$ (Hauck et al., 2013) which is not well constrained to evaluate the velocity of the mantle crossing of FeS-rich blobs precisely), the primitive core mantle boundary (CMB) might be an important reactive zone. Mg-rich sulfides, formed during the cooling of the molten mantle, could react at the CMB with the FeS-rich outer core to produce (Fe,Mg)S sulfides as we observed in the present work (cf. reaction (6)). These sulfides, which might remain stable at the CMB would then create a slight increase of the deep mantle density just before the outer layer of the core. Such a density increase close to the CMB has indeed been reported in Hauck et al. (2013) and might also be interpreted as “a basal mantle layer of unspecified composition” (Hauck et al., 2013). Based on these previous results and ours, we propose that the CMB might contain a mixture of Fe–Mg-rich sulfide, pyroxene, and likely quartz.

If EC-like materials (with ~33 wt% Fe) were the main precursors of Mercury, then how did the planet obtain its large ratio of metal to silicate (~60–75 wt%, e.g. Hauck et al., 2013)? It could be due to the blasting off of the mantle during a giant impact (e.g. Benz et al., 2007). This hypothesis is not in conflict with the relatively high abundances of K at the surface of Mercury (Peplowski et al., 2011); due to the very reducing conditions of Mercury, K could be more chalcophile than volatile (McCubbin et al., 2012). It is also possible that Mercury’s precursors are simply not sampled in the meteorite collections, as might be the case for the Earth (e.g. Righter and O’Brien, 2011). These unknown Mercurian materials could be close to the mineralogy and chemistry of EC but with at least one significant difference: their metallic proportions.

4.2. The budget of iron in the primitive mantle of Mercury

The Fe budget of Mercury’s primitive mantle can be understood through its distribution between the three main phases that were present during differentiation: silicate, sulfides (from troilite to Mg–Ca-bearing sulfides) and metal. The knowledge of the partition coefficients of Fe between metal and silicate $D^Fe_{metal/silicate}$, between metal and Mg–Ca-rich sulfide $D^Fe_{metal/Mg-sulfide}$, between troilite and silicate $D^Fe_{FeS/silicate}$, and finally between troilite and Mg–Ca-rich sulfide $D^Fe_{FeS/Mg-sulfide}$, is therefore essential. Since the $D^Fe_{metal/silicate}$ reached 36 and 3.6 in the most and the least reduced samples, respectively. If Mercury formed from EC-like materials, then the Mg–Ca–Fe-bearing sulfides would account for a range of ~1 wt% to ~9 wt% Fe abundance in the primitive mantle. On the other hand, if Mercury formed from a precursor which initially contained ~70 wt% metal like CB (Bencubbin-type) chondrites (Brown and Elkins-Tanton, 2009), then the Fe content associated with Mg–Ca–Fe-bearing sulfides based on $D^Fe_{metal/Mg-sulfide}$ could theoretically range from ~2 wt% up to ~19 wt% in the primitive mantle. However, CB chondrites contain less sulfur than EC, with 0.5 to 1.5 vol.% of troilite and no Ca-rich and Mg-rich sulfides (Krot et al., 2003), which would significantly limit the ability of such a mechanism to store Fe in Mercury’s mantle. With $D^Fe_{FeS/Mg-sulfide}$ obtained from our work (1.5 $\leq D^Fe_{FeS/Mg-sulfide} \leq 2.6$, cf. Table 5), we can estimate the range of Fe that can be incorporated in (Mg,Fe)CaS sulfides in equilibrium with FeS. If Mercury formed from EC-like materials, and if FeS equilibrated with (Mg,Fe)CaS, then those Mg-bearing sulfides would account for ~3.6 wt% to ~5.6 wt% Fe in the primitive mantle. All these results demonstrate the potentially central role played by (Mg,Fe)CaS sulfides in the global chemistry of Mercury’s mantle.

4.3. The behavior of sulfur in the primitive mantle of Mercury

Based on the isothermally equilibrated samples, we can infer the sulfur content of reduced silicate melts in a range of temperature-$f_{O_2}$ (~1 GPa) conditions relevant to mantle formation during differentiation (Fig. 4). The results can be compared to those from similar chemical systems found in the literature (Berthet et al., 2009; McCoy et al., 1999; Siebert et al., 2004;
Fig. 4. Concentration of S in quenched silicate melts as a function of (a) oxygen fugacity relative to IW buffer ($\Delta$IW) and (b) temperature; (c) Temperature dependency of sulfur content in the silicate melts obtained from enstatite chondrite systems around 1 GPa. Assuming a linear dependency of Log(S in wt%) with Log $f_O^2$ relative to IW, we found: $S$(wt$%) = -1.9 \pm 0.3 (10000/T) + 14 \pm 3$ around $-2 < \Delta$IW $< -1$, and $S$(wt$%) = -2 \pm 0.3 (10000/T) + 20 \pm 4$ around $-6 < \Delta$IW $< -4$. (d) Log $D_i^{metal-silicate melt}$ as a function of $f_O^2$. Our results are compared with data obtained at higher pressure since $D_i^{metal-silicate melt}$ has no pressure dependence at low pressure ($P < 5$ GPa). These data confirm a linear decrease of Log $D_i^{metal-silicate melt}$ with $f_O^2$. On the same graph, Log $D_i^{FeS-silicate melt}$ is also plotted as a function of $f_O^2$.

Rose-Weston et al., 2009; Kilburn and Wood, 1997; Holzheid and Grove, 2002; Chabot and Agee, 2003; Li and Agee, 2001; Gaillard et al., 2013). The sulfur content in EC-like silicate melts at $\sim$1 GPa strongly depends on $f_O^2$ but also on temperature ($T$). The maximum concentration of sulfur in the silicate melt is $\sim$9 wt% when the $f_O^2$ reaches 5 log units below IW (IW-5), meaning that even for $f_O^2$ lower than IW-5, no more sulfur enrichment occurs with $f_O^2$ going down. This sulfur saturation limit seems to be constant with $T$ below IW-5, but it may increase with pressure, since McCoy et al. (1999) found only $\sim$4 wt% of sulfur in the quenched silicate liquids of the EC Indarch at atmospheric pressure. Below this upper limit, the logarithm of the sulfur content of reduced silicate melts log($S_{silicate-melt}$) varies linearly with log $f_O^2$ or with $1/T$. Log($S_{silicate-melt}$) can thus be fitted by a straight line. This trend shows how important it is to isolate the influence of $f_O^2$ from that of $T$. Below IW-5, the maximum S content in the silicate melts is mostly temperature-independent, meaning that a small planetary body could store up to $\sim$9 wt% S in its mantle melts during the course of differentiation. We used the results shown in Figs. 4a and 4b to model the evolution of the sulfur content in silicate melts with compositions relevant to EC systems at 1 GPa, as a function of $T$ (Fig. 4c). In this model, we assumed that the linear increase with temperature of the sulfur content in silicate melts with $f_O^2$ ranging from 2 to 1 log unit below IW (Fig. 4a) remains valid at higher temperatures as it does at lower $f_O^2$s. Fig. 4c illustrates two important results for planetary differentiation in general. First, the sulfur solubility limit in silicate melts even as oxidizing as the [IW-1, IW-2] range might be reached around 2700$^{\circ}$C. This means that there is no need for extremely reducing conditions to keep large amounts of sulfur in a molten mantle, since very high temperatures could produce the same result. Such conditions may have been produced early in the history of the Solar System, for example by the decay of short-lived radionuclides. Secondly, a planetary body made, like Mercury, mainly of reduced material such as EC should retain a large amount of sulfur in the molten part of its mantle after undergoing a large
impact melting event. This silicate melt would release most of its sulfur during cooling by crystallizing Mg–Ca-rich sulfides (cf. Fig. 3), hence providing a reservoir of sulfur in the mantle (Fig. 4) and, later possibly in the volcanic surface layers as suggested in Zolotov et al. (2013). In order to understand the distribution of S between the core and the mantle of Mercury, we also plotted the partition coefficient of S between metal and silicate melt $D_{S}^{metal/silicate}$ and between FeS and silicate melt $D_{FeS/silicate}$ as a function of $fO_2$ (Fig. 3d). Fig. 4d confirms a linear decrease of Log $D_{FeS/silicate}$ with $fO_2$ and shows a clearly different behavior between $D_{FeS/silicate}$ and $D_{metal/silicate}$ under reducing conditions. Below IW-4, $D_{FeS/silicate}$ is below 1, indicating that S becomes lithophile due to the S enrichment of the silicate melt under such a low $fO_2$. In parallel, $D_{metal/silicate}$ stays above 1 under the same conditions. Our $D_{FeS/silicate}$ values range from ≈4.5 to 13 (cf. Table 5), meaning that if FeS equilibrated with the silicate melt of the mantle, the silicate part of the mantle could store a maximum range of ~3 to ~8 wt% of S. These results imply that the inner metallic part of the Mercurian core can only store between ~0.02 to ~1 wt% of S, i.e. much less than what could potentially be stored in the mantle. $D_{metal/silicate}$ is found to range between 0.8 and 0.9 (Table 5). We used these partition coefficients to estimate the amount of S that can be incorporated in (Mg,Fe,Ca)S sulfides in equilibrium with FeS. If EC materials, in which FeS and Mg–Ca–Fe-bearing sulfides are present, equilibrate at high pressure (HP) and high temperature (HT), then (Mg,Fe,Ca)S would account for a maximum of ~5.8 wt% S abundances in sulfides.

4.4. Chemical evolution of Mg–Fe–Ca-rich sulfides in Mercury’s primitive mantle

Whereas Ca-rich sulfides appear to dominate MESSENGER data (cf. Fig. 1), Mg–Fe–Ca-rich sulfides (richer in Mg than in Ca) are more abundant in our samples. This chemical difference is mainly explained by the compositional evolution of EC silicate liquids during cooling, which can be compared with the cooling of a possible differentiating magma ocean during the formation of Mercury. The initial melt (which has an EC composition) is always richer in Mg and poorer in Ca than the residual liquid after the onset of the crystallization process (Stockstill-Cahill et al., 2012). The residual liquid is thus enriched in Ca and Al and it also retains a high sulfur concentration (Table 4, Fig. 5). With ongoing crystallization (forming Mg-rich pyroxenes and Mg–Fe-rich sulfides), which additionally depletes the liquid in Mg, the last sulfides to form upon reaching the surface would be richer in Ca than those formed deeper at higher temperature (Fig. 5). Furthermore, the Raman spectroscopic study of Avril et al. (2013) performed on different sulfides (from high HP–HT experiments like our runs and from enstatite meteorites) indicate that at HP–HT Mg-rich or Ca-rich sulfides have the same Raman signature as ninnerite or oldhamite of EC as well as the differentiates aubrites implying that such sulfides: (i) do not have HP–HT polymorphs between 1 atm to 1.5 GPa and 20 to 1500 °C, (ii) are not destabilized by any other phases present at HT and/or HP. This result shows that the sulfides formed in our runs can remain stable up to the surface of primitive Mercury. Finally, once at the surface of the planet, such sulfides are likely to survive the harsh physico-chemical conditions (Vaughan et al., 2013).

4.5. The chemical data of MESSENGER

Our results on the formation of Mg–Fe–Ca-rich sulfides extrapolated to Mercury provide a simple explanation for the high Fe and S concentrations required in the Mercurian mantle to explain the Fe/Si and S/Si surface data (Fig. 1). Indeed, these Mg–Fe–Ca-bearing sulfides can be sufficiently abundant to account for most of the indigenous Fe. For example, the Fe content of the pseudoeutectic “pyroxene + (Mg,Fe,Ca)S” assemblage observed in sample #H170 yields an Fe/Si ratio of ~0.12. This is consistent with values obtained by MESSENGER (~0.05 ≤ Fe/Si ≤ ~0.1. cf. Fig. 1). If the highest abundances of Ca and Fe detected by MESSENGER at the surface of Mercury are due to Fe–Fe-bearing sulfides (e.g. Nittler et al., 2011; Weider et al., 2012), it is then possible to estimate the abundance of this phase with the help of our experimental data, which let us estimate the amount of Fe and Ca that can be stored in the silicate phase. We used an average Si abundance of ~25 wt% (as previously done in Weider et al., 2012 and consistent with our EC-like system) in order to derive the range of Fe, Ca and S concentrations at the surface of Mercury based on MESSENGER data. By subtracting the abundances of silicate-stored Ca and Fe from the minimum and maximum Ca and Fe present at the surface of Mercury based on MESSENGER data, we can determine the excess of these two elements that would need to be stored in (Ca,Fe)S (~2 to ~6 wt% and ~1 to ~2 wt% resp.). Such an abundance of Ca and Fe corresponds to a ~2 to ~6 wt% range for the S necessary to make the (Ca,Fe)S sulfides, which is consistent with the ~1.5 to ~6–7 wt% interval deduced directly from MESSENGER data. Our results thus support the interpretation of Nittler et al. (2011), Weider et al. (2012), and Zolotov et al. (2013) that Ca and Fe are mostly stored in sulfides at the surface of Mercury. It should also be noted that the range for S concentration cited above is comparable to the ~5 wt% S in EH chondrites (Yanai et al., 1995), which supports the idea that EC are the best precursor identified so far for Mercury while CB chondrites, another suggested precursor (Brown and Elkins-Tanton, 2009), would contain insufficient S.

5. Conclusion

The present experimental study performed using reducing conditions may be considered as provides a relevant model for the differentiation of proto-Mercury, from melting (during accretion and subsequent impacts) to later cooling and crystallization. Our experiments show that Mg–Fe–Ca-rich sulfides must have formed as crystallization products of the molten silicate part of Mercury’s mantle, which sequestered large amounts of iron and sulfur in conjunction with troilite before and during core segregation (Fig. 5). Moreover, these Mg–Ca-rich sulfides may contain significant amounts of iron depending on the oxygen fugacity and temperature. Consequently, the behavior of iron in the primitive mantle during the differentiation of Mercury was inferred from its distribution between metal (or troilite) and Mg–Fe–Ca-rich sulfides rather than by its partitioning between metal (or troilite) and silicates. In addition to explaining the retention of iron and sulfur, the crystallization of Mg–Fe–Ca-bearing sulfides along with that of Mg-pyroxyene would have modified the relative distribution of calcium and magnesium with depth due to their chemical evolution (from more Mg-rich towards more Ca-rich). The primitive CMB would represent also a reactive zone where Mg-rich sulfides, formed during the cooling of the molten mantle, might react with the FeS-rich outer core to produce (Fe,Mg)S. These sulfides might remain stable at the CMB, even after the total crystallization of the mantle, and would create a slight increase of the deep mantle density before the outer layer of the core as suggested recently (Hauck et al., 2013). Our experimental data thus agree with the MESSENGER chemical data in demonstrating the importance of sulfides in retaining iron and sulfur at the surface of Mercury and they confirm the relevance of EC system experimental studies to model this planet.
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