



Sulfur solubility in reduced mafic silicate melts: Implications for 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 an empirical parameterization to predict SCSS in Mercurian magmas as a function of oxygen fugacity (fO_2), temperature, pressure and silicate melt composition. SCSS being not strictly a redox reaction, our expression is fully 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.

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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 mete-

orites (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 (<2 wt.%; Weider et al., 2014). They are also unusually enriched in sul-

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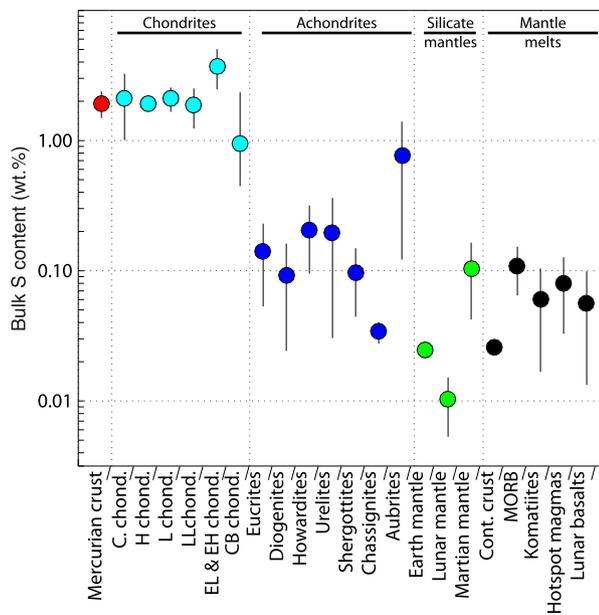


Fig. 1. Sulfur concentrations in the Mercurian crust, chondrites, achondrites, silicate mantles and crusts of terrestrial planets and primary mantle derived melts. Symbols show average concentrations and vertical bars show the 1σ standard deviations. The data for the Mercurian crust were calculated using the MESSENGER data presented by Weider et al. (2015). The complete list of references and number of analyses used in the compilation are given in Appendix. C = Carbonaceous; Chond. = chondrite; Cont. = continental.

fur (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 correlations between S and Ca–Mg observed in Mercurian lavas (Weider et al., 2012). Understanding the origin of high sulfur concentrations at the surface of Mercury is important to better constrain the structure of the planet and the distribution of sulfur amongst the different reservoirs (mantle, core and crust), the mechanisms of explosive volcanism (Kerber et al., 2009; Thomas et al., 2014a; Weider et al., 2016), and the formation of the hollows (sub-kilometer scale shallow depressions surrounded by bright deposits) which may have formed during sublimation of volatiles (Blewett et al., 2013; Thomas et al., 2014b).

The high sulfur concentrations in lavas, together with their low Fe contents and the large metal/silicate ratio of Mercury are strong evidence for accretion and differentiation of the planet under highly reducing conditions (< IW-3; IW = iron-wüstite oxygen fugacity buffer; Malavergne et al., 2010; McCubbin et al., 2012; Zolotov et al., 2013). However, any interpretation of magmatic processes on Mercury and, in particular, the behavior of sulfur in magmas are presently very difficult because of the very limited number of experimental studies performed under oxygen fugacity conditions relevant to Mercury (McCoy et al., 1999; Berthet et al., 2009; Chabot et al., 2014; Malavergne et al., 2014; Vander Kaaden and McCubbin, 2016). In this study, we present the results of 100 new, high-temperature, low- to high-pressure (1 bar to 4 GPa), experiments performed under highly reducing

conditions (IW-1.5 to IW-9). Experiments were performed on compositions representative of the basalts and the mantle of Mercury. We investigate sulfur distribution in coexisting silicate melt, sulfide melt and metallic melt and use our experimental data to build a predictive model of sulfur solubility in silicate melt as a function of intensive parameters (temperature, pressure, oxygen fugacity). We then discuss sulfur transport from the mantle to the surface of Mercury, the redox conditions of the mantle and sulfur partitioning between the metallic core and the silicate mantle, with implications for the formation of a FeS layer at the mantle–core boundary.

2. Experimental and analytical procedures

2.1. Choice and preparation of starting compositions

Experiments were performed on three silicate compositions (Table 1) that were equilibrated with a Fe-bearing metallic phase and a sulfide phase. Silicate compositions were chosen to match (1) lavas of the Northern Volcanic Plains (NVP), (2) the high-Mg terrane (HMg) of the ICP-HCT and (3) a composition representative of the silicate fraction of an enstatite chondrite (EH). NVP and HMg compositions are based on geochemical data presented by Weider et al. (2012). For NVP, we used 34 X-Ray Spectroscopy (XRS) measurements and calculated median values for the Mg/Si, Al/Si and Ca/Si ratios and re-calculated the compositions on an oxide basis. For minor elements (TiO₂, MnO and K₂O), we used data from Nittler et al. (2011) and Peplowski et al. (2012). We considered a Na/Si ratio of 0.20 (Peplowski et al., 2014), leading to ~7 wt.% Na₂O in the NVP composition. For some experiments, we also used a Na-free NVP composition. For HMg, we prepared a starting composition corresponding to the median composition of the High-Mg terrane of the ICP-HCT. We used 49 XRS measurements with a Mg/Si ratio greater than 0.6. We considered a Na/Si ratio of 0.06 (~2.7 wt.% Na₂O) and 0.1 wt.% K₂O. For the EH starting material, we used the silicate composition of the Indarch meteorite (McCoy et al., 1999; Berthet et al., 2009).

Silicate compositions were produced from high-purity oxides and carbonates. Mixtures were decarbonated at 900 °C for 10 hrs. The reagents were then mixed under ethanol. Silicate compositions were mixed with metallic and sulfide materials produced with FeS, S and Fe in different proportions (Table 1). For the sulfur source, we used FeS, FeS + S or S because CaS was not stable during preparation of the starting materials. We used several combinations of the silicate/metal/sulfide mixture (Table 1; Supplementary Dataset 1). The total Fe content in our experiments ranges from 15–25 wt.%, which is lower than the bulk Fe content of the planet (~65 wt.%; Hauck et al., 2013) and higher than the Fe content of Mercurian lavas (0–2 wt.%; Weider et al., 2014).

The intrinsic oxygen fugacity (f_{O_2}) of the samples was reduced by adding Si metal powder to the silicate starting material (Berthet et al., 2009; Cartier et al., 2014a; Malavergne et al., 2014). In most experiments, we varied the Si/SiO₂ ratio (0–0.5) in order to control f_{O_2} without affecting cation ratios of the starting compositions. In other experiments, we added additional Si (total of 20 and 50 wt.% Si) to reach highly reducing conditions.

2.2. Experiments, analytical methods and oxygen fugacity

Low-pressure (1 bar) experiments were performed in a Gero gas-mixing furnace in evacuated silica tubes at the University of Hannover. Medium-pressure experiments (0.1–0.3 GPa) were performed in large volume internally heated pressure vessels (IHPV) at the University of Hannover (Germany). Argon was used as the pressure medium. High-pressure experiments (1 to 4 GPa)

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