The redox state, FeO content, and origin of sulfur-rich magmas on Mercury

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[1] MErcury Surface, Space ENVironment, GEOchemistry, and Ranging (MESSENGER) orbital observations of Mercury have revealed elevated S abundances, Ca-S and Mg-S correlations, and a low upper limit for ferrous iron in surface silicates. These data indicate the presence of Ca and/or Mg sulfides in volcanic rocks and a low oxygen fugacity (fO2) in their parental magmas. We have evaluated coupled fO2 and fS2 values and FeO contents in Mercury’s magmas from silicate-sulfide equilibria and empirical models for silicate melts and metallurgical slags. The evaluated fO2 at 1700–1800 K is 4.5 to 7.3 log10 units below the iron-wüstite buffer. These values correspond to 0.028–0.79 wt% FeO, implying that Fe must be also present in sulfides and metal and are also consistent with the composition of the partial melt of an enstatite chondrite. This derived upper limit for FeO is substantially lower than the limits obtained from reflectance measurements of Mercury’s surface materials. The low fO2 and FeO values provide new constraints for igneous processes on Mercury as well as the formation, evolution, and internal structure of the innermost planet.


1. Introduction

[2] Both telescopic and Mariner 10 observations of the spectral reflectance of Mercury indicate a low FeO content (< ~3–6 wt%) in surface silicates [e.g., Vilas, 1988; Blewett et al., 1997; Robinson and Taylor, 2001; Boynton et al., 2007; Denevi and Robinson, 2008]. Observations obtained by the MESSENGER Surface, Space Environment, GEOchemistry, and Ranging (MESSENGER) spacecraft during its flybys of Mercury supported these results and indicated an upper limit on the FeO content in surface silicates of 2–4 wt% [McClintock et al., 2008]. The low upper limit for FeO is consistent with the low overall iron content of Mercury’s surface (0.2–4.5 wt%, depending on location) subsequently determined from orbital measurements by MESSENGER’s X-Ray Spectrometer (XRS) and Gamma-Ray Spectrometer (GRS) [Nittler et al., 2011; Weider et al., 2012; Starr et al., 2012; Evans et al., 2012].

[3] MESSENGER imaging and elemental remote sensing observations show that a substantial fraction of Mercury’s surface consists of volcanic deposits [Head et al., 2009, 2012; Weider et al., 2012]. Therefore, the low FeO content in surface silicates could indicate unusually reduced (oxygen deficient) conditions in parental magmas and magma source regions in Mercury’s mantle. The apparent shift of the FeO = Fe2+ + 0.5 O2 equilibrium toward Fe0 metal signifies a low fugacity of oxygen (fO2) in magmas on Mercury. The low FeO content in surface silicates also implies a strongly reduced composition for the materials from which Mercury accreted, indicating the presence of low-fO2 environments in the inner portions of the solar nebula.

[4] Chemical and mineralogical characterization of enstatite chondrites [Keil, 1968], along with experimental data in chemical and metallurgical literature, indicates that low fO2 can restrain the lithophile behavior of some elements (e.g., Mg, Cu, Ti, U, Th, Na, and K) and favor their bonding with S, if it is available. Therefore, speciation and concentration of these elements and S in Mercury’s surface materials can be used to constrain the oxidation state of their parental magmatic systems [Nittler et al., 2011; McCubbin et al., 2012]. In turn, the behavior of elements in the interior of Mercury can be assessed if fO2 values are known [e.g., Malavergne et al., 2010].

[5] The low FeO content in Mercury’s silicates is consistent with the unusually high S concentrations (~1–6 wt%) in surface materials detected by MESSENGER XRS and
GRS instruments [Nittler et al., 2011; Weider et al., 2012; Starr et al., 2012; Evans et al., 2012]. The high S content could reflect the anomalously high (up to ~10 wt%) solubility of sulfide S at fO2 values more than 2 log10 units below that for the iron-wüstite (IW, Fe-Fe0.947O) buffer (fO2 < IW-2) [e.g., Richardson and Fincham, 1954; Fogel et al., 1996; McCoy et al., 1999; Berthet et al., 2009]. These experimental data show that the high solubility of S in silicate/oxide melts is mainly caused by the association of S with Ca, Mg, and Fe, which behave as lithophile elements at more oxidized conditions. Indeed, positive correlations between Ca and S and between Mg and S in surface materials on Mercury suggest the presence of Ca and Mg sulfides [Nittler et al., 2011; Weider et al., 2012], which are common in enstatite chondrites [Keil, 1968; Brearley and Jones, 1998]. These chondrites are often considered among the analogs of Mercury’s precursory materials because they are rich in the FeO-poor Mg silicate enstatite and their partial melts are similar in composition to Mercury’s surface materials as measured by MESSENGER XRS data [Wasson, 1988; Burbine et al., 2002; Taylor and Scott, 2003; Nittler et al., 2011]. The weak absorption feature at 0.6 μm reported for some high-albedo younger areas on Mercury is consistent with the presence of Mg and/or Mn sulfides [Vilas et al., 2012]. A possible correlation between S and Fe seen in XRS data (Figure 1) and some interpretations of Mercury’s reflectance spectra [Fernazza et al., 2010; Blewett et al., 2013] both suggest the presence of troilite (FeS) in surface materials. These observations agree with an earlier prediction of sulfides at Mercury’s surface [Sprague et al., 1995]. By analogy with enstatite chondrites, sulfides containing Ni, Cr, Ti, K, and Na may also be present.

[6] Abundant experimental data and theoretical deductions for the metal-oxide and sulfate-oxide equilibria show that the concentration of FeO in silicate/oxide melts depends on fO2 [e.g., Roeder, 1974; Ariskin et al., 1993; Liu et al., 2001; O’Neill and Eggins, 2002; Wade et al., 2012], and the concentration (solubility) of S in these melts is affected by both fO2 and fS2 [e.g., Richardson and Fincham, 1954; Nzotta et al., 1999; Shankar et al., 2006; Taniguchi et al., 2009]. These dependencies are also functions of melt composition and temperature. Therefore, the possible high abundance of sulfides and the low FeO content of surface silicates constrain the petrology and redox state of Mercury’s magmas and igneous rocks. Here we present an evaluation of the fugacity of O2 and S2 and the corresponding FeO contents in typical magmas on Mercury. In particular, we have determined upper limits on fO2 from reported upper limits on FeO in surface silicates. From concentrations of S obtained by MESSENGER measurements, we evaluated fO2 on the basis of data from metallurgical slags. From the fO2 values so inferred, we have constrained the FeO contents of magmas and volcanic rocks. We also discuss here the implications of these results for igneous processes on Mercury and the formation, evolution, and internal structure of the planet.

2. Fugacities of S2 and O2, and FeO and S Contents of Magmas on Mercury

2.1. Approaches

[7] We have made use of several independent methods to evaluate fS2, fO2, and FeO contents in magmas on Mercury. We have considered thermochemical equilibria of sulfides with metals, oxides, and silicates. The values of fO2 and fS2 were evaluated from equilibrium constants of corresponding reactions and assumed activities of chemical species. In addition, we used empirical dependencies inferred from petrologic experiments and the literature on metallurgical slags that connect the FeO concentration with fO2 and the S content with fS2 and fO2 in silicate/oxide melts saturated with respect to Fe0 metal. These numerical dependencies are functions of melt composition and temperature but not the activities of species. All evaluations have been based on the assumption that the chemical and mineralogical compositions of Mercury’s surface materials inferred from spacecraft measurements correspond to the characteristics of the planet’s igneous rocks and their parental melts.

[8] The fugacity of S2 is a fundamental parameter related to the speciation and concentration of sulfur in melts. It is linked to the redox state (fO2) because these two fugacities control the partitioning of metals between sulfide and oxide species, as discussed below. Because fS2 values have not been measured experimentally for reduced silicate magmas, we have evaluated fS2 from the equilibrium constants of metal-sulfide equilibria

\[ 2\text{MS} = 2\text{M} + 2\text{S}_2(g), \]

where M is a metal (section 2.2). Our assumption is that fS2 values in Mercury’s melts do not exceed fS2 in equilibrium with the least stable metal sulfide. The estimated upper limits on fS2 have been further applied to constrain fO2 from coupled fO2-fS2 relations (sections 2.4 and 2.5).

[9] The upper limits on the FeO content of surface silicates obtained from spectral reflectance observations of surface materials [e.g., McClintock et al., 2008] were used to evaluate upper limits on fO2 in corresponding magmas (section 2.3). This evaluation was made with the empirical approach of

Figure 1. Concentrations of S and Fe in Mercury surface materials detected with MESSENGER XRS [Nittler et al., 2011], obtained for an assumed Si abundance of 25 wt%. The dashed line corresponds to the Fe/S weight ratio in troilite. Other XRS data [Weider et al., 2012] provide some support for the Fe-S correlation along the FeS line. Note that the two data points well removed from the trend are repeated measurements of a single region, which may be an outlier.
Figure 2. Partial pressure (p) of S$_2$ in equilibrium with sulfides at 0.1 MPa. The data refer to equilibrium as expressed in equation (1), where M is metal and MS and M are condensed phases with unity activities. The $p_{S_2}$ values are identical to $f_{S_2}$. The data correspond to equilibrium constants calculated at a standard pressure of 0.1 MPa from thermodynamic data of Pankratz et al. [1987] and Robie and Hemingway [1995]. The FeS data also represent the $p_{S_2}$ in the Fe-FeS system [Guillermet et al., 1981]. The data show the lower stability of FeS than for other sulfides.

Ariskin et al. [1993] that links $fO_2$, FeO molar content, and the silicate composition of Fe$^0$-saturated silicate melts. Although this method is based on a fit of experimental data for $S$-depleted melts, it does not consider the activities of FeO and Fe$^0$ in melts and leads to $fO_2$ evaluations comparable with those from other approaches [e.g., McCubbin et al., 2012].

$\text{MgO(melt)} + 0.5 \ S_2 = \text{MgS(melt)} + 0.5 \ \text{O}_2$  

(2)  

where $a$ denotes activity. We calculated the equilibrium constants of several oxide-sulfide equilibria to evaluate the dependencies of coupled $fO_2$ and $fS_2$ on the activities of oxides and sulfides. In addition, the assumed presence of some crystalline silicates in magmas permits the consideration of silicate-sulfide equilibria. In such cases, the activities of oxides are controlled by the coexisting silicates, and coupled $fS_2$-$fO_2$ relations are functions of sulfide activity and temperature. Therefore, we evaluated $fS_2$-$fO_2$ relations in melts from silicate-sulfide equilibria for appropriate sulfide activities and temperatures (section 2.4).

Another approach for estimating the relationship between $fO_2$ and $fS_2$ is to use empirical data on the sulfide capacity ($C_S$) of metallurgical slags, defined as

$$C_S = (S\%) \frac{fO^{1.5}_2}{fS^{2.7}_2}$$  

(3)

where S% is the wt % of S in a slag [Richardson and Fincham, 1954]. In other words, sulfide capacity is a constant in the equation that connects S solubility in Fe$^0$-metal-saturated oxide melts (slags) with $fO_2$ and $fS_2$. The composition and temperature dependence of $C_S$ has been determined from numerous experiments at controlled $fS_2$-$fO_2$ conditions and can be calculated with published empirical models [e.g., Taniguchi et al., 2009]. Many of these models require the knowledge of optical basicity [Duffy, 1996], which depends on the oxide composition of the melt and reflects its acid-base properties. $C_S$ strongly correlates with optical basicities of slags [Shankar et al., 2006]. We evaluated optical basicities and sulfide capacities of melt compositions for Mercury, and we calculated coupled $fS_2$-$fO_2$ relations for appropriate temperatures with equation (3) (section 2.5). The results have been compared with $fS_2$-$fO_2$ data obtained from silicate-sulfide equilibria (section 2.4).

[12] The $fO_2$ values in melts were then estimated from coupled $fS_2$-$fO_2$ values and $fS_2$ constrained from equilibrium, expressed as in equation (1). Finally, the FeO content in magmas and igneous rocks was evaluated from the FeO-$fO_2$ relations inferred for melts on Mercury after Ariskin et al. [1993] (section 2.6).

[13] The evaluations of $fO_2$, $fS_2$, and FeO contents were performed at 1600–1800 K. The temperature of 1800 K is close to the estimated liquidus temperature for Mercury’s silicate melts [Stockstill-Cahill et al., 2012]. At 1600–1700 K, crystalline Mg silicates may coexist with silicate and immiscible sulfide melts, as inferred from melting experiments with the Indarch (EH4) enstatite chondrite (EC) [McCoy et al., 1999]. Partial melts of enstatite chondrites are widely considered as analogs of magmas on Mercury [e.g., Burbine et al., 2002; Nittler et al., 2011; Stockstill-Cahill et al., 2012]. Therefore, this temperature range is appropriate for evaluations of coupled $fS_2$ and $fO_2$ from silicate-sulfide equilibria. The majority of the metallurgical data used here are for temperatures at and above ~1700 K. Therefore, temperatures between 1700 and 1800 K are most suitable for the evaluation of $fS_2$ and $fO_2$ from metallurgical slag data. Our evaluations obtained from different approaches are compared at 1700 K.

2.2. Constraints on $fS_2$ in Magma

[14] The high S content in Mercury’s rocks implies a high solubility of $S$ in silicate melts. Some magmatic S could occur in immiscible sulfide liquids, as observed in partial melts of the Indarch EC at temperatures less than 1700 K [McCoy et al., 1999]. The $fS_2$ of Mercury’s magmas could be controlled by equilibria of dissolved and/or immiscible sulfides with $S_2$-dominated gas. The less stable sulfide species would disproportionally contribute to the value of $fS_2$. The stability of metal sulfides increases in the order Fe, Mn, Mg, and finally Ca. This sequence is seen in the decreasing equilibrium partial pressure ($p$) of $S_2$ in sulfide vaporization reactions at 1700 K (FeS, 10.6 Pa; MnS, 10$^{-3.3}$ Pa; MgS, 10$^{-6.1}$ Pa; CaS, 10$^{-17.6}$ Pa) and is also illustrated in Figure 2. FeS, as the least stable sulfide, would have a relatively large effect on $fS_2$, and the $fS_2$ value for the FeS-Fe melt sets an upper limit for silicate melts on Mercury. However, the presence of coexisting sulfide and Fe-metal melts in EC melting experiments [McCoy et al., 1999] together with a Fe-S correlation in Mercury surface materials (Figure 1) imply $fS_2$ values near the Fe-FeS melt equilibrium.

2.3. The $fO_2$ in Magma from Upper Limits on the FeO Content of Surface Silicates

[15] The empirical equation of Ariskin et al. [1993] was used to calculate the $fO_2$ values as a function of the FeO
content for silicate compositions that might represent Mercury’s magmas, following Stockstill-Cahill et al. [2012] (Table 1). Two compositions represent the northern volcanic plains (NVP) and a mix of intercrater plains and heavily cratered terrain (IcP-HCT), and a third S-free composition is a normalized partial melt of the Indarch EC. All three compositions led to similar coupled FeO abundance (0.25 wt %) in a partial melt of the Indarch enstatite chondrite. The calculations were performed with the approach of Arikin et al. [1993] and are depicted in Figure 3. The FeO contents evaluated from equation (5) for that approach are for the S-free compositions for northern volcanic plains (NVP) and intercrater plains and heavily cratered terrain (IcP-HCT) (Table 1). The FeO values evaluated from sulfide capacities of compositions NVP and IcP-HCT (Table 1) are shown in Figures 4 and 5 for $f_O$ at the Fe-FeS buffer. The corresponding FeO contents evaluated from FeO-$f_O$ relationships can be seen in Figure 3.

For the upper limit of 4 wt % FeO in surface silicates [McCointock et al., 2008], the evaluated $f_O$ value is IW-2.9 to IW-3.1 (Figure 3). If all Fe in surface materials (0.2–4.5 wt %) [Nittler et al., 2011; Evans et al., 2012; Starr et al., 2012; Weider et al., 2012] occurs in ferrous silicates, the evaluated values are IW-3.3 to IW-3.5 for an average of 2 wt % Fe (2.6 wt % and ~2.1 mol % FeO). For a partial melt of the Indarch enstatite chondrite with 0.25 wt % FeO [McCoy et al., 1999], the evaluated $f_O$ value is IW-5.2. The same value is obtained for the lowest value of 0.19 wt % Fe (0.24 wt % FeO) reported from MESSENGER electron-induced X-ray fluorescence data [Starr et al., 2012].

### 2.4. Coupled $f_S$ and $f_O$ from Silicate-Sulfide Equilibria

The melting experiments with the Indarch EC sample reveal that crystals of the Mg silicates enstatite (En, Mg$_2$Si$_2$O$_6$) and forsterite (Fo, Mg$_2$SiO$_4$) coexist with silicate and sulfide melts [McCoy et al., 1999]. The mid-infrared spectral features for Mg silicates on Mercury (see Boynton et al. [2007] for a review), the Mg-rich composition of surface materials, and the observed Mg-S correlation [Nittler et al., 2011; Weider et al., 2012] imply similar occurrences in Mercury’s magmas. We thus assume that $f_S$ and $f_O$ in the magmas are linked in silicate-sulfide equilibrium, so that

$$\text{Mg}_2\text{SiO}_4(\text{solid}) + 0.5 \; \text{S}_2 = \text{MgS(melt)} + 0.5 \; \text{Mg}_2\text{Si}_2\text{O}_6(\text{solid}) + 0.5 \; \text{O}_2.$$ (4)
to 0.6 for admixtures of FeS and MnS observed in chondritic (EH3) niningrite. Because the enstatite-forsterite coexistence (0.5 En + MgO = Fo) determines aMgO in the melt (0.21 at 1700 K), identical results were obtained for the oxide-sulfide equilibria given by equation (2).

[20] Lower temperatures and analogous considerations for Ca and Mn silicate-sulfide equilibria lead to lower fO2 values. An admixture of Ca or Mn into pyroxene would lead to lower fO2 than for pure enstatite. It follows that the evaluations for equilibria in equations (4) and (2) set an upper limit to fO2 at a specified fS2 value. At the value for fS2 in equilibrium with the Fe-FeS melt [Guillermet et al., 1981], the fO2 value is IW-5.6 at 1700 K (Figure 4a, Table 2). Analogous evaluations at 1800 K make less sense because of a lack of crystalline silicates and/or immiscible sulfide liquids at near-liquidus conditions [McCoy et al., 1999; Stockstill-Cahill et al., 2012].

2.5. Coupled fS2 and fO2 from Sulfide Capacity Data

[21] Although magma-like compositions have not been explored in multiple metallurgical slag experiments, we have obtained consistent sulfide capacity (CS) values for Mercury’s melts from five empirical models [Sosinsky and Sommerville, 1986; Young et al., 1992; Nzotta et al., 1999; Shankar et al., 2006; Taniguchi et al., 2009] (Table 3). With each of these models, CS was calculated as a function of melt composition and temperature. The lack of experimental data on CS for magma-like compositions could in part account for the diversity of calculated CS values.

[22] The fS2-fO2-S% relations calculated with equation (3) for CS data averaged for the five models (Table 3) are shown in Figures 4b, 4c, and 5. The relations are slightly different for the NVP and IcP-HCT compositions, whereas the results for the Indarch partial melt composition are similar to those for the IcP-HCT composition. At an fS2 value appropriate to the Fe-FeS buffer, the evaluated fO2 values for NVP and IcP-HCT are in good agreement with those obtained for equilibrium as expressed in equation (5) (Table 2). However, the use of high Na2O (4 wt %) abundances for NVP and IcP-HCT compositions [Evans et al., 2012] leads to more oxidized fO2 values, higher by 0.6 and 0.4 log units, respectively. The fO2 value obtained for the Indarch melt (IW-6.2 ± 0.56 at 1700 K) agrees with the value of IW-5.9 evaluated by Malavergne et al. [2010] for the data of McCoy et al. [1999] for 1773 K melt.

[23] The coupled S%-fO2 relations obtained from CS data for Mercury’s NVP and IcP-HCT compositions are not in complete agreement with petrologic experiments on S solubility [McCoy et al., 1999; Malavergne et al., 2007a; Berthet et al., 2009] (Figure 5). Most of the experimental data indicate higher fO2 for a given S abundance. This discrepancy may reflect a range of temperature and pressure conditions and melt compositions, a systematic discrepancy in calculations of CS from slag models applied to magmatic compositions which differ from typical slags, uncertain fS2 conditions in petrologic experiments, and the adopted fS2 value in our calculations. Formally, the petrologic data could be matched within the framework of the slag CS model if the experimental value of fS2 were higher than at the Fe-FeS buffer. Comparison of our results with petrologic data, however, shows that fS2 in EC melts and magmas on Mercury cannot be less than that at Fe-FeS

Figure 4. Relations among fO2 and fS2 for silicate melts on Mercury. (a) The fO2 and fS2 values are set by equilibrium expressed by equations (4) and (5) at two values for the activity of MgS. The dashed lines correspond to the fS2 values in the Fe-FeS system [Guillermet et al., 1981]. fS2 may not exceed these values in magmas on Mercury (see text). The intersections of the silicate-sulfide equilibrium lines with fS2 lines (open circles) set the fO2 values shown in Table 2. (b and c) Relations between fO2 and fS2 in Mercury melts evaluated with equation (3) and with the S contents and CS values shown in Tables 1 and 3. Brackets denote statistical uncertainties in the calculated values. The intersections of the inclined lines with the horizontal fS2 lines for the Fe-FeS system determine fO2 values (see Table 2).

[18] The fugacities fS2 and fO2 are variables in the expression for the equilibrium constant

\[ K_s = \frac{a_{MgS}^{0.5} f_{O2}^{0.5}}{a_{FeS} f_{S2}} \]  

where a denotes the activity of a solid species. Figure 4a shows the fO2-fS2 conditions for equilibrium (4) with \( K_s \) calculated from standard thermodynamic properties (at 0.1 MPa) of the respective species [Pankratz et al., 1987; Robie and Hemingway, 1995]. The activity of the silicates was assumed to be unity, reflecting the presence of FeO-poor Mg silicates observed in mid-infrared spectra of Mercury [Boynton et al., 2007; Sprague et al., 2009] and in the products of EC melting experiments [McCoy et al., 1999]. The activity of MgS was varied from unity for the pure condensed phase to 0.6 for admixtures of FeS and MnS observed in chondritic (EH3) niningrite. Because the enstatite-forsterite coexistence (0.5 En + MgO = Fo) determines aMgO in the melt (0.21 at 1700 K), identical results were obtained for the oxide-sulfide equilibria given by equation (2).
equilibrium. By this comparison, our $f_{\text{O}_2}$ values are appropriate estimates rather than upper limits. The lack of information on $S_2$ in petrologic experiments, however, limits the strength of this argument. Further experiments on S solubility in magma-like melts at fixed $S_2$ and $f_{\text{O}_2}$ will help to reconcile the discrepancy noted here and will further constrain the redox state of magmas on Mercury.

### 2.6. FeO Content in Melts and Igneous Rocks

[23] The concentration of FeO in partial melts and corresponding igneous rocks has been evaluated from the FeO-$f_{\text{O}_2}$ relations established for Mercury’s surface compositions with the approach of Ariskin et al. [1993] (Figure 3). The evaluated $f_{\text{O}_2}$ range of IW-6.4 to IW-5.1 for NVP and IcP-HCT compositions with 1.5 and 2.3 wt% $S$, respectively, corresponds to 0.07–0.44 wt% FeO in melts at 1700–1800 K (Table 2). These evaluated FeO contents are close to the 0.25 wt% FeO reported for partial melt of Indarch at 1700 K [McCoy et al., 1999]. The match of the calculated and experimental FeO values provides some validation of our numerical approaches. Therefore, the $f_{\text{O}_2}$ values of ~IW-5 and 0.44 wt% FeO are taken to be upper limits that supersede other evaluations presented in Table 2.

[24] For a range of S abundances on Mercury of 1.2–4 wt% and with $S_2$ at the Fe-FeS buffer, the evaluated $f_{\text{O}_2}$ value is between IW-4.5 and IW-7.3 at 1700–1800 K, including uncertainties in $C_S$ (Figure 5). These $f_{\text{O}_2}$ values correspond to FeO concentrations of 0.028–0.79 wt% (~0.023–0.65 mol%) in melts and igneous rocks. This range reflects variations in silicate composition, S content, and uncertainties in the data.

### 3. Implications of Low $f_{\text{O}_2}$ and High S Content in Mercury’s Surface Material

[25] The upper limits on $f_{\text{O}_2}$ obtained above confirm earlier inferences [e.g., Robinson and Taylor, 2001; Nittler et al., 2011; McCubbin et al., 2012] about strongly reducing conditions in Mercury’s igneous systems. The derived low concentration of FeO in silicates is less than upper limits evaluated from spectral reflectance measurements [e.g., Vilas, 1988]. The evaluated concentration of FeO in silicates is generally lower than the Fe concentrations reported from XRS [Nittler et al., 2011; Weider et al., 2012] and GRS data [Evans et al., 2012]. Therefore, Fe must also be present as troilite, as an FeS admixture in Mg-rich sulfides, and possibly in the metallic form. Both metal and sulfides could have separated and crystallized from cooling magma at near-surface conditions [cf. McCoy et al., 1999]. The low $f_{\text{O}_2}$ values exclude ilmenite (FeTiO₃) as a major darkening surface mineral [cf. Riner et al., 2010; Zolotov, 2011].

[26] The strong effect of $f_{\text{O}_2}$ on S solubility at fugacities less than ~IW-2.5 implies that the variable S content observed on Mercury may reflect redox heterogeneity of the igneous systems on the planet. However, evaluations from $C_S$ data show that although the IcP-HCT regions are relatively enriched in S, Mg, and Ca, they may not be more reduced than the NVP areas (Figures 4b, 4c, and 5 and Table 2). The solubility of S at $f_{\text{O}_2} <$ IW-1 could increase with temperature [Malavergne et al., 2012], and the high temperatures implied by the Mg-rich IcP-HCT melts (Table 1) may have contributed to the elevated S contents. Higher S concentrations may also reflect efficient assimilation of crustal S-bearing minerals by high-temperature melts, as observed in komatites [Bekker et al., 2009]. Condensation of S-bearing species emitted from hot lavas with mantle or assimilated S may also play a role.

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**Table 3. Optical Basicity ($\Lambda$) and Sulfur Capacity ($\log_{10} C_S$) of Mercury and a Possible Analog Composition**

<table>
<thead>
<tr>
<th>Model</th>
<th>Northern Volcanic Plains ($\Lambda = 0.564$)</th>
<th>Intercrater Plains and Heavily Cratered Terrain ($\Lambda = 0.580$)</th>
<th>Indarch Melt ($\Lambda = 0.573$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1600 K</td>
<td>1700 K</td>
<td>1800 K</td>
</tr>
<tr>
<td>SS86</td>
<td>$-5.69$</td>
<td>$-5.39$</td>
<td>$-5.12$</td>
</tr>
<tr>
<td>YO92</td>
<td>$-6.30$</td>
<td>$-5.87$</td>
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</tr>
<tr>
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<td>$-5.75$</td>
<td>$-5.18$</td>
</tr>
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<td>$-5.31$</td>
<td>$-4.89$</td>
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<td>TA09</td>
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<td>$-5.24 \pm 0.24$</td>
<td>$-4.49 \pm 0.26$</td>
</tr>
</tbody>
</table>

*aOptical basicity and $C_S$ data correspond to S-free compositions of silicate melts (Table 1). Optical basicities were calculated after Duffy [1996] and used to calculate $C_S$ for five independent models for metallurgical slags. The uncertainties given for average $C_S$ reflect the differences in values obtained from the five models, SS86, Soinosky and Sommerville [1986], YO92, Young et al. [1992], NZ99, Nzotta et al. [1999], SH06, Shankar et al. [2006], TA09, Taniguchi et al. [2009].

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**Figure 5.** The solubility of S in reduced silicate melts as a function of $f_{\text{O}_2}$. The solid lines show the values evaluated from sulfide capacities of melts (Table 3) at $S_2$ controlled by Fe-FeS melt equilibrium at 1700 K (Table 2). The uncertainties reflect the range of $C_S$ values. The solid symbols show $f_{\text{O}_2}$ at S contents depicted in Table 1. The open symbols show petrologic experimental data performed at different temperatures, pressures, and melt compositions. Note that $S_2$ is not specified for these experiments. The dashed lines show the range of S concentrations in surface materials on Mercury [Nittler et al., 2011]. These data determine $f_{\text{O}_2}$ for the range of S contents in Mercury materials (Table 2).
The Th/U ratio in Mercury materials is also in disagreement with an explanation for the high K/Th ratio (8000 ± 3200 [Peploski et al., 2012]) involving a strong partition of Th into core sulfides as discussed by McCubbin et al. [2012]. High-pressure experimental data on the sulfide-oxide partitioning behavior for Th would further constrain redox conditions at the time of core formation [McCubbin et al., 2012]. The possible redistribution of K in surface materials by thermal or other surface processes should be taken into account in the interpretation of the K/Th ratio [Peploski et al., 2012].

The high S contents in surface materials and the corresponding low fO2 in magmas imply that Mercury accreted from reduced materials (FeO-poor silicates, Mg and Ca sulfides, Si-rich Fe-Ni metal) broadly similar to the constituents in enstatite chondrites [Nittler et al., 2011]. Although enstatite chondrites have the lowest Mg/Si ratio among chondrite groups, and an even lower Mg/Si ratio may be expected on Mercury (though the surface composition may not reflect the bulk ratio because of magmatic processes and Si in the core). For example, sulfidation of Mg and Ca silicates by S-rich gas released from Fe-FeS melts in the early inner solar system would lead to temperature-resistant Ca and Mg sulfides and also may result in the loss of Mg gas [Lehner et al., 2013]. Fe metal left after evaporation of S from the Fe-FeS melt might have contributed to Mercury’s unusually high bulk density.

Although a low FeS/(CaS + MgS + Fe) ratio in materials accreted by Mercury is consistent with the measured surface composition, such a ratio needs to be reconciled with the possible presence of a dense solid layer beneath the silicate mantle that could be rich in FeS and/or FeO [Smith et al., 2012]. At the lowest fO2 values inferred here, Fe-Si core compositions could be more favorable than an Fe-S-Si composition [e.g., Berthet et al., 2009]. The Fe-Si compositional end-member does not exhibit the liquid-liquid immiscibility that could segregate a liquid FeS layer at the top of the core that may later have (partially) solidified.

Despite a major sequestration of Fe-FeS melts into the core, dissolved sulfur should have remained abundant in reduced silicate melts during and after differentiation (e.g., in a magma ocean). The dominance of silicates at the surface of Mercury is not consistent with the large-scale separation of low-density Ca and Mg sulfides by flotation in silicate magma. This inference is consistent with the lower crystallization temperature of sulfides than of Mg silicates and sulfide melt separation only at a small length scales [McCoy et al., 1999]. In other words, because...
sulfides crystallize after substantial crystallization of silicates, they may not float in high viscosity, crystal-rich magma despite their buoyancy. The likely presence of Fe in Mg-and/or Ca-rich sulfide melts increases their density and further restricts their buoyancy. In contrast to immiscible FeS-rich melts, Mg-Ca-Fe-sulfide melts should not sink in magma chambers or thick lava flows. Therefore, S concentration in surface materials may represent S dissolved within the silicate melt at the time of partial melting (except in cases when crustal S is assimilated). We conclude that the high S solubility in reduced melts can account for the observations without major sulfide separation through flotation. It follows that Ca, Mg, and Fe sulfides were imbedded in the initial solidified mantle. Subsequent partial melting of the mantle would have mobilized sulfur into silicate melts that eventually erupted at the surface, where sulfides crystallized later than major silicate phases.

4. Concluding Remarks

[33] The elevated concentrations of S in surface materials on Mercury, along with low FeO content in surface silicates, indicate that the magmas that formed volcanic rocks on Mercury were strongly reduced. Both upper limits on the FeO content and the high S concentrations in surface materials have been used to evaluate fO2 in magmas. The fO2 values estimated from Mg-silicate-sulfide equilibrium and sulfide capacity data on metallurgical slags lead to similar results. The average fO2 in magmas on Mercury is estimated to lie between ~5 and ~6.5 log units below the iron-wüstite buffer. This fO2 range corresponds to FeO concentrations of 0.07–0.44 wt%, which are markedly less than upper limits obtained from spectral reflectance measurements. Spatial variations of fO2 could be between IW-7.3 and IW-4.5, possibly reflecting differences in the S abundance and the silicate composition. Mercury’s northern volcanic plains could be slightly more reduced than surrounding regions, although the difference is not statistically significant. The evaluated fO2 values and FeO contents in volcanic rocks are consistent with the presence of Mg and/or Ca sulfides together with troilite and Fe0-metal as products of the crystallization of erupted lavas, but ilmenite is excluded by this argument.

[34] The fO2 values of ~5–7 log units below the IW buffer are similar to fO2 values estimated for the canonical solar nebula [e.g., Grossman et al., 2008; Lehtinen et al., 2013; Jurac et al., 1995]. It is likely, therefore, that Mercury’s precursory materials were not oxidized in the inner solar nebula, in contrast to those from which the asteroids and other terrestrial planets formed (except for the parent bodies of enstatite chondrites).

[35] The Th/U ratio in surface materials is not much different from that on other solid planetary bodies [Peplowski et al., 2011] and could be inconsistent with fO2 < IW-6 ± 0.5, at which Th and U may separate during differentiation. Experiments on fO2-dependent sulfide-silicate fractionation of Th will further constrain fO2 on Mercury.

[36] The fO2 values obtained from Mercury’s S contents and slag-based sulfide capacity data are lower than estimates derived from petrologic experiments that provide data on S solubility in FeS-saturated melts. The discrepancy may reflect the inapplicability of slag models to magma compositions on Mercury, uncertain values of fS2 in petrologic experiments, and/or other factors. Therefore, we encourage experimental investigations of sulfide-silicate melt partitioning of S at controlled fS2 and fO2 to obtain sulfide capacity data for magma compositions directly relevant to conditions on Mercury. Further evaluation of igneous systems on Mercury will also depend on understanding the scale of surface processes that modify volcanic rocks and redistribute volatile species.

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