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

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ABSTRACT

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.

1. Introduction

The recent results obtained from the MErcury Surface, Space ENvironment GEochemistry 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

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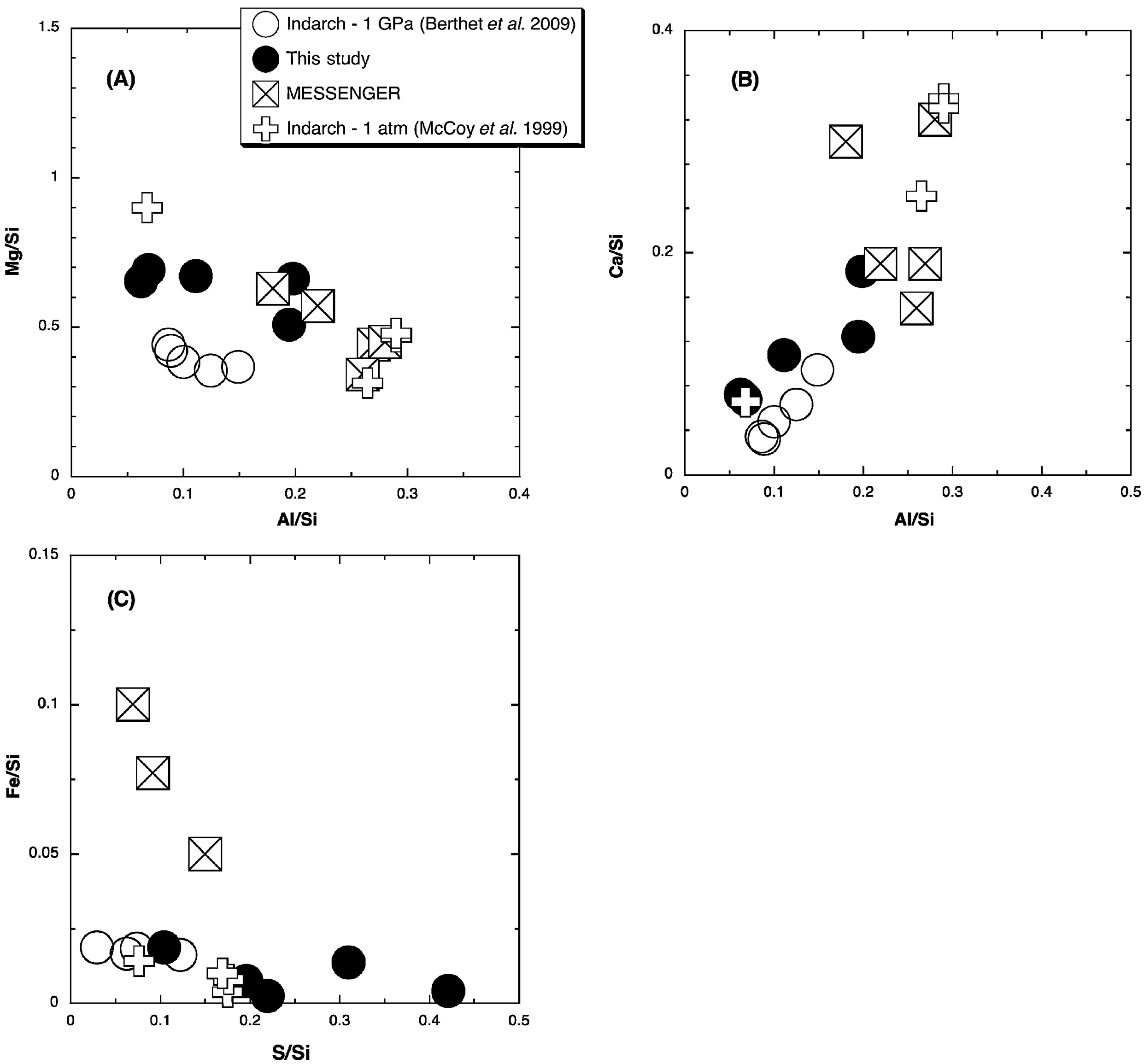

Fig. 1. Mg/Si (a), Al/Si and Ca/Si (b), Fe/Si and S/Si (c) mass ratios for Mercury obtained from the average MESSENGER data (Nittler et al., 2011; Weider et al., 2012; Starr et al., 2012; Evans et al., 2012) compared with enstatite chondrite Indarch (samples obtained at 1 GPa with fO_2 ranging between 4 to 5 log units below IW (Berthet et al., 2009)); samples obtained at 1 atm with fO_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 ($\sim 0.05 \leqslant (\mathrm{Fe/Si})_{\mathrm{MESSENGER}} \leqslant \sim 0.1$) are still much higher than those in the silicate melts produced experimentally as shown in Fig. 1 ($(\mathrm{Fe/Si})_{\text{silicates of EC}} \sim 0.015$, 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 (fO_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