The fate of sulfide during decompression melting of peridotite – implications for sulfur inventory of the MORB-source depleted upper mantle

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A B S T R A C T

Magmatism at mid ocean ridges is one of the main pathways of S outflux from deep Earth to the surface reservoirs and is a critical step in the global sulfur cycle, yet our understanding of the behavior of sulfide during decompression melting of the upper mantle is incomplete. In order to constrain the sulfur budget of the mantle and reconcile the sulfur and chalcophile element budget of mantle partial melts parental to primitive mid-ocean ridge basalts (MORBs), here we developed a model to describe the behavior of sulfide and Cu during decompression melting by combining the pMELTS thermodynamic model and empirical sulfur contents at sulfide concentration (SCSS) models, taking into account the effect of the presence of Ni and Cu in sulfides on SCSS of mantle-derived melts. Calculation of SCSS along melting adiabat at mantle potential temperature of 1380 °C with variable initial S content in the mantle indicates that the complete consumption or partial survival of sulfide in the melting residue depends on initial S content and degree of melting. Primitive MORBs (Mg# > 60) with S and Cu mostly concentrated in 800–1000 ppm and 80–120 ppm are likely mixture of sulfide undersaturated high degree melts and sulfide saturated low degree melts derived from depleted peridotite containing 100–200 ppm S. Model calculations to capture the effects of variable mantle potential temperatures (1280–1420 °C) indicate that for a given abundance of sulfide in the mantle, hotter mantle consumes sulfide more efficiently than colder mantle owing to the effect of temperature in enhancing sulfide solubility in silicate melt, and higher mantle temperature stabilizing partial melt with higher FeO* and lower SiO_2 and Al_2O_3, all of which generally enhance sulfide solubility. However, sulfide can still be exhausted by ~10–15% melting with bulk S of 100–150 ppm in the mantle when T_P is as low as 1300 °C. We also show that although variation of $D_{Cu}^{peridotite/melt}$ and initial Cu in the mantle can all affect the Cu concentration of primitive MORBs, 100–200 ppm S in the MORB source mantle can satisfy both S and Cu geochemistry of partial melts parental to ocean floor basalts.

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1. Introduction

Sulfur (S) is one of the major magmatic volatiles and plays an important role in the planetary differentiation, elemental partitioning, volcanism, and long to short term habitability of the planetary surficial environment. In particular, S in the deep Earth has bearing on the early accretion and core formation process (e.g., Dasgupta et al., 2009; Fei et al., 1997; Labidi et al., 2013; Li et al., 2016; Wood and Halliday, 2005), storage and distribution of chalcophile and siderophile elements (e.g., Buono et al., 2013; Li and Agee, 2001, 1996; Li and Audétat, 2012), origin and storage of other key volatile such as carbon (Li et al., 2016; Tsuno and Dasgupta, 2015), and potentially buffering the canonical Nd/Pb ratio in MORB and OIB (e.g., Hart and Gaetani, 2016, 2006). Yet the constraints on the S budget of the upper mantle are limited and come from very different assumptions and approaches. First, estimates based on peridotite xenoliths vary from <10 to >300 ppm and might not be representative of S content of the mantle as S in xenoliths could be affected by metasomatic processes (e.g., Lorand and Luguet, 2016). Moreover, estimates from global MORB geochemistry, though may yield narrower range of 100–300 ppm, are often based on fundamentally different assumptions. For example, many studies used constancy of S/Dy ratio in MORBs to obtain the S content of the source (Saal et al., 2002; Salters and Stracke, 2004; Shimizu et al., 2016); this assumes that sulfur does not fractionate from Dy during magmatic processes,

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which can happen if sulfide is absent or exhausted by melting. However, MORB glasses which underwent variable degree of crystal fractionation, up to at least ~9 wt.% MgO show clear evidence of sulfide saturation, both from the presence of immiscible sulfide globules (e.g., Czamanske and Moore, 1977; Francis, 1990; Kanehira et al., 1973; Mathez, 1976) and from trends of chalcophile element concentration and ratios (e.g., Jenner et al., 2015; Jenner and O'Neill, 2012). The sulfide saturation of MORBs poses a challenge to directly use them to probe mantle sulfur abundance because irrespective of the abundance of sulfide phases in the mantle, MORBs would always yield saturation values. To circumvent the issue of MORBs sulfide saturation, Nielsen et al. (2014) obtained mantle sulfur abundance using a constant Ce/Tl ratio in global MORBs, to argue that both clinopyroxene and sulfide are present in a constant ratio through melting interval. Although chalcophile elements are commonly used to constrain the behavior of sulfur during partial melting (e.g. Le Roux et al., 2015; Nielsen et al., 2014), covariation of S and chalcophile elements concentration in the orogenic lherzolites and other primitive upper mantle (PUM) related S-rich xenoliths (Harvey et al., 2016; Lorand and Luguet, 2016) demonstrate that the budget of chalcophile elements (e.g., Cu, Se) covary strongly with S inventory of the mantle. But no study thoroughly tracked the fate of sulfur and chalcophile elements together through melting of a sulfide-bearing mantle, taking into account that the mantle domains with elevated S likely also has elevated abundance of chalcophile elements.

Compared to the sub-aerial lavas, S degassing is inhibited in mid ocean ridge basalts (MORBs) both by its water poor nature and the high eruption pressures beneath the ocean (Saal et al., 2002; Wallace and Edmonds, 2011). Therefore, S signature of primitive MORBs could be particularly useful to constrain the S budget of the Earth's depleted mantle (DM) and the main S flux from the Earth's mantle, especially if primitive MORBs and mantle-derived primary melt that evolves to form MORBs are sulfide undersaturated. Given the paucity of primitive MORB glasses at MgO > 9–10 wt.% and the fact that all MORBs suffered variable extent of fractionation, it is necessary to evaluate through forward modeling whether mantle melting could consume sulfide, i.e., how S behaves during melting in the Earth's upper mantle.

In this study, we first compiled S, major elements and other related trace elements geochemistry of MORBs from previous studies to gain insight as to what the sulfur and other chalcophile element abundances could be in partial melts parental to MORBs. Then we coupled thermodynamic calculations of isentropic decompression melting (Ghiorso et al., 2002) with existing sulfur solubility models to track the S contents in the partial melt and the mode of residual sulfide in the mantle source of variable sulfur content as a function of melting. We also modeled the fractionation of Cu, a chalcophile element whose partitioning behavior among various mantle phases including sulfide during partial melting is better known compared to others. The behavior of Cu was modeled assuming both a fixed value of source Cu content, independent of sulfur heterogeneity in the source and a coupled variation of Cu and S source abundances to see whether an internally consistent set of inferences can be reached about the geochemistry of S and Cu in partial melt parental to MORB and the DM. The goals of this study was to (1) construct a framework to constrain the fate of S and Cu during isentropic decompression melting of a sulfide-bearing depleted upper mantle peridotite as a function of bulk mantle S content and mantle potential temperatures; and (2) by comparing compiled S of less differentiated MORBs (Mg#>60) to the modeling results, to estimate the S abundance in MORB source mantle.

1.1. Data compilation and observations

S, Cu, Se and major elements data of a total of 425 basalts from ocean ridges and fracture zones were considered from Pacific, Atlantic and Indian ocean basins (Jenner and O'Neill, 2012; Labidi et al., 2014; le Roux et al., 2006; Shimizu et al., 2016; Yi et al., 2000). For each sample, S, major elements and related trace elements, if available, are obtained in the same basaltic glass. Compositional systematics of the compiled data are plotted in Fig. 1. Only major elements and S are plotted if Cu and Se data are not available (e.g., samples from NEPR by le Roux et al., 2006, and Indian Ocean spreading ridge by Yi et al., 2000). The main observations in Fig. 1 is that the concentration of S broadly increases from ~750–1000 ppm to ~2000 ppm with increasing FeO* from ~7.5 wt.% to ~14–15 wt.% and decreasing Mg# (molar MgO/(MgO + FeO*) × 100) from ~65–70 to ~45. Similarly, Cu and Cu/Se ratio also show a broad decrease with decreasing Mg#, clearly up to Mg# of 60. Similar observation has been made in previous studies where Cu, Cu/Se, Ag/Se show a clear monotonic decrease with decreasing MgO at MgO ≤ 9 wt.% (Jenner et al., 2015, 2012; Jenner and O'Neill, 2012). These trends can be explained by sulfide saturation and fractionation during differentiation of MORBs (Wallace and Carmichael, 1992; Wallace and Edmonds, 2011), which is supported by many observations of Fe–Ni–Cu–S–O sulfide globules in MORBs up to Mg# of 60–63 (e.g., Czamanske and Moore, 1977; Francis, 1990; Kanehira et al., 1973; Mathez, 1976; Patten et al., 2012, 2013). However, Cu concentration and Cu/Se ratio in the less differentiated basaltic glasses do not show systematic decrease with decreasing Mg#, which would be expected if all of them are sulfide saturated (Fig. 1d and 1e). Indeed in the ocean floor basalt dataset of Jenner and O'Neill (2012) and as shown in Jenner et al. (2012, 2015), the decreasing trend of Cu, Cu/Se, and Ag/Se with decreasing MgO appears to cease at MgO ≥ 9 wt.%. At MgO ≥ 9 wt.%, i.e., basalts that are closer in composition to primary magma in equilibrium with the mantle, Cu, Cu/Se, and Ag/Se show no apparent variation (see Fig. 9 of Jenner et al., 2012, 2015). These observations may suggest that the partial melts of DM that lead to MORBs are sulfide undersaturated. To test whether mantle partial melt with similar S and Cu contents as the most primitive MORBs can be generated within the framework of MORB source melting, we take a range of 800–1000 ppm for S and 80–120 ppm for Cu defined by Mg#>60 (Fig. 1b and 1e) as the reference S and Cu concentrations. These ranges are conservative and in good agreement with studies that constrain S and Cu contents of least differentiated MORBs (e.g., Jenner et al., 2012, 2010; Labidi and Cartigny, 2016).

Because the key goal of this study is to evaluate whether the S and Cu contents of primitive MORBs that approach primary mantle melt compositions are produced by sulfide saturation or undersaturation, it is critical to consider whether any other process can modify the S (and Cu) contents of MORBs. Though S in the MORB is generally less degassed as described before, low solubility of CO_2 in basaltic magma can result in significant CO_2 degassing during magma ascent (Dixon et al., 1995). At low pressure (>1.5 kbars), partition coefficient of S between vapor and silicate melt can dramatically increase from 10 to 1000 with decreasing pressure (e.g., Webster and Botcharnikov, 2011). Thus, S concentration of basaltic melt would be affected if the melt is in equilibrium with abundant CO_2–H_2O vapor at pressures lower than 1.5 kbars. By comparing P_{sat} (CO_2–H_2O fluid saturation pressure) and P_{coll} (pressure of sample collection) from Shimizu et al. (2016), we are able to identify some vapor undersaturated samples from this study, which are highlighted in red in Fig. 1 and Fig. 2. Fig. 1 and 2 show that the S concentration of vapor undersaturated samples are in the same range as the other samples at similar MgO contents. Therefore, we