



Fe²⁺–Mg partitioning between olivine and basaltic melts: Applications to genesis of olivine-phyric shergottites and conditions of melting in the Martian interior

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ABSTRACT

Fe²⁺–Mg partitioning between olivine and basaltic melt, expressed by the exchange coefficient, $K_{D_{ol-melt}}^{Fe-Mg}$ [$= (X_{melt}^{Mg}/X_{olivine}^{Mg}) / (X_{melt}^{Fe^{2+}}/X_{olivine}^{Fe^{2+}})$] is widely used to check if a rock composition may represent a mantle-derived magma, to demonstrate equilibrium between coexisting olivine and groundmass in mafic-ultramafic systems, both in experiments and in natural assemblages, and to constrain liquid lines of descent where olivine is the dominant fractionating phase. However, $K_{D_{ol-melt}}^{Fe-Mg}$ of 0.30, which is appropriate for understanding most terrestrial basalts petrogenesis may not apply for Martian basalts as $K_{D_{ol-melt}}^{Fe-Mg}$ is known to depend strongly on the melt compositions and Martian systems produce basalts that are distinctly richer in iron than terrestrial basalts. Here we compiled experimental data on olivine–melt equilibria of Martian and terrestrial basalt compositions to parameterize the effect of magma composition on $K_{D_{ol-melt}}^{Fe-Mg}$ and derive the $K_{D_{ol-melt}}^{Fe-Mg}$ applicable for Martian magmatic systems. We find that the equilibrium relationship between olivine and basaltic melt in Martian systems is described by $K_{D_{ol-melt}}^{Fe-Mg}$ of 0.35 ± 0.01 .

Applying the newly parameterized values of $K_{D_{ol-melt}}^{Fe-Mg}$ to olivine-phyric shergottites suggest that the only known Martian meteorites where the olivine cores and the bulk composition are in equilibrium and therefore could represent magma compositions are: Yamato 980459, NWA 5789, and NWA 2990. LAR 06319, which has been suggested to represent a near magma composition, actually contains ~11 wt.% excess olivine. All other ol-phyric shergottites contain significant excess olivine (20–52 wt.%). Further, assuming that the basalts analyzed by the Mars Exploration Rovers at Gusev crater and the Bounce Rock in Meridiani Planum lie on olivine control lines, we have used our newly parameterized $K_{D_{ol-melt}}^{Fe-Mg}$ to estimate primary magmas in equilibrium with the model Martian mantle. Application of geothermobarometers to new primitive magma compositions suggest that basalt generation in the Martian mantle occurs at greater depths and higher temperatures than previously thought.

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1. Introduction

Olivine is the dominant mineral in the upper mantle of both Earth and Mars, but the composition of olivine in each mantle (~Fo_{89–91} vs ~Fo₇₇ respectively) is significantly different owing to distinctly different iron content and Mg# of the two bulk mantles (e.g., Agee and Draper, 2004; Bertka and Fei, 1998; Dreibus and Wänke, 1985; McDonough and Sun, 1995; Workman and Hart, 2005). Despite the differences in bulk mantle chemistry, basalts from the Earth and Mars are both olivine saturated. Because olivine is such an important mineral during basalt genesis, an enormous effort has been placed on understanding Fe²⁺–Mg partitioning between olivine and magma for terrestrial compositions (e.g., Beattie et al., 1991; Ford et al., 1983; Jones, 1984, 1988; Kushiro and Mysen, 2002; Kushiro and Walter, 1998; Matzen et al., in press; Mibe

et al., 2006; Roeder and Emslie, 1970; Toplis, 2005). Terrestrial models of Fe²⁺–Mg partitioning between olivine and basaltic melt, expressed by the distribution coefficient $K_{D_{ol-melt}}^{Fe-Mg}$ of 0.30 have then been applied to Martian systems to: check if a composition represents a mantle-derived magma, verify that experiments in mafic-ultramafic systems approach equilibrium, and constrain liquid line of descent where olivine is the dominant fractionating phase (e.g., Bunch et al., 2009; Irving et al., 2010; Médard and Grove, 2006; Musselwhite et al., 2006; Peslier et al., 2010; Shearer et al., 2008). The use of $K_{D_{ol-melt}}^{Fe-Mg} = 0.30$ for Martian petrogenesis may not be valid, however, as $K_{D_{ol-melt}}^{Fe-Mg}$ is dependent on numerous factors including melt and olivine composition as well as oxygen fugacity (e.g., Filiberto et al., 2009; Kushiro and Walter, 1998; Matzen et al., in press; Mibe et al., 2006; Toplis, 2005). In particular, Martian basalts are distinctly richer in FeO compared to terrestrial basalts (Fig. 1) (e.g., Dreibus and Wänke, 1987; McSween, 1994; Treiman et al., 2000), equilibrium olivine in the Martian mantle or in equilibrium with model Martian basalts is also much less magnesian compared to primary olivine for terrestrial compositions (Bertka and Holloway, 1994b, a), and Martian basalts genesis likely take place at a

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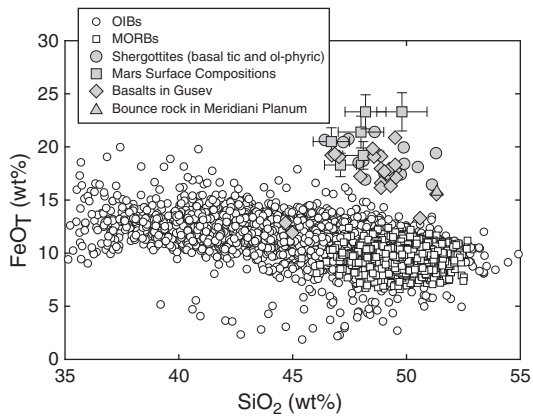


Fig. 1. FeO_T versus SiO_2 for Shergottites (olivine-phyric and basaltic shergottites), basalts analyzed in Gusev Crater, Bounce rock in Meridiani Planum, and Average Martian Surface compositions (Taylor et al., 2010) compared with terrestrial MORBs (Mid-Ocean Ridge Basalts) and OIBs (Ocean Island basalts). Data for Mars basalts (shergottites, Gusev Crater basalts, and Bounce Rock) used for this comparison come from: Barrat et al. (2002), Basu Sarbadhikari et al. (2009), Bunch et al. (2009), Gellert et al. (2006), Goodrich (2003), Greshake et al. (2004), Gross et al. (2011), Lodders (1998), Meyer (2010), Mikouchi et al. (2001), Ming et al. (2008), Peslier et al. (2010), Rieder et al. (2004), Shearer et al. (2008), Squyres et al. (2007), Taylor et al. (2002), Usui et al. (2008b), and Wadhwa et al. (2001). Data for OIBs are taken from GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/>) and those for MORBs from PetDB (<http://www.petdb.org/>). All the terrestrial data are filtered to $8 < \text{MgO} < 16$ wt.%.

distinctly lower oxygen fugacity (\sim QFM to IW oxygen fugacity buffer) than typical terrestrial basaltic magmas (e.g., Goodrich et al., 2003; Herd, 2003; Herd et al., 2002; Shearer et al., 2006).

Our knowledge of Martian basaltic geochemistry, and hence Martian interior, comes mainly from two data sets: Martian meteorites (shergottites, nakhlites, chassignites, and ALH84001) (e.g., McSween and Treiman, 1998; Meyer, 2010; Treiman, 2005) and remotely analyzed basalts on the surface of Mars (e.g., Gellert et al., 2006; McSween et al., 2006; Rieder et al., 2004; Squyres et al., 2007). Martian meteorites range from basaltic (shergottites) through cumulate (nakhlites, chassignites and ALH84001) rocks and are relatively young (1.3–0.17 Ga, e.g., Jones, 1984, 2007; Nyquist et al., 2001; Treiman, 2005) with the exception of ALH84001 (4.5 Ga, Nyquist et al., 2001). Rocks from the surface also range from basaltic through cumulate rocks (e.g., Dreibus et al., 2007; McSween et al., 2006; Ming et al., 2008; Squyres et al., 2006) but are much older (\sim 3.65 Ga) than shergottites (Arvidson et al., 2003; Greeley et al., 2005) and have significantly different chemistry than basaltic shergottites (Filiberto et al., 2006; McSween et al., 2009; Taylor et al., 2006).

Olivine-phyric shergottites are a significant and important subgroup of Martian shergottites (Goodrich, 2002). They contain large olivine crystals with lesser orthopyroxene and chromite grains set in a fine-grained matrix mainly pigeonite and plagioclase (e.g., Basu Sarbadhikari et al., 2009; Goodrich, 2002, 2003; Gross et al., 2011; Usui et al., 2008b). Compared with the basaltic shergottites (with no phenocrystic olivines), they have relatively high bulk rock MgO compositions which has led previous researchers to suggest that they could represent primitive mantle melts (Goodrich, 2002; Gross et al., 2011; Musselwhite et al., 2006; Usui et al., 2008b). However, it is clear from experimental results and textural studies, that at least some of the olivine-phyric shergottites contain excess olivine, although the nature of olivine accumulation, phenocrystic vs. xenocrystic, is highly debated (e.g., Filiberto et al., 2010b; Goodrich, 2003; Shearer et al., 2008; Zipfel et al., 2000).

Basalts have also been analyzed on the surface of Mars in both Gusev Crater (e.g., Squyres et al., 2004) and Meridiani Planum (Rieder et al., 2004). Mineralogically they contain olivine, pyroxene, magnetite, and plagioclase based on Mössbauer spectroscopy and thermal emission spectroscopy (Mini-TES) (e.g., Christensen et al., 2004a, b; McSween

et al., 2008; Ming et al., 2008; Morris et al., 2006a, b). Based on experimental results Humphrey and Fastball have been suggested to represent near-basaltic magma compositions (Filiberto et al., 2008; Filiberto et al., 2010a; Monders et al., 2007), Fastball has been shown likely to be a primitive mantle derived melt (Filiberto et al., 2010a), and it is debated how much fractionation Humphrey has seen on its way to the surface (Filiberto et al., 2008; Monders et al., 2007).

Martian basalts (both surface basalts and shergottites) are significantly richer in FeO than terrestrial basalts (Fig. 1) which will affect Fe–Mg partitioning between olivine and melt (e.g., Filiberto et al., 2009; Kushiro and Mysen, 2002; Kushiro and Walter, 1998; Mibe et al., 2006; Toplis, 2005). We will review the known bulk compositional effects on $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ and the problems with using an incorrect $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ value for determining whether a given basalt represents a magma composition and the conditions of formation in the mantle.

1.1. Compositional effects on $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$

Roeder and Emslie (1970) studied the temperature dependence of olivine–melt Fe^{2+} –Mg partitioning in their seminal work. They concluded that both temperature and bulk composition have minor effects on Fe^{2+} –Mg partitioning, and that a $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ value of 0.30 was appropriate for all known basaltic compositions. Since then, there have been many more experimental studies on wider ranges of basaltic compositions and recent works have emphasized that $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ is not a constant value but experimental values range from 0.17 to 0.45 (Toplis, 2005). Numerous factors have been identified to explain this large range but most studies have focused on the effect of melt composition (e.g., Filiberto et al., 2009; Gee and Sack, 1988; Jones, 1988; Kushiro and Mysen, 2002; Kushiro and Walter, 1998; Longhi et al., 1978; Matzen et al., in press; Mibe et al., 2006; Sack et al., 1987; Takahashi, 1978; Toplis, 2005). In fact, the first study to point out compositional effects on $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ was a study on lunar basalts which are typically richer in FeO than terrestrial basalts (Longhi et al., 1978). These works have suggested that melt structure, Fe- and Mg-activity, Ti- and Al-speciation, SiO_2 content, alkali contents, dissolved water, and oxygen fugacity may all have an effect on Fe–Mg exchange between olivine and melt. Therefore, it is vital to know the correct $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ for a bulk composition before modeling a given planetary system. Using an inappropriate $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ for Martian petrology becomes particularly problematic when modeling: 1) whether a bulk Martian meteorite composition is in equilibrium with its olivine-phenocrysts and 2) the pressures and temperatures of basalt formation in the Martian mantle.

1.2. Modeling olivine-phyric Martian basalts equilibrium

Identifying samples that may represent a magma composition derived from the mantle is key to understanding thermal and compositional evolution of any terrestrial planet. To demonstrate whether a Martian meteorite could represent a basaltic magma or a cumulate, Fe^{2+} –Mg partitioning between olivine megacryst cores and the bulk meteorite composition has been used (e.g., Bunch et al., 2009; Gross et al., 2011; Irving et al., 2010; Peslier et al., 2010; Shearer et al., 2008). Note that, because we are focusing on olivine–basaltic melt partitioning in this study, we have chosen only those samples that contain olivine and are classified as basaltic or near basaltic in composition. We have excluded basaltic shergottites (no olivine phenocrysts) as well as nakhlites (clinopyroxenites), chassignites and Algonquin-class rocks (dunites) and ALH84001 (orthopyroxenite). Fig. 2 shows bulk Mg# of olivine-phyric shergottite compared with the Fo content of the olivine megacryst cores modified from Shearer et al. (2008) (bulk compositional data in Supplemental Table 1). Also plotted is the equilibrium line for a $K_{\text{Dol-melt}}^{\text{Fe-Mg}}$ of 0.30 (Roeder and Emslie, 1970) commonly used to understand Martian basalts petrogenesis.

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