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Experimental determination of CO_2 content at graphite saturation along a natural basalt-peridotite melt join: Implications for the fate of carbon in terrestrial magma oceans

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ABSTRACT

Knowledge of the carbon carrying capacity of peridotite melt at reducing conditions is critical to constrain the mantle budget and planet-scale distribution of carbon set at early stage of differentiation. Yet, neither measurements of CO_2 content in reduced peridotite melt nor a reliable model to extrapolate the known solubility of CO_2 in basaltic (mafic) melt to solubility in peridotitic (ultramafic) melt exist. There are several reasons for this gap; one reason is due to the unknown relative contributions of individual network modifying cations, such as Ca^{2+} versus Mg^{2+}, on carbonate dissolution particularly at reducing conditions. Here we conducted high pressure, temperature experiments to estimate the CO_2 contents in silicate melts at graphite saturation over a compositional range from natural basalts toward peridotite at a fixed pressure (P) of 1.0 GPa, temperature (T) of 1600 °C, and oxygen fugacity ($\log fO_2 \sim \text{IW} + 1.6$). We also conducted experiments to determine the relative effects of variable Ca and Mg contents in mafic compositions on the dissolution of carbonate. Carbon in quenched glasses was measured and characterized using Fourier transform infrared spectroscopy (FTIR) and Raman Spectroscopy and was found to be dissolved as carbonate (${CO_3}^{2-}$). The FTIR spectra showed ${CO_3}^{2-}$ doublets that shifted systematically with the MgO and CaO content of silicate melts. Using our data and previous work we constructed a new composition-based model to determine the CO_2 content of ultramafic (peridotitic) melt representative of an early Earth, magma ocean composition at graphite saturation. Our data and model suggest that the dissolved CO_2 content of reduced, peridotite melt is significantly higher than that of basaltic melt at shallow magma ocean conditions; however, the difference in C content between the basaltic and peridotitic melts may diminish with depth as the more depolymerized peridotite melt is more compressible. Using our model of CO_2 content at graphite saturation as a function of P–T–fO_2-melt composition, we predict that a superliquidus shallow magma ocean should degas CO_2. Whereas if the increase of fO_2 with depth is weak, a magma ocean may ingas a modest amount of carbon during crystallization. Further, using the carbon content of peridotite melt at $\log fO_2$ of IW and the knowledge of C content of Fe-rich alloy melt, we also consider the core–mantle partitioning of carbon, showing that ${D_C}^{\text{metal/peridotite}}$ of a shallow magma ocean is generally higher than previously estimated.

1. Introduction

In order to constrain the contents, distribution, and evolution of volatiles, such as carbon, in the terrestrial planets, their behavior during Earth's accretion and magma ocean (MO) differentiation needs to be better understood. In particular, we must know the capacity and partitioning behavior of C between the silicate MO, the metallic core, and the early atmosphere (e.g., Armstrong et al., 2015; Chi et al., 2014; Dasgupta, 2013; Dasgupta et al., 2013; Hirschmann, 2012; Li et al., 2015). As both the atmosphere and core would interact with the silicate MO during early differentiation/metal-silicate separation in terrestrial planets, the carbon concentration of the three main reservoirs is heavily influenced by the ability of the MO to dissolve C. Fundamentally, the carbon concentrations of the three reservoirs are linked through the storage capacity of the silicate MO.

For one part, equilibrium between the early atmosphere and the MO will control the partial pressure of carbon in the proto-atmosphere which will in turn influence how much C will dissolve

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in the near-surface portion of a convecting MO (e.g., Elkins-Tanton, 2008; Hirschmann, 2012). If the CO_2 concentration of the MO increases with depth, as is the CO_2-pressure relationship at oxidizing conditions, a parcel of the MO that is brought upward will degas into the early atmosphere regardless of the CO_2 partial pressure. However, if the CO_2 concentration of the MO decreases with depth, which is the basis of the 'carbon pump' hypothesis (e.g., Dasgupta, 2013; Dasgupta et al., 2013; Hirschmann, 2012) and is thought to occur under more reducing conditions, i.e., at graphite/diamond saturation (e.g., Holloway et al., 1992), a MO parcel in equilibrium with the atmosphere will actually draw down CO_2 from the atmosphere. Once this parcel is carried deeper and the melt capacity drops, graphite or diamond will precipitate and could be sequestered in the deeper MO or mantle, effectively increasing the initial carbon budget of the mantle.

For the other part, the equilibration of Fe-rich alloy melt and the MO near its base would control the relative distribution of C between the metallic core and the early silicate mantle. Depending on the oxidation path that the Earth followed during accretion and core formation, the Earth may have evolved from a highly reduced condition, e.g., at a $\log fO_2 \leq 4$ log units below the iron-wüstite (IW) buffer where any carbon present would be partitioned into the metallic phase (Chi et al., 2014; Dasgupta et al., 2013; Li et al., 2015), to more oxidized conditions, e.g., IW-2 to IW-1.5 (e.g., Righter and Ghiorso, 2012; Rubie et al., 2011), to the modern day upper mantle near IW+5 (near the fayalite-magnetite-quartz (FMQ) buffer). During MO crystallization, the Earth may have remained at a $\log fO_2$ around the IW buffer, i.e., ≤IW+2, where the stable carbon phase is likely graphite or diamond.

For both the vapor (atmosphere)-melt (MO/mantle) and metal (core)-melt (MO/mantle) partitioning, knowledge of the carbon capacity at reducing conditions is key, i.e., the concentration of CO_2 in a MO at graphite/diamond saturation. The carbon carrying capacity of silicate melt is controlled by pressure (P), oxygen fugacity (fO_2), hydrogen fugacity (fH_2) or water content, temperature (T), and silicate composition (Holloway et al., 1992; Li et al., 2015). These factors will affect concentration as well as speciation, e.g., carbonate ($CO_3{}^{2-}$), methane (CH_4), carbon monoxide, carbonyl (Li et al., 2015; Stanley et al., 2014; Wetzel et al., 2013), though for the fO_2 relevant for the late stage of MO, the chief species of carbon in silicate melt is thought to be carbonate (e.g., Li et al., 2015). Despite the recognition that knowing the volatile concentrations in the MO is critical to constrain the origin and early distribution of volatiles in terrestrial planets, the carbon carrying capacity in general, and of CO_2 in particular, has not been directly measured for relevant MO compositions and conditions. Hence one of the most critical data to constrain the role of carbon in a MO is the content of CO_2, dissolving as $CO_3{}^{2-}$, in peridotite melt.

Current estimates of CO_2 contents of relatively depolymerized, peridotite melt come from two types of studies and models. One set of previous studies, performed mostly at oxidizing conditions, i.e., several orders of magnitude higher fO_2 than those imposed by the presence of Fe-rich metal, attempted to constrain C contents of ultramafic melts by measuring bulk carbon of the quenched material (e.g., with beta-track mapping; Mysen et al., 1975; Mysen et al., 1976) or gas chromatography (Brey, 1976; Brey and Ryabchikov, 1994). Other techniques, such as FTIR or SIMS, are limited when measuring dissolved volatile concentrations in ultramafic compositions, as these compositions do not quench to glasses at the cooling rate achieved by standard solid-media devices, but rather a mix of quench crystals and glass (e.g., Fig. 1; Dasgupta et al., 2013), making analysis difficult to impossible. The other set of studies extrapolated from measured CO_2 solubility in quenched, glassy mafic/basaltic compositions by using a compositional parameter such as NBO/T (e.g., Brooker et al., 2001a), where NBO/T is a silicate compositional parameter of the ratio of non-bridging oxygens (NBO) to tetrahedrally coordinated cations (T). However, using only NBO/T may not reliably take into account the effects of different network modifiers, such as Ca^{2+} and Mg^{2+} on CO_2 solubility, because within the mafic compositions the variation in NBO/T is commonly tied to variation of CaO; whereas extrapolation to ultramafic compositions occurs through a large increase of MgO content with little change in CaO (Fig. 1). Previous CO_2 solubility data at oxidizing conditions, i.e., at CO_2-rich vapor saturation, suggest that there may be a cation preference of the dissolution of carbonate with Ca^{2+}–$CO_3{}^{2-}$ complexes forming preferentially to K_2^+–, Na_2^+–, and Mg^{2+}–$CO_3{}^{2-}$ complexes (Dixon, 1997; Spera and Bergman, 1980), possibly indicating that an increase in Ca over Mg in a melt would have corresponding increase in dissolved CO_2. However, the relative roles of Mg^{2+} and Ca^{2+} on CO_2 solubility in silicate melt still remain ambiguous (Chi et al., 2014; Mallik and Dasgupta, 2014; Stanley et al., 2012). Chi et al. (2014) argued that increasing MgO in basaltic melt at a fixed CaO should enhance CO_2 solubility, by comparing the C contents of silicate glasses with similar CaO (11.2 versus 11.8 wt.%) but different MgO (8.6 versus 13.8 wt.% MgO) at graphite saturation. Mallik and Dasgupta (2013, 2014) also concluded that the CO_2 content of basaltic melt increases with MgO content using the olivine-basaltic melt Fe–Mg K_D as a proxy for MgO, which they interpreted as complexation of dissolved $CO_3{}^{2-}$ with MgO in the melt. On the contrary, Stanley et al. (2012) observed no appreciable difference in the CO_2 solubility between two martian basalts of different MgO contents (~11 and 19 wt.%) at a similar P–T–fO_2 conditions, and these authors concluded that MgO has a minor role in affecting CO_2 solubility due to the potential for Mg to act as a network former as well as the more familiar network modifier (e.g., Brooker et al., 2001b; Guillot and Sator, 2011). However, their lower MgO composition had ~1 wt.% more CaO than the higher MgO composition, which may be enough to counteract the effect of MgO on CO_2 solubility.

While there are currently several models that include the effects of P, T, and silicate composition (Duan, 2014; Ghiorso and Gualda, 2015; Iacono-Marziano et al., 2012; Papale et al., 2006; Shishkina et al., 2014), they are limited by the conditions of the calibration data, and therefore limited in their ability to extrapolate beyond the conditions of the experiments. Of primary note is the fO_2 of the majority of the previous experiments, which lie between the FMQ buffer and FMQ+4 (or IW+3 to IW+8), a significantly higher fO_2 than that of a MO, i.e., the compositional dependence of these models may only be valid for vapor-silicate melt equilibria. While these fO_2 are appropriate for modern day magmatic processes (e.g., melting at mid-ocean ridges FMQ±1, and melting in subduction zones ≥FMQ), the early Earth's MO stage during or soon after core formation and metal-silicate equilibration was characterized by fO_2 several log units lower than the present day, closer to the IW buffer. One model that does consider more reducing conditions is that of Holloway et al. (1992), who combined an empirical equation for graphite oxidation as a function of P and T with the experimentally-derived thermodynamic parameters ($\ln(K^0)$, ΔV, ΔH) from Pan et al. (1991) for carbonate dissolution in a tholeiitic composition ($P = 0.1-1.5$ GPa, $T = 1170-1600\,^\circ C$) to create an equation to calculate CO_2 as a function of P, T, and absolute $\log fO_2$ over the range of $P = 0.0001$ (1 bar)–3 GPa, $T = 1000-1700\,^\circ C$, and $\log fO_2$ at or below the carbon–carbon dioxide (CCO) buffer. However, since this model was calibrated for only a tholeiitic composition, it cannot predict the CO_2 content of more ultramafic melts.

Here we performed a series of high pressure–temperature experiments on a range of compositions spanning from basalt toward the peridotite compositional field. By studying the compo-