Experimental Constraints on the Solubility and Partitioning of Carbon between Metallic and Silicate Melt in a Shallow Magma Ocean

By

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Earth Science Department

RICE UNIVERSITY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Science

APPROVED, THESIS COMMITTEE

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ABSTRACT

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The budget and origin of carbon in Earth and other terrestrial planets are debated and one of the key unknowns is the fate of carbon during early planetary processes including accretion, core formation, and magma ocean (MO) crystallization. Here we determine, experimentally, the solubility of carbon in coexisting Fe-Ni alloy melt and basaltic silicate melt in shallow MO conditions, i.e., at 1-3 GPa, 1500-1800 °C. Oxygen fugacity of the experiments, estimated based on Fe (in metallic alloy melt)-FeO (in silicate melt) equilibrium, varied between ~IW-0.4 and IW-1.0, where IW refers to the oxygen fugacity imposed by the coexistence of iron and wüstite. Four different starting mixes, each with 7:3 silicate:metal mass ratio and silicate melt NBO/T (estimated proportion of non-bridging oxygen with respect to tetrahedral cations) ranging from 0.81 to 1.54 were studied. Concentrations of carbon in the alloy melt were determined using electron microprobe whereas carbon contents of quenched basaltic glasses were determined using secondary ionization mass spectrometry (SIMS). Identification of carbon and hydrogen-
bearing species in silicate glasses was performed using Raman and Fourier Transformed Infrared (FTIR) spectroscopy.

Our results show that carbon in the metallic melt varies between 4.39 and 7.43 wt.% and increases with increasing temperature and modestly with increasing pressure but decreases with increasing Ni content of the alloy melt. Carbon concentration in the silicate melts, on the other hand, varies from 11±1 ppm to 111±7 ppm and is negatively correlated with pressure but positively correlated with temperature, the NBO/T (non-bridging per tetrahedron, an index of the depolymerization of the silicate melt), the oxygen fugacity and the water content of the silicate melts. Raman and FTIR results show that at our experimental conditions, carbon in silicate melt is dissolved both as hydrogenated species and CO$_2^-$ . The calculated carbon partition coefficient $D_{\text{metal/silicate}}^C$ varies from 510±53 to 5369±217 and varies systematically as a function of $P$, $T$, $f_{O_2}$, water content and the composition of the silicate melt. The range of $D_{\text{metal/silicate}}^C$ measured in our study with carbonated and hydrogenated carbon species in silicate melt is similar to that reported in literature for experiments where carbonyl complexes are chief carbon species in silicate melts. An empirical parameterization was derived using the data from this and existing studies such as

$$\ln[D_{\text{metal/silicate}}^C] = a/T + b \cdot P/T + c \cdot \ln(f_{O_2}) + d \cdot (\text{nbo/T}) + e$$

where $a = -39110$, $b = 1541$, $c = -0.683$, $d = -1.06$, $e = 14.102$, the temperature is in Kelvins, and the pressure is in GigaPascals. Using this parameterization and the estimated conditions for the base of the MOs, we estimate the average $D_{\text{metal/silicate}}^C$ value for Earth, Mars, and the Moon. The deep MO of Earth results in the strongest depletion of its
silicate carbon budget, followed by Mars with intermediate depth MO, and then the Moon with a shallow MO. We predict that the lunar mantle carbon budget not too dissimilar to that of the Earth’s upper mantle might have been set by equilibrium core-mantle fractionation in MO, whereas for Earth, later processes such as ingassing from proto-atmosphere and late-stage accretion of volatile-rich material was necessary for delivery of carbon and other volatiles. Finally, the comparison of our predicted value of $D_C^{\text{metal/silicate}}$ for deep terrestrial MO with similar constraints on $D_N^{\text{metal/silicate}}$ from literature suggests that the apparent depletion of nitrogen relative to carbon for the Earth’s mantle or bulk silicate Earth and the Earth’s upper mantle is unlikely to be caused by preferential partitioning of nitrogen to alloy melt during core formation.
Acknowledgments

I appreciate the supervision and the discussions from my committee: Prof. Rajdeep Dasgupta, Prof. Cin-Ty A. Lee and Prof. Adrian Lenardic and I have special thanks to Prof. Cin-Ty A. Lee for his suggestions about my career.

I also appreciate my fellow labmate Megan Duncan for her significant help on the part of FTIR as well as others. I also thank the rest of my labmates: Dr. Kyusei Tsuno, Dr. Sebastian Jego, Ananya Mallik and Shuo Ding for their suggestions, discussion and encouragement with me. Dr. Peter Luffi had extensive discussions with me through many aspects of this thesis. I thank him for his ideas and time.

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Many thanks for Kevin Righter providing the Knippa basalt powder and thanks to Brian Monteleone, Ray Guillemette, and Gang Liang for their assistance during SIMS, EPMA, and Raman analyses, respectively. The work received funding from a Packard fellowship for Science and Engineering and a NASA grant to Prof. Rajdeep Dasgupta.
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1. INTRODUCTION

Constraining the behavior of volatile elements during accretion in general and in a magma ocean in particular, is critical in understanding the initial stage for further evolution of volatile cycles in terrestrial planets. The fate of carbon during core-mantle and mantle-proto-atmosphere fractionation in a magma ocean in particular might be key because of carbon’s role in building a habitable planet and the origin of life. The origin of mantle carbon is also critical because of the element’s role on the process of partial melting in the mantle (e.g., Dasgupta, 2013; Dasgupta and Hirschmann, 2006; Dasgupta et al., 2013b; Falloon and Green, 1989; Stagno et al., 2013; Wyllie and Huang, 1976) and impacting the dynamical, geophysical, and geochemical properties of asthenosphere and lithosphere-asthenosphere transition in particular (Dasgupta et al., 2007; Dasgupta et al., 2013b). Mantle of Earth is thought to be one of the largest reservoirs of terrestrial carbon (Dasgupta, 2013; Dasgupta and Hirschmann, 2010; Javoy et al., 1982; Sleep and Zahnle, 2001) and similar argument regarding the mantle budget of volatiles in general and carbon in particular perhaps can be made for other terrestrial planets such as Mars and the Moon (Hauri et al., 2011; Lodders and Fegley, 1997; Morgan and Anders, 1979); if such a budget of mantle carbon was established during early differentiation and metal-silicate separation of planets, then planetary mantles might have started imposing a long-term control on the exospheric chemistry and climate of terrestrial planets since soon after core formation, whereas if mantle was mostly devoid of carbon during early differentiation and post-core formation, its influence on long-term climate was likely minor early on. It is also plausible that a difference in carbon partitioning behavior in a core-forming
magma ocean stage might have forced Earth to evolve differently than other terrestrial planets such as Mars (Kuramoto, 1997).

Carbon fractionation in a core-forming magma ocean was not only critical for the further geochemical evolution of the mantle-atmosphere system but also for the geochemistry and physical properties of alloy liquid outer core and for nature and properties of crystalizing inner core. This is because on one hand the presence of carbon in the alloy liquid affects the partitioning of other siderophile elements between magma ocean and alloy liquid (Jana and Walker, 1997; 1999; Wood and Halliday, 2010; Wood et al., 2013) on another carbon also affects siderophile element fractionation during crystallization of possible inner core solids (e.g., Buono et al., 2013; Chabot et al., 2006; Hayden et al., 2011). Furthermore, the presence of carbon as a light element would also affects the density and other physical properties of the outer core alloy liquid (Poirier, 1994) and possible inner core solids, especially if carbide phases are stabilized (e.g., Gao et al., 2011; Lord et al., 2009; Mookherjee, 2011; Wood, 1993). Whether iron carbides can crystallize as inner core solids also critically depends on the carbon content of the bulk core.

Partition coefficient of carbon between Fe-rich, metallic alloy melt and silicate melt, $D_{C^{metal/silicate}}$ is a key quantity that must have influenced the initial carbon budget of the silicate fraction of the terrestrial planets versus that in the metallic core (Dasgupta, 2013; Dasgupta et al., 2013a; Dasgupta and Walker, 2008; Hirschmann, 2012; Kuramoto and Matsui, 1996). However, no quantitative framework yet exists that allows prediction of $D_{C^{metal/silicate}}$ as a function of key variables relevant for core-mantle equilibration at a
magma ocean condition. Recent studies with vastly different approaches and assumptions produced disparate estimates of $D_{C}^{\text{metal/silicate}}$ relevant for terrestrial magma ocean with value as low as $\sim 9$ (Zhang and Yin, 2012) and as high as $10^4$-$10^6$ (Hirschmann, 2012), with values in between ($\sim 10^4$) (Dasgupta and Walker, 2008). Furthermore, for many of these studies, it remains unclear how the $D_{C}^{\text{metal/silicate}}$ value should vary as a function of MO conditions. Much needed experimental constraints on partitioning of carbon between multi-component, Fe-rich alloy melt and mafic-ultramafic silicate melt, $D_{C}^{\text{metal/silicate}}$, also remained scarce (Dasgupta et al., 2013a). To build on the recent experiments of Dasgupta et al. (2013a), here we present results from new high pressure experiments on the solubility of carbon in coexisting Fe-Ni alloy melt and basaltic silicate melt in order to quantify the effect of pressure ($P$), temperature ($T$), oxygen fugacity ($fO_2$), and silicate melt composition on $D_{C}^{\text{metal/silicate}}$. Using the data from this study and those available from literature, we develop an empirical parameterization that allows calculation of $D_{C}^{\text{metal/silicate}}$ as a function of magma ocean depth, temperature, oxygen fugacity, and composition. We use this parameterization to predict the nature of carbon fraction during core forming processes of the Earth, Mars, and the Moon. Our predictions of different fractionation behavior of carbon between core and mantle as a function of the difference in intrinsic conditions of magma ocean have implications on the volatile inventory and further geochemical and dynamical evolution of Earth and other terrestrial planets.
2. Methods

2.1 Starting Materials

Four different, homogeneous starting mixes, each with 7:3 silicate:metal mass ratio, with silicate melt NBO/T (estimated proportion of non-bridging oxygen with respect to tetrahedral cations) ranging from 0.81 to 1.54 were studied (Table 1). All experiments employed a metallic mix of 95 wt.% Fe-5 wt.% Ni. However, for one set of experiments, the metal-silicate mix was pre-fired at 300 °C, which led to partial oxidation of the metallic iron and enhancement of FeO in the silicate fraction and Ni in the metallic fraction (see below).

Table 1. Composition of silicate starting material

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>NiO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>NBO/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>H251</td>
<td>50.5(3)</td>
<td>0.93(3)</td>
<td>15.9(3)</td>
<td>0.03(2)</td>
<td>9.06(17)</td>
<td>0.23(3)</td>
<td>8.63(13)</td>
<td>-</td>
<td>11.2(1)</td>
<td>3.01(3)</td>
<td>0.10(3)</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>Knippa</td>
<td>40.3(1)</td>
<td>3.34(1)</td>
<td>11.0(2)</td>
<td>0.07(0)</td>
<td>11.55(9)</td>
<td>0.19(1)</td>
<td>13.75(9)</td>
<td>-</td>
<td>11.82(6)</td>
<td>3.17(5)</td>
<td>1.79(3)</td>
<td>0.81(1)</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Four different silicate mixtures that are used in this study are the following –

(1) A synthetic, tholeiitic basalt (ThB) with a relatively low NBO/T (Table 1) as used in the study of Dasgupta et al.(2013a);

(2) A synthetic basalt similar to ThB but with higher FeO* content as well as NBO/T of the silicates (Oxidized-ThB). This batch of starting materials was produced by loading
the capsules with metal-silicate mixes and then keeping the capsules in a 300 °C oven overnight before the experiments;

(3) Natural, alkalic Knippa basalt (Lewis et al., 1993) as used in many previous metal-silicate partitioning studies (e.g., Chabot et al., 2005; Dasgupta et al., 2013a; Righter et al., 2010), without dehydrating the composition (Knippa-H);

(4) Knippa basalt dehydrated at 1000 °C and \( fO_2 = \text{QFM-1} \) for 6 hours using a CO-CO\(_2\) Deltech gas mixing furnace (Knippa). For all the starting mixes except (2) the homogeneous mixtures of metal and silicate fractions were stored in a desiccator before loading into capsules and subjecting to high \( P-T \) conditions.

2.2. High Pressure-Temperature Experiments

Experiments were conducted using an end-loaded piston cylinder device at the experimental petrology laboratory of Rice University from 1 to 3 GPa and 1500-1800 °C using graphite capsules (Table 2). MgO spacers surrounded by a cylindrical graphite heater and a half-inch outer diameter BaCO\(_3\) pressure cell, wrapped in a lead foil were used to contain the capsule. The experimental pressure calibration and thermal gradient for this experimental assembly is given in Tsuno and Dasgupta (2011). During each run, temperature was monitored and controlled using a type-C thermocouple. Experiments were pressurized first at room temperature and then heated at the rate of 100 °C/min. In order to reduce porosity in the graphite capsules and prevent leakage of metallic melt, experiments were held at 900 °C, i.e., at a temperature lower than the expected
temperature of formation of Fe-Ni-C alloy melt, for 3 h then raised to the desired, nominal temperature of the experiment. The experimental durations were varied as a function of target temperatures, 1500 °C runs were held for 3 h, 1600 °C runs for 2 h, 1700 °C runs for 1 h, and 1800 °C runs for 0.5 h. All experiments were terminated by cutting off power to the heater and then slowly decompressed to recover the sample. Before extracting the graphite capsule from the assembly, its location relative to the entire pressure cell and with respect to the thermocouple was documented. Experiments were rejected if breakage of the graphite capsule lid and contamination of the experimental sample with thermocouple wires or MgO spacers were apparent.

After each experiment, recovered capsule was sectioned into two halves using a diamond saw or a wire saw and both halves were mounted in Crystal Bond® for polishing. Polished surface of one half was analyzed using Raman spectroscopy, electron microprobe, and ion microprobe (SIMS) and the other half of the sample was doubly polished for Fourier transformed infrared (FTIR) spectroscopy.
Table 2. Summary of experimental run conditions

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Silicate Composition</th>
<th>$P$ (GPa)</th>
<th>$T$ (°C)</th>
<th>$\log f_{O_2} (\Delta IW)^a$</th>
<th>$\log f_{O_2} (\Delta IW)^b$</th>
<th>NBO/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>B61</td>
<td>Oxidized-ThB</td>
<td>2.0</td>
<td>1700</td>
<td>-1.19</td>
<td>-0.60</td>
<td>1.20</td>
</tr>
<tr>
<td>B74</td>
<td>Oxidized-ThB</td>
<td>2.0</td>
<td>1800</td>
<td>-1.01</td>
<td>-0.37</td>
<td>1.22</td>
</tr>
<tr>
<td>B76</td>
<td>Oxidized-ThB</td>
<td>3.0</td>
<td>1600</td>
<td>-1.09</td>
<td>-0.44</td>
<td>1.13</td>
</tr>
<tr>
<td>B73</td>
<td>Oxidized-ThB</td>
<td>3.0</td>
<td>1700</td>
<td>-1.14</td>
<td>-0.50</td>
<td>1.21</td>
</tr>
<tr>
<td>B77</td>
<td>Oxidized-ThB</td>
<td>3.0</td>
<td>1800</td>
<td>-1.14</td>
<td>-0.47</td>
<td>1.15</td>
</tr>
<tr>
<td>B110</td>
<td>ThB</td>
<td>1.0</td>
<td>1500</td>
<td>-1.59</td>
<td>-1.02</td>
<td>0.84</td>
</tr>
<tr>
<td>B109</td>
<td>ThB</td>
<td>1.0</td>
<td>1600</td>
<td>-1.57</td>
<td>-0.97</td>
<td>0.85</td>
</tr>
<tr>
<td>B95</td>
<td>ThB</td>
<td>1.0</td>
<td>1700</td>
<td>-1.61</td>
<td>-1.02</td>
<td>0.83</td>
</tr>
<tr>
<td>B112</td>
<td>ThB</td>
<td>1.0</td>
<td>1800</td>
<td>-1.45</td>
<td>-0.81</td>
<td>0.90</td>
</tr>
<tr>
<td>B100</td>
<td>ThB</td>
<td>2.0</td>
<td>1500</td>
<td>-1.58</td>
<td>-0.91</td>
<td>0.82</td>
</tr>
<tr>
<td>B106</td>
<td>ThB</td>
<td>2.0</td>
<td>1600</td>
<td>-1.57</td>
<td>-0.88</td>
<td>0.82</td>
</tr>
<tr>
<td>B105</td>
<td>ThB</td>
<td>2.0</td>
<td>1700</td>
<td>-1.59</td>
<td>-0.93</td>
<td>0.83</td>
</tr>
<tr>
<td>B111</td>
<td>ThB</td>
<td>2.0</td>
<td>1800</td>
<td>-1.58</td>
<td>-0.93</td>
<td>0.90</td>
</tr>
<tr>
<td>B102</td>
<td>ThB</td>
<td>3.0</td>
<td>1500</td>
<td>-1.56</td>
<td>-0.95</td>
<td>0.82</td>
</tr>
<tr>
<td>G212</td>
<td>ThB</td>
<td>3.0</td>
<td>1600</td>
<td>-1.55</td>
<td>-0.87</td>
<td>0.84</td>
</tr>
<tr>
<td>B117</td>
<td>ThB</td>
<td>3.0</td>
<td>1700</td>
<td>-1.60</td>
<td>-0.95</td>
<td>0.81</td>
</tr>
<tr>
<td>B115</td>
<td>ThB</td>
<td>3.0</td>
<td>1800</td>
<td>-1.54</td>
<td>-0.84</td>
<td>0.84</td>
</tr>
<tr>
<td>B172</td>
<td>Knippa</td>
<td>1.0</td>
<td>1600</td>
<td>-1.56</td>
<td>-0.97</td>
<td>1.51</td>
</tr>
<tr>
<td>B170</td>
<td>Knippa</td>
<td>3.0</td>
<td>1600</td>
<td>-1.52</td>
<td>-0.90</td>
<td>1.44</td>
</tr>
<tr>
<td>B141</td>
<td>Knippa-H</td>
<td>1.0</td>
<td>1500</td>
<td>-1.53</td>
<td>-0.83</td>
<td>1.48</td>
</tr>
<tr>
<td>B149</td>
<td>Knippa-H</td>
<td>1.0</td>
<td>1600</td>
<td>-1.49</td>
<td>-0.77</td>
<td>1.54</td>
</tr>
<tr>
<td>B136</td>
<td>Knippa-H</td>
<td>1.0</td>
<td>1700</td>
<td>-1.53</td>
<td>-0.78</td>
<td>1.54</td>
</tr>
<tr>
<td>B135</td>
<td>Knippa-H</td>
<td>1.0</td>
<td>1800</td>
<td>-1.44</td>
<td>-0.62</td>
<td>1.50</td>
</tr>
<tr>
<td>B133</td>
<td>Knippa-H</td>
<td>2.0</td>
<td>1500</td>
<td>-1.51</td>
<td>-0.72</td>
<td>1.49</td>
</tr>
<tr>
<td>B144</td>
<td>Knippa-H</td>
<td>2.0</td>
<td>1600</td>
<td>-1.51</td>
<td>-0.75</td>
<td>1.53</td>
</tr>
<tr>
<td>B131</td>
<td>Knippa-H</td>
<td>2.0</td>
<td>1700</td>
<td>-1.56</td>
<td>-0.74</td>
<td>1.51</td>
</tr>
<tr>
<td>B134</td>
<td>Knippa-H</td>
<td>2.0</td>
<td>1800</td>
<td>-1.56</td>
<td>-0.76</td>
<td>1.43</td>
</tr>
<tr>
<td>B142</td>
<td>Knippa-H</td>
<td>3.0</td>
<td>1500</td>
<td>-1.51</td>
<td>-0.71</td>
<td>1.43</td>
</tr>
<tr>
<td>B148</td>
<td>Knippa-H</td>
<td>3.0</td>
<td>1600</td>
<td>-1.65</td>
<td>-0.84</td>
<td>1.40</td>
</tr>
<tr>
<td>B145</td>
<td>Knippa-H</td>
<td>3.0</td>
<td>1700</td>
<td>-1.52</td>
<td>-0.75</td>
<td>1.43</td>
</tr>
<tr>
<td>B143</td>
<td>Knippa-H</td>
<td>3.0</td>
<td>1800</td>
<td>-1.49</td>
<td>-0.71</td>
<td>1.45</td>
</tr>
</tbody>
</table>
a. $f_{O_2}$ with respect to the iron-wüstite (IW) buffer calculated assuming ideal solution behavior of metallic and silicate melts;

b. $f_{O_2}$ with respect to the iron-wüstite (IW) buffer calculated assuming non-ideal solution behavior of Fe in metallic melts and FeO in silicate melts.

Runs in italics are re-reported from Dasgupta et al. (2013a) with $f_{O_2}$ recalculated based on the methodology outlined in the text.

2.3. Analytical Procedure

We used electron probe microanalyzer for measuring the major and minor element compositions of coexisting metallic and silicate melts and carbon abundance of metallic melt, Raman spectroscopy to acquire information about the speciation of dissolved C-O-H species and ion probe to analyze bulk carbon concentration in the quenched silicate glasses. Below we detail the procedure for each of the analytical techniques used.

2.3.1. Electron probe microanalysis (EPMA)

Quantitative compositional analyses of major and minor element chemistry of silicate melts were carried out on a four spectrometer, Cameca SX 50 electron microprobe in Texas A&M University and the composition of coexisting metallic melts was determined using Cameca SX 100 electron microprobe in NASA-Johnson Space Center (NASA-JSC). Determination of elemental distribution and checking for potential contamination were done using an Imix Princeton Gamma Tech (PGT) energy dispersive spectrometer (EDS) coupled to the Cameca SX 50 probe. Quantitative analyses of silicate melts were carried out on carbon-coated samples using a 10-20 micron diameter electron beam, an accelerating voltage of 15 kV, beam currents of 10 nA for major (Si, Al, Fe, Mg, Ca) and volatile minor elements (Na, K) and
200 nA for non-volatile minor elements (Ti, Cr, Mn, Ni, P). An Indian Ocean basalt glass was used as analytical standard for all elements in the silicate part.

For analyzing the metallic melts, the protocol of Dasgupta and Walker (2008) and as followed in a number of recent studies (Dasgupta et al., 2009; Dasgupta et al., 2013a; Sanloup et al., 2011; Walker et al., accepted), was adopted. Carbon coat from the silicate melt analysis session was first thoroughly removed by re-polishing the samples using 0.3 micron alumina powder on a lapidary wheel and then the sample was coated with 25-30 nm thick aluminum (Al) using a CRC-150 sputter coater at Rice University. For every analytical session, samples were coated along with pure Ni metal, pure Fe metal, and experimentally-synthesized stoichiometric cementite, Fe₃C standards, to minimize the differential CKα X-ray absorption by the Al-coating between the standard and the unknown samples. To minimize carbon blank concentration, which commonly results from the sample surface contamination owing to deposition organic molecules from the sample chamber, an anti-contaminant device cooled with liquid N₂ was used. An order of magnitude improvement of the vacuum in the sample chamber was noticed because of the use of the anti-contaminant device. Analytical condition for metal melt analysis was 10 kV accelerating voltage, 90-100 nA beam current, and 30-50 micron beam diameter, and counting time of 10 s at peak and 5 s at each background. Pure Fe metal standard was analyzed to evaluate blank value of carbon at the beginning and the end of every analytical session and background carbon content, analyzed on Fe remained ~0.6 wt.%.

2.3.2. Raman Spectroscopy

Raman spectroscopy was used (1) to distinguish the glassy portion of the quenched melt pool from any possible non-glassy quenched melt with fine dendritic texture and (2) to constrain the nature of C-O-H species dissolved in the silicate glasses. A Renishaw inVia Raman microscope, housed at the Shared Equipment Authority of Rice University and equipped with a 514 nm laser was used. Using a 50× objective lens and working power of 15.6 mW, spectra in the frequency range of 200-4500 cm⁻¹ were collected with 1
cm\(^{-1}\) resolution. Spectrum at each point was accumulated five times and the exposure time was set to 30 seconds to increase the signal-to-noise ratio. For each sample, the spectra were averaged, smoothed, and the backgrounds subtracted. Characteristic peaks of CH\(_4\) were then treated with a single-peak-fitting so that peak height and full width at half maximum (FWHM) can be quantified.

2.3.3. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy, using a Thermo Nicolet Fourier Transform Infrared Spectrometer, was performed on a subset of our silicate glass samples to quantify the concentration of dissolved H\(_2\)O as OH\(^-\) and detect and quantify carbon dissolved as CO\(_3^{2-}\), if present. Experimental glasses were doubly polished to thicknesses of 150-400 μm, and cleaned with acetone before analysis. Spectra were recorded with 4 cm\(^{-1}\) resolution, from 650 to 4000 cm\(^{-1}\), averaging 128 scans. A nitrogen purge was used to eliminate atmospheric gases with backgrounds collected before every analysis. A peak attributed to water was detected at 3530 cm\(^{-1}\) (O-H stretching). Peaks attributed to dissolved carbonates were detected at 1510 and 1420 cm\(^{-1}\). The total dissolved water content of experimental glasses was determined from the intensity of O-H stretching at 3530 cm\(^{-1}\). Peak heights and areas were measured with linear backgrounds. Total dissolved carbonates of experimental glasses were determined from the intensity of the ν\(_3\) antisymmetric stretch bands of the carbonate doublets.

Dissolved volatile concentrations were quantified using the Beer-Lambert law:

\[
C_i = 100 \times M_i \times A_j / (d \rho \epsilon_j)
\]

where \(C_i\) is the concentration of volatile \(i\) in the sample, \(M_i\) is it's molecular weight (44.01 g mol\(^{-1}\) for CO\(_2\) and 18.02 g mol\(^{-1}\) for H\(_2\)O), \(A_j\) is the absorption of peak \(j\) (peak height or area measured from the spectrum in cm\(^{-1}\) or cm\(^2\)), \(d\) is the thickness of the sample (in cm), \(\rho\) is the density of the sample (in g L\(^{-1}\)), etc.
and $\varepsilon_j$ is the absorption coefficient for the peak from previous studies (in L mol$^{-1}$ cm$^{-1}$ for linear absorption coefficient and in L mol$^{-1}$ cm$^{-2}$ for integrated absorption coefficient) (Table 3) (Dixon and Pan, 1995; Dixon et al., 1995; Fine and Stolper, 1986; Jakobsson, 1997; Stolper, 1982). Absorption coefficients for the carbonate peaks were chosen based on silicate composition, i.e. basanite for the Knippa samples (Dixon and Pan, 1995) and basalt for the ThB samples (Fine and Stolper, 1986). However, using the carbonate $\varepsilon$ calculation determined by Dixon and Pan (1995), both sets of silicate compositions should have roughly the same values for $\varepsilon$, which are nearly identical to the basalt $\varepsilon$ values from Fine and Stolper (1986). Sample thickness was measured using a digital micrometer (ID-C125EXB Mitutoyo Digimatic Indicator). Sample density was an average of the calculation methods of Silver (1988), and Lange and Carmichael (1987). Density was calculated for each experiment from the average compositions of glasses determined by EPMA.
Table 3. Linear ($\varepsilon$) and integrated ($\varepsilon^*$) absorption coefficients used in this study, with compositions of glasses from which they were determined.

<table>
<thead>
<tr>
<th>Band (cm(^{-1}))</th>
<th>Species</th>
<th>$\varepsilon$ (Lmol(^{-1})cm(^{-1}))</th>
<th>Ref.</th>
<th>$\varepsilon^*$ (Lmol(^{-1})cm(^{-2}))</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>3530</td>
<td>OH, H(_2)O</td>
<td>63 a</td>
<td></td>
<td>32000 b</td>
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<tr>
<td>1420</td>
<td>CO(_3^{2-})</td>
<td>281 c1</td>
<td></td>
<td>27700 d</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>387 c2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>375 e</td>
<td></td>
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</tr>
<tr>
<td>1510</td>
<td>CO(_3^{2-})</td>
<td>284 c1</td>
<td></td>
<td>27730 d</td>
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<td></td>
<td>387 c2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>375 e</td>
<td></td>
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<table>
<thead>
<tr>
<th>wt. %</th>
<th>a</th>
<th>c</th>
<th>d</th>
<th>e</th>
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<td>46.00</td>
<td>54.55</td>
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<tr>
<td>MnO</td>
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<td>0.23</td>
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<td>0.16</td>
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<tr>
<td>MgO</td>
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<td>9.06</td>
<td>2.95</td>
<td>10.76</td>
</tr>
<tr>
<td>CaO</td>
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<td>6.96</td>
<td>11.40</td>
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<tr>
<td>Na(_2)O</td>
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<td>4.33</td>
<td>3.95</td>
<td>2.30</td>
</tr>
<tr>
<td>K(_2)O</td>
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<td>1.32</td>
<td>1.28</td>
<td>0.10</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.19</td>
<td>0.27</td>
<td>1.02</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100.15</td>
<td>99.80</td>
<td>99.19</td>
<td>97.57</td>
</tr>
</tbody>
</table>

\(^a\) Dixon et al. (1995), \(^b\) Stolper (1982), \(^c\) Dixon and Pan (1995),
\(^d\) Jakobsson et al. (1997), \(^e\) Fine and Stolper (1986)

2.3.4. **Secondary Ionization Mass Spectrometry (SIMS)**

SIMS analysis of carbon was conducted using a Cameca IMS 1280 ion microprobe at Woods Hole Oceanographic Institution. Polished samples were mounted in indium substrate in an aluminum dish and were thoroughly cleaned with Milli-Q water and were dried in a vacuum oven at ~100°C. Samples were then coated with gold (~4 nM thick), and stored under vacuum for at least 24 hours prior to be inserted in the airlock of the instrument.
A beam of $^{133}$Cs$^+$ ions with a current of 1 – 1.5 nA and with energy of 12 kV was focused to a spot of approximately 10 μm in diameter and was rastered over an area of 30 x 30 μm. Negatively charged secondary ions were accelerated to energy of 10 kV into a double-focusing mass spectrometer. A mechanical aperture was placed on the focal plane of the secondary ion optics, such that the central 15 x 15 μm area of the beam-rastered area was analyzed. A mass-resolving power (MRP) of ~6000 was used for complete separation of $^1$H$^{16}$O$^-$ from $^{17}$O$^-$ (required MRP = 4700).

During each analytical session, calibration curves for H$_2$O and CO$_2$ were obtained by replicate measurements of $^{12}$C/$^{30}$Si and $^1$H$^{16}$O/$^{30}$Si ratios in standard glasses of basaltic composition. CO$_2$ and H$_2$O concentrations in the standards were obtained by FTIR spectroscopy and/or manometry (e.g. Helo et al., 2011). The number of spots analyzed on each sample is listed in Table 2. For each spot, we had 240 s of pre-sputtering period, followed by measurements of at least 10 cycles of ion intensities. During each cycle, a sequence of $^{12}$C, $^1$H$^{16}$O and $^{30}$Si was recorded and intensity ratio of $^{12}$C/$^{30}$Si and $^1$H$^{16}$O/$^{30}$Si were converted to C and H (reported as H$_2$O) concentration using the calibration curves. Signal stability during 10 cycles of measurements was monitored carefully, since surface contamination generally produces decreasing intensities with time. For spots with intensity decrease greater than 10% were considered “contaminated” and rejected. In a selected number of samples, quenched silicate melt was composed of both glassy and dendritic matte domains (Fig. 1). To evaluate whether volatile-abundance measured from the heterogeneous, dendritic domains yield concentrations similar to those obtained from glasses, both domains were analyzed from three experiments (B142, B143, and B145). Analyzed spots from the dendritic matte always resulted in a factor of ~2-10 higher carbon contents. Hence, relatively low $D_{\text{metal/silicate}}^c$ values obtained from few non-glassy, ultramafic compositions in the study of Dasgupta et al. (2013a) may be lower bounds and in this study we only consider carbon analyses from silicate glasses for constraining bulk solubility and deriving $D_{\text{metal/silicate}}^c$. 
3. RESULTS

3.1. Texture and phase equilibrium

Experiments with all starting materials generated glassy silicate pool, in which Fe-Ni-rich alloy blobs were embedded (Fig. 1).

Figure 1: Representative back-scattered electron images of immiscible metallic and silicate melt. (a) Quenched texture of coexisting metallic and silicate melt in a graphite capsule with silicate composition ThB (Table 1) (Run no. B95: 1 GPa, 1700 °C). Under this condition, the silicate melt quenched into a glass and the metallic melt quenched into a heterogeneous mass of Fe-rich alloy (lighter domains) inter-fingered with blades of Fe-rich carbides (acicular darker domains) shown in the inset. In contrast, silicate melt with composition Knippa-H shown in (b) (Run no. B142: 3 GPa, 1500 °C) quenched into partly glassy and partly non-glassy, quenched crystal aggregates. Partly glassy and partly quenched dendritic texture of silicate melt such as in this experiment allowed us to evaluate the reliability of SIMS analysis of carbon from heterogeneously quenched, dendritic silicate matte (see text for details).

Some low NBO/T synthetic basalt samples at 3 GPa or some high NBO/T natural basalt (Knippa) at 2 and 3 GPa also produced some domains of the melt pool with quenched crystals, which is distinct from
glass by their morphology and boundaries can easily be identified dividing the quenched aggregates from glassy domains (Fig. 1b). The dendritic mattes of quenched crystals, where present, were along the interfaces between silicate glassy pool and capsule walls or alloy blobs. One experiment, B102, at 3 GPa and 1500 °C, also produced residual garnet \([\text{Ca}_{0.6}\text{Mg}_{1.5}\text{Fe}_{0.9}\text{Al}_2(\text{SiO}_4)_3]\) at the base of the capsule. Alloy melts, in all experiments, quenched into fine mass of Fe-Ni alloy interspersed by the blades of Fe-rich carbides (inset of Fig. 1a).

### 3.2. Major element composition and ‘water’ content of silicate melts

The major element composition of silicate glasses varies with pressure and temperature and deviates slightly from the composition of starting material listed in Table 1. Somewhat elevated concentrations of FeO* in the silicate melts suggests that the iron-nickel alloys are oxidized during each run. Runs with the ThB produced glasses with ~47 wt.% SiO\(_2\), ~8 wt.% MgO, ~16 wt.% Al\(_2\)O\(_3\), ~14 wt.% FeO*, which gives the NBO/T (non-bridging oxygen per tetrahedron) between 0.8 and 0.9. The experiments with Knippa basalt produced glasses with ~39 wt.% SiO\(_2\), ~13 wt.% MgO, ~11 wt.% Al\(_2\)O\(_3\), ~14 wt.% FeO* and NBO/T between 1.4 and 1.55. The ThB basalts, previously oxidized before run, produced glasses with a more varied composition of ~40-43 wt.% SiO\(_2\), ~8 wt.% MgO, ~14 wt.% Al\(_2\)O\(_3\), ~21-25 wt.% FeO* and NBO/T ~1.2.

The energy dispersive spectra from quenched crystal-bearing domains were similar to those from glassy domains; however, average major element compositions were obtained from glassy spots only.

Total H content, expressed as H\(_2\)O and measured using SIMS, for ThB is ~0.6 wt. % and for oxidized- ThB is ~0.5 wt.%. The Knippa basalts without the dehydration step (Knippa-H) have the highest H\(_2\)O contents, 1.5-2.0 wt.% and the dried Knippa basalts (Knippa) have H\(_2\)O contents of ~0.3-0.4 wt.%.
3.3. Composition of metallic melts and estimation of oxygen fugacity

The Fe content in most metallic melt is ~88 wt.% but has the lowest values in those previously oxidized samples, ranging from 86.66-87.58 wt.%. The Ni content is mostly ~5 wt.% but has the highest values in the oxidized samples, ~7 wt.% and up to 7.71 wt.%.

3.3.1. Oxygen fugacity during experiments

The oxygen fugacity, $f_{O_2}$, was calculated from the coexistence of Fe-rich metallic melt and silicate melt with finite FeO* content, using the following equilibrium –

$$\text{FeO (silicate melt) = Fe (metal alloy melt) + 0.5O}_2$$

from which the $f_{O_2}$ of the experiment relative to the $f_{O_2}$ of the iron-wüstite buffer (IW) can be expressed as

$$\Delta IW = 2\log(a_{\text{FeO}}/a_{\text{Fe}}) = 2\log(X_{\text{FeO}} \cdot \gamma_{\text{FeO}} / X_{\text{Fe}} \cdot \gamma_{\text{Fe}})$$

$a_{\text{FeO}}$ represents the activity of FeO component in the silicate melt phase; $a_{\text{Fe}}$ represents the activity of Fe component in the metallic alloy melt phase; $X_{\text{FeO}}$ and $X_{\text{Fe}}$ are the molar fractions of FeO in the silicate melt and Fe in the metallic melt, respectively; $\gamma_{\text{FeO}}$ and $\gamma_{\text{Fe}}$ are the activity coefficients of FeO in the silicate melt and Fe in the metallic melt. Oxygen fugacity calculations using both ideal ($\gamma_{\text{FeO}}$ and $\gamma_{\text{Fe}}$ are equal to 1; $f_{O_2}^{\text{ideal}}$) and non-ideal solution models ($f_{O_2}^{\text{non-ideal}}$) were performed and calculated $f_{O_2}$ values using both approaches are reported in Table 1. The $f_{O_2}$ calculations using the non-ideal solution model were performed assuming $\gamma_{\text{FeO}}$ of ~1.5 (Holzheid et al., 1997; O’Neill and Eggins, 2002). The interaction parameter approach and the method described in Ma (2001) were used to determine the activity coefficients $\gamma_{\text{Fe}}$. In this approach, interaction parameters $\varepsilon_{ij}$ were used to describe the thermodynamic behavior of each component in the metallic alloy solution and specifically Fe in our case. The activity coefficient of Fe, $\gamma_{\text{Fe}}$ with the $N$-1 solutes
(i) in a metallic solution containing \( N \) components (three in our case, i.e., Fe, Ni, and C) can be expressed as

\[
\ln \gamma_{\text{Fe}} = (\varepsilon_C^C (X_C + \ln(1-X_C)) + (\varepsilon_N^N (X_N + \ln(1-X_N)))
\]

\[
-\varepsilon_N^C X_N X_C (1+ \frac{\ln(1-X_N)}{X_N} + \frac{\ln(1-X_C)}{X_C})
\]

\[
+\varepsilon_N^C X_N X_C (1+ \frac{\ln(1-X_N)}{X_N} + \frac{1}{1-X_C}) X_C X_N (1+ \frac{\ln(1-X_C)}{X_C} + \frac{1}{1-X_N}))
\]

\[
+ \frac{1}{2} \varepsilon_N^C X_N^2 X_C^2 (\frac{1}{1-X_N} + \frac{1}{1-X_C} - 1)
\]

\[
-\varepsilon_N^C X_N^2 X_C^2 ((\frac{1}{1-X_N} + \frac{1}{1-X_C} + \frac{X_N}{2(1-X_N)^2} - 1) + (\frac{1}{1-X_C} + \frac{1}{1-X_N} + \frac{X_C}{2(1-X_C)^2} - 1)
\]

where \( \varepsilon_N^N = 0.12; \varepsilon_C^C = 12.81; \varepsilon_N^N = \varepsilon_C^C = 0.92 \), for a reference temperature of 1873 K and taken from the of Siebert et al. (2011). \( \varepsilon_i^j \) values were extrapolated to our experimental temperatures following the relationship:

\[
\varepsilon_i^j(T) = \frac{T^0}{T} \varepsilon_i^j(T^0)
\]

where \( T \) is the temperature of interest and \( T^0 \) is the temperature at which the tabulated values apply.

The \( \varepsilon_i^j \) approach takes into account the effects of temperature, but not those of pressure, due to the lack of high-pressure data. This along with the extrapolation of interaction parameters values to different temperatures is a potential source of error while calculating \( \gamma_{\text{Fe}} \).
Except the experiments that started with oxidized synthetic basalt, most runs give $f_{O_2}^{\text{ideal}} \sim \text{IW}-1.6$ and $f_{O_2}^{\text{non-ideal}} \sim \text{IW}-0.7-\text{IW}-0.8$. The oxidized synthetic basalts, in contrast, have $f_{O_2}^{\text{ideal}}$ ranging from $\text{IW}-1.19$ to $\text{IW}-1.01$ and $f_{O_2}^{\text{non-ideal}}$ ranging from $\text{IW}-0.50$ to $\text{IW}-0.37$. The absolute $f_{O_2}$ of each experiment was calculated based on the high $P-T$ calibration of the IW-buffer by Campbell et al. (2009).
Table 2. Composition of immiscible silicate and metallic melt

<table>
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<tr>
<th>Run no.</th>
<th>B61</th>
<th>B74</th>
<th>B76</th>
<th>B73</th>
<th>B77</th>
<th>B110</th>
<th>B95</th>
<th>B112</th>
<th>B100</th>
<th>B106</th>
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<td></td>
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<tr>
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<td>5/3</td>
<td>5/1</td>
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### Silicate melt

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### Metallic melt

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$\Delta C_{C_{non-ideal} - C_{ideal}}$

| 3211 (750) | 2259 (314) | 1049 (68) | 802 (116) | 575 (30) | 1476 (74) | 876 (34) | 1030 (27) | 656 (14) | 1818 (108) | 998 (108) | 820 (81) |
\( n \) is the number of measurements averaged to obtain the composition reported. For silicate melts, \( n \) of 5/3 should be read as 5 spots measured using EPMA and 3 spots measured using SIMS. All of the values are in wt.% unless otherwise stated. Values in parentheses are 1s standard deviation based on replicate analyses and given in last digit cited; 42.0(3) should be read as 42.0±0.3 wt.%.

\( \theta_{\text{metal/silicate}} \) is the partition coefficient of carbon between metallic melt and silicate melt and derived by dividing the concentration of carbon (by weight) in metallic melt measured by EPMA by the concentration of carbon (by weight) in silicate melt measured using SIMS.

\*FeO* content is determined using EPMA as \( \text{Fe}^{2+} \).

\*\*C_{\text{ideal}} \) is the calculated concentration of carbon dissolved in the silicate melts as \( \text{CO}_2 \) by using the model of Holloway et al. (1992) and oxygen fugacity based on an ideal solution assumption.

\( \delta C_{\text{non-ideal}} \) is the calculated concentration of carbon dissolved in the silicate melts as \( \text{CO}_2 \) by using the model of Holloway et al. (1992) and oxygen fugacity based on a non-ideal solution assumption.
3.4. Carbon Concentration at Graphite Saturation (CCGS) in the metallic melt

The carbon concentration in the metallic alloy melt varies from ~4.5 wt.% to 7.5 wt.% and at a given pressure, C content in alloy melt increases with increasing temperature (Figure 2), similar to the estimates of C solubility in pure Fe-melt by Chipman (1972), Wood (1993), and Siebert et al. (2011). However, the 1σ error in absolute C concentration, based on replicate microprobe analyses, remains high owing to heterogeneity in the quench aggregates and within error one may argue for a very small temperature dependence on C solubility over this temperature interval of 1500 to 1800°C, similar to the data set of Dasgupta and Walker (2008). We note, however, following the argument of Dasgupta et al. (2013a), that the absolute carbon contents in the Fe-Ni alloy melt measured in this study is likely a better representation of C-solubility owing to the fact that the metal melt blobs are isolated from the graphite capsules by silicate melt pool and hence the bias of over or undersampling of quenched graphite is minimized.

For most of our isothermal experimental series, pressure also appears to have a modest positive effect on carbon solubility; however, 1800 °C experiments with Knippa-H composition and 1500 °C experiments with ThB composition appears to inconsistent with this observation (Figure 2). The partial lack of clarity of the pressure effect on solubility in this study is owing to the fact that the pressure range of our study is too small and recent study with somewhat wider range of pressure produced better resolved positive effect of pressure on carbon solubility in Fe-rich alloy melt (Dasgupta et al., 2013a). Similar to the observation Dasgupta et al. (2013a), our dataset also shows a decrease in carbon solubility with increasing Ni content of alloy melt. For example, at
same $P$-$T$, oxidized-ThB-experiments yield metallic melt with higher Ni and lower C content whereas ThB-experiments with somewhat lower Ni content in the alloy melt yield greater average C solubility. In Figure 3 we show how at each pressure of 1, 2, and 3 GPa, the carbon solubility in the alloy melt varies as a function of Ni content of the alloy.

**Figure 2:** Carbon concentrations in graphite-saturated, Fe-rich metallic alloy melts as a function of temperature at different pressures. (a) Alloy melts in equilibrium with synthetic basalt ‘ThB’ and oxidized synthetic basalt ‘Oxidied-ThB’ and (b) alloy melts equilibrated with hydrated and dehydrated Knippa basalts, i.e., ‘Knippa-H’ (this study) and ‘Knippa’ (Dasgupta et al., 2013a).
Figure 3: Carbon contents in graphite-saturated, Fe-Ni-C alloy melt as a function of Ni content of alloy melt at (A) 1 GPa, (B) 2 GPa, and (C) 3 GPa. At each pressure the data are grouped by temperature. Data come from this study and from Dasgupta et al. (2013a). We note that apart from the outlier of 3 GPa, 1500 °C datum, which shows too low C-solubility at a relatively low Ni content of the alloy melt, C solubility diminishes with increasing Ni content. Also, at a given Ni content and pressure, C solubility increases with increasing temperature.
3.5. Carbon concentration at graphite saturation (CCGS) in the silicate melt

The carbon concentration at graphite saturated (CCGS) in the silicate melts increases with temperature, depolymerization index of the silicate network (NBO/T), and water content of the silicate melt, and decreases with pressure (Figure 4 and 5). For example, at 2 GPa, with the increase of temperature from 1500 to 1800 °C, the CCGS of ThB composition increases from 12±1 ppm to 33±1 ppm. Similarly, at 2 GPa, the CCGS of the Knippa-H composition increases from 43.7±0.5 ppm to 110±2 ppm as the temperature increases from 1500 to 1800 °C. At a fixed temperature, for example at 1500 °C, the CCGS of ThB composition decreases from 14.71±0.05 ppm to 9.1±0.1 ppm as the pressure increases from 1 to 3 GPa. Similarly, for the Knippa-H composition, with pressure increase from 1 to 3 GPa at 1500 °C, the CCGS decreases from 55±4 ppm to 36±2 ppm. These trends are similar to those observed in the study of Dasgupta et al. (2013a).

In addition to the effect of P and T, the present study also documents that CCGS increases with increasing oxygen fugacity. The oxidized-ThB compositions ($f_{O_2}^{\text{non-ideal}} \sim \text{IW-0.37–IW-0.6}$) have systematically higher CCGS than the ThB compositions ($f_{O_2}^{\text{non-ideal}} \sim \text{IW-0.81–IW-1.02}$). For example, at 1700 °C and 2 GPa, the CCGS in the oxidized-ThB is 92±9 ppm, while at the same P-T condition, non-oxidized ThB composition contains 20±2 ppm C. Similarly, at 1800 °C and 3GPa, the carbon content of graphite-saturated oxidized-ThB (Run No. B77) is 58±3 ppm, which is distinctly higher than 27±4 ppm, the CCGS in the non-oxidized ThB.
Figure 4: Carbon concentrations at graphite saturation in the silicate melt from our starting materials. (a) tholeiitic basalt, ‘ThB’ and oxidized tholeiitic basalt, ‘ThB-oxidized’, (b) water-rich, alkalic basalt, ‘Knippa-H’ and water-poor, alkalic basalt, ‘Knippa’ from Dasgupta et al. (2013a).
Figure 5: Carbon concentrations at graphite saturated silicate melt from our starting materials (ThB, Oxidized-ThB, and Knippa-H) versus NBO/T, a melt depolymerization index. Also plotted for comparison are bulk carbon analysis from the study of Dasgupta et al. (2013a), i.e., compositions Knippa, MAR, and MT-7C.
3.6. Speciation of C-O-H volatiles

3.6.1. Results of Raman spectroscopy

Raman spectra were collected from the glassy domains of all samples to constrain the speciation of dissolved carbon-bearing species in general and especially to detect those that are IR-inactive in particular. The presence or absence of various Raman-active volatile species were confirmed by comparing the locations of peaks with the frequencies of characteristic vibrations of those species found from literature (Bley et al., 1997; Brooker et al., 1999; Kadik et al., 2004; Mysen et al., 2009; Mysen and Yamashita, 2010; Socrates, 2011; Wetzel et al., 2013).
Figure 6: Average Raman spectra of graphite-saturated silicate melts with different starting compositions. (a) Isobaric experiments at 1 GPa and variable temperatures with tholeiitic basalt, ThB, (b) isobaric experiments at 2 GPa and variable temperatures with water-rich alkali basalt, Knippa-H, (c) isothermal experiments at 1600 °C and variable pressures with water-rich (Knippa-H) and water-poor (Knippa) alkalic basalt (Dasgupta et al., 2013a) at 1 and 3 GPa. Vertical dashed lines mark the wave numbers for characteristic peaks of various volatile species based on Socrates (2004). Panel (d) shows peak heights as a function of temperature for 2917 cm⁻¹ peak, which is thought to represent dissolved molecular CH₄ or methyl group bonded to silicate network.
In our silicate glass, the Raman spectra are featured by three highly visible peaks at wavenumbers 400-600 cm\(^{-1}\), 600-800 cm\(^{-1}\) and 800-1150 cm\(^{-1}\) in the low frequency range, which could be observed in all aluminosilicate glasses (Figure 6a, b and c; Kadik et al., 2004). However, the exact frequencies and the intensities of the framework vibration bands vary significantly based on glass composition (Kadik et al., 2004; Neuville and Mysen, 1996). The three peaks of silicate glass with ThB (Figure 6a) composition are at ~519 cm\(^{-1}\), ~732 cm\(^{-1}\) and ~984 cm\(^{-1}\), respectively. Among them, the ~984 cm\(^{-1}\) is much sharper and more prominent than the other two. The three peaks of silicate glass with Knippa-H composition (Figure 6b and 6c), however, are at ~571 cm\(^{-1}\), ~768 cm\(^{-1}\) and ~955 cm\(^{-1}\). Both of ~768 cm\(^{-1}\) and ~955 cm\(^{-1}\) peaks are tall but the ~571 cm\(^{-1}\) appears more compressed. Brooker et al. (1999) also suggested the presence of Fermi doublet of molecular CO\(_2\), at ~1380 cm\(^{-1}\) and ~1268 cm\(^{-1}\), which is not found in any of our silicate glass. Brooker et al. (1999) assigned a peak at ~1075 cm\(^{-1}\) for carbonate groups, which was not detected in our samples either. However, the visibility potential of carbonate peak has to be diminished by the most striking peak of silicate frameworks appearing in this range.

In the high frequency range, the most striking peak is the asymmetric one of H\(_2\)O or OH\(^{-}\) at ~3600 cm\(^{-1}\), with peak height clearly positively correlated with the bulk H contents measured using SIMS (Fig. 6c). Mysen et al. (2009) observed two additional peaks in the high frequency range that he assigned to carbon bearing species, the one of alkyne group at ~3300 cm\(^{-1}\) and the other of methane or methyl group at ~2900 cm\(^{-1}\). Both of these peaks are observed in our samples within this range. The ~2900 cm\(^{-1}\) peak heights are plotted in Figure 5d and it can be observed that they correlate positively with
temperature and total hydrogen content (e.g., Knippa-H experiments at a given P-T produce greater peak heights for CH₄ than the Knippa experiments) and negatively with pressure.

3.6.2. Results of FTIR spectroscopy

Our experiments were not designed to yield systematic FTIR data. In particular, preparing doubly polished thin sections from intimately mixed metal-silicate assemblages posed significant challenge. Yet we obtained FTIR data for a subset of our experimental glasses from this study and the study of Dasgupta et al. (2013a) covering all the compositions and under similar $P$-$T$-$f_{O_2}$ conditions (Fig. 7; Table 5). The FTIR spectra confirm that all of our experimental glasses are variably water-bearing with strong asymmetric peaks at ~3500 cm$^{-1}$ indicating that water is primarily dissolved as OH. Very small doublets for CO$_3^{2-}$ have been observed at 1420 and 1510 cm$^{-1}$ for both Knippa and ThB compositions, with Knippa compositions showing stronger peaks for carbonate-doublets than those observed for ThB (Fig. 7). However, no discernible peak for Fe-carbonyl was observed at 2110 cm$^{-1}$, similar to the findings of Wetzel et al. (2013).

Comparison of total H contents, determined using SIMS with H$_2$O contents determined using FTIR suggests that for ThB, oxidized-ThB, and Knippa the entire budget of hydrogen are, within error, present as dissolved hydroxyl/water (Table 4 and 5). Whereas for Knippa-H, total hydrogen determined using SIMS (Table 4) clearly exceeds those accounted for by dissolved hydroxyl alone (Table 5), suggesting the possibility of the presence of molecular hydrogen and/or methane in these samples, with
the presence of the latter being consistent with the Raman spectroscopic observation mentioned above.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Comp.</th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>H₂O (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>H (ppm)</th>
<th>CO₃⁻&lt;sup&gt;b&lt;/sup&gt; (ppm)</th>
<th>C (ppm)</th>
<th>CO₂&lt;sup&gt;c&lt;/sup&gt; (ppm)</th>
<th>C (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B109</td>
<td>ThB</td>
<td>1.0</td>
<td>1600</td>
<td>0.49 (2)</td>
<td>274 (11)</td>
<td>4 (3)</td>
<td>1.0 (9)</td>
<td>5 (4)</td>
<td>1.4 (12)</td>
</tr>
<tr>
<td>B112</td>
<td>ThB</td>
<td>1.0</td>
<td>1800</td>
<td>0.50 (1)</td>
<td>279 (8)</td>
<td>36 (10)</td>
<td>9.6 (27)</td>
<td>48 (13)</td>
<td>13.1 (36)</td>
</tr>
<tr>
<td>G212</td>
<td>ThB</td>
<td>3.0</td>
<td>1600</td>
<td>0.51 (0)</td>
<td>284 (1)</td>
<td>2 (3)</td>
<td>0.5 (7)</td>
<td>2 (4)</td>
<td>0.6 (10)</td>
</tr>
<tr>
<td>B149</td>
<td>Knippa-H</td>
<td>1.0</td>
<td>1600</td>
<td>0.99 (4)</td>
<td>554 (22)</td>
<td>41 (10)</td>
<td>11.1 (27)</td>
<td>51 (16)</td>
<td>13.8 (44)</td>
</tr>
<tr>
<td>B135</td>
<td>Knippa-H</td>
<td>1.0</td>
<td>1800</td>
<td>1.10 (9)</td>
<td>613 (51)</td>
<td>51 (16)</td>
<td>13.8 (44)</td>
<td>114 (21)</td>
<td>31.0 (56)</td>
</tr>
<tr>
<td>B172</td>
<td>Knippa</td>
<td>1.0</td>
<td>1600</td>
<td>0.22 (2)</td>
<td>121 (9)</td>
<td>17 (5)</td>
<td>4.7 (13)</td>
<td>23 (6)</td>
<td>6.3 (18)</td>
</tr>
<tr>
<td>B170</td>
<td>Knippa</td>
<td>3.0</td>
<td>1600</td>
<td>0.16 (1)</td>
<td>91 (8)</td>
<td>26 (3)</td>
<td>7.1 (8)</td>
<td>34 (4)</td>
<td>8.4 (11)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Water concentrations were calculated using absorption coefficients from Dixon et al. (1995) given in Table 3.

<sup>b</sup>CO₃⁻ concentrations were calculated as CO₂ using basalt absorption coefficients from Fine and Stolper (1986) given in Table 3.

<sup>c</sup>CO₂ concentrations were calculated as CO₂ using basanite absorption coefficients from Dixon and Pan (1995) given in Table 3.

For errors given in parentheses are based on spot to spot variation in FTIR analyses and given as last digit cited; for example, 0.20 (2) wt.% should be read as 0.20 ± 0.02 wt%. Major element compositions and CCGS of the runs in italics were reported in Dasgupta et al. (2013a).
Figure 7: FTIR spectra of silicate glasses from a subset of our experiments and those from Dasgupta et al. (2013a) covering different basalt compositions and hydration but similar P-T-\( f_\text{O}_2 \) conditions. (B) and (D) show the spectral range shaded in (A) and (C) to highlight the carbonate doublets.
4. DISCUSSION

4.1. Mechanisms of Carbon’s solution in the silicate melt

The mechanism of carbon dissolution in the silicate melt is critical to understand the variation of CCGS or bulk carbon solubility at graphite saturation with oxygen fugacity, melt NBO/T, water content of silicate melt, and pressure and temperature. Because carbon solubility is affected by carbon speciation, the latter also affects partition coefficient of carbon between alloy melt and silicate melt.

Previous studies have documented that carbon dissolves as carbonate ions in basalts under oxidized condition (e.g., log $f_O_2$ ~QFM±2) but solubility of carbonates decreases with decreasing oxygen fugacity (Holloway et al., 1992; Pawley et al., 1992) and under core-forming, reduced magma ocean, carbon solution may be dominated by other reduced species such methane, methyl groups, polyyne, and carbonyl (Ardia et al., 2013; Dasgupta et al., 2013a; Mysen et al., 2009; Wetzel et al., 2013). A key question is what were the relative proportions of different carbon-bearing species dissolved in MO of terrestrial planets and how they varied as a function of various intensive variables.

To constrain the relative contributions of carbon dissolved as $CO_3^{2-}$ versus carbon dissolved as methane (-CH$_3$) or alkyne (C$_n$H$_{2n-2}$) or other species in our glasses we compared the bulk carbon contents measured using SIMS with $CO_3^{2-}$ contents estimated using (1) FTIR and (2) the model of Holloway et al. (1992), which can be used to predict the solubility of $CO_3^{2-}$ in basalts at graphite-saturated conditions, as function of $P$-$T$-$f_O_2$. 

Figure 8: (a) Calculated carbon concentrations dissolved as $\text{CO}_3^{2-}$ in the silicate, based on the calibration of Holloway et al. (1992) and using the $f_{O_2}$ estimates based on the non-ideal solution assumption (see text) versus total carbon concentration, i.e., bulk CCGS, determined using SIMS. (b) Carbon concentrations dissolved as $\text{CO}_3^{2-}$ as determined using in a subset of our experiments and from those reported in Dasgupta et al. (2013a) (Table 4) versus the bulk CCGS measured using SIMS. The black line marks the locus where the total carbon content and those dissolved as carbonates are estimated to be equal. Both (a) and (b) suggest that there are other carbon species present besides $\text{CO}_3^{2-}$ that contribute to total carbon solubility at graphite saturation in metal-saturated, reduced (<IW) MOs.
From the positive correlation between carbonate solubility and NBO/T (non-bridging oxygen per tetrahedron – a depolymerization index of silicate melts) (Brooker et al., 2001) might suggest that at similar conditions, dissolved \( \text{CO}_3^{2-} \) may contribute more to the CCGS for more depolymerized compositions. The thermodynamic model of Holloway (1992), however, was not developed to factor in any melt compositional effect on \( \text{CO}_3^{2-} \) solubility at graphite saturation. Our limited FTIR data, however, do indicate that under similar conditions Knippa compositions (NBO/T ~1.4) have higher \( \text{CO}_3^{2-} \) compared to those in ThB (NBO/T ~0.8) (Table 5). For example, at 1 GPa and 1600 °C graphite saturated ThB contains only ~1.4 ppm C dissolved as \( \text{CO}_3^{2-} \), whereas at the same \( P-T \), Knippa contains 6.3 ppm C dissolved as \( \text{CO}_3^{2-} \). Furthermore, Knippa composition with greater water content (Knippa-H: ) but the same condition contains even greater proportion of carbon, i.e., 13.8 ppm C, dissolved as \( \text{CO}_3^{2-} \). Therefore, these data suggest that even under reduced conditions more depolymerized mafic-ultramafic melts likely dissolve more \( \text{CO}_3^{2-} \) compared to tholeiitic basalts and greater amount of water in basaltic melt enhances \( \text{CO}_3^{2-} \) dissolution similar to those documented at more oxidized conditions for a wide variety of silicate compositions (Duncan and Dasgupta, in press; Eggler and Rosenhauer, 1978).

Although the available FTIR data indicate that only a fraction of total dissolved carbon is \( \text{CO}_3^{2-} \), because we do not have reliable FTIR data from all our samples, we also employed the Holloway et al. (1992) model to estimate the proportion of dissolved
in all our experimental glasses. Carbon dissolved as carbonates is expected to increase with temperature and oxygen fugacity and decrease with pressure, similar to what we observe in our total dissolved carbon. However, our total C contents, measured using SIMS, remain higher than those as carbonates alone derived from the Holloway et al. (1992) model (Fig. 8A). This is consistent with our Raman spectra where we find evidence of hydrogenated carbon species, such as CH₄ or methyl group and alkyne groups in our glasses.

One of the chief uncertainties of the Holloway et al. (1992) model, however, is that there needs to be an independent $f_{O_2}$ estimate to calculate $CO_3^{2-}$ solubility at graphite saturation at a given P-T. Comparison of total carbon versus those as carbonates estimated using the non-ideal solution assumption suggests that ~15.2-15.5% of total carbon in the Knippa basalts, ~10.9-64.0% of total carbon in Knippa-H basalts, ~33.1-87.6% of total carbon in ThB basalts, and ~34.3%-96.1% of total carbon in oxidized-ThB basalts can be in the form of dissolved $CO_3^{2-}$ (Fig. 8A). However, if we use the $f_{O_2}$ estimates based on the ideal solution model, the contribution of $CO_3^{2-}$ to the total dissolved C becomes significantly smaller (Table 2). Our limited FTIR data suggest that the true concentrations of $CO_3^{2-}$ may be somewhere in between those estimated using $f_{O_2}$ estimates based on non-ideal and ideal solution model for melts. This suggests that the proportion of $CO_3^{2-}$ relative to the total dissolved carbon in terrestrial MOs, i.e., at reduced conditions ($f_{O_2} \leq IW-1$), may be small but non-negligible and $CO_3^{2-}$ may
contribute as much as 5-25% for relatively dry tholeiitic basalt and alkali basalt whereas as much as 12-24% for alkali basalts with high \( f_{\text{H}_2\text{O}} \) and \( f_{\text{H}_2} \) (Fig. 8B; Table 5).

4.2. Partition coefficient of carbon between metallic alloy melt and silicate melt

By combining the results of carbon concentration in the metallic and the silicate melt, we calculate partition coefficients of carbon between metallic alloy melt and silicate melt, \( D_{\text{C}}^{\text{metal/silicate}} \). Experimental \( D_{\text{C}}^{\text{metal/silicate}} \) in the present study varies from 510±53 (Run no. B74, oxidized synthetic basalt, 2 GPa, 1800 °C) to 5369±217 (Run no. B102, hydrated Knippa basalt, 3 GPa, 1500 °C). It increases with increasing pressure, but decreases with increasing temperature, silicate melt NBO/T, oxygen fugacity, and water content of the silicate melts (Figure 9).

\[ \text{Figure 9: Partition coefficient of carbon between metallic melt and silicate melt, } D_{\text{C}}^{\text{metal/silicate}} \text{ plotted as a function of temperature. (a) 70 wt.% ThB + 30 wt.% Fe-Ni mix and oxidized aliquot of 70 wt.% ThB + 30 wt.% Fe-Ni mix. (b) 70 wt.% Knippa-H + 30 wt.% Fe-Ni mix and 70 wt.% Knippa + 30 wt.% Fe-Ni mix.} \]
There is no particular correlation of $D_{\text{metal/silicate}}^C$ observed with metallic melt carbon content for a given silicate melt composition. $D_{\text{C}}^\text{metal/silicate}$, however, shows a strong negative correlation with carbon content in silicate melt, i.e., it decreases exponentially with increasing carbon in silicate melt (Figure 10).

**Figure 10:** Experimental $D_{\text{C}}^\text{metal/silicate}$ values from this study and previous studies (Dasgupta et al., 2013a) as a function of carbon content in the silicate melt.
Given the fact that $D_{C}^{\text{metal/silicate}}$ scales with CCGS, one of the key considerations is how relevant our CCGS values are as they depend in turn on the speciation of C in the melt. In our experimental glasses, C is dissolved as a mixture of $\text{CO}_3^{2-}$, molecular $\text{CH}_4$ or $\text{CH}_3$, and possibly CO in the more oxidized (Oxidized-ThB) experiments. Therefore, we believe that our $D_{C}^{\text{metal/silicate}}$ values and the parameterization developed below are applicable to a wide range of MO conditions and carbon speciation and the parameterization likely works even if the dominant species of carbon is other clusters such Fe-carbonyl (Wetzel et al., 2013).

4.2.1. Parameterization of $D_{C}$

Our experiments were conducted over a limited range of $P$-$T$-$fO_2$-composition space and magma ocean of terrestrial planets extend to much more extreme conditions, particularly in terms of depth, temperature, and silicate melt composition. Therefore, in order to apply our partitioning data to magma ocean of Earth and/or other planetary bodies, a quantitative parameterization is needed such that a reasonable extrapolation can be made.

An empirical parameterization was derived using the data from this study and those from Dasgupta et al. (2013a). Because carbon analyses in heterogeneously quenched dendritic matte have larger uncertainty, experiments with only glassy silicate melt pool were taken from the study of Dasgupta et al. (2013a). The following equation describes,
within ~5% error bounds, the average $D_{\text{metal/silicate}}$ values measured in a total 31 experiments (Figure 9; 25 new experiments reported in this study and 6 from the study of Dasgupta et al. (2013a).

$$\ln[D_{\text{metal/silicate}}] = a/T + b \cdot P/T + c \cdot \ln(fO_2) + d \cdot (\text{nbo}/T) + e \quad \text{(Eqn. 1)}$$

where $a = -39110$, $b = 1541$, $c = -0.683$, $d = -1.06$, $e = 14.102$, the temperature is in Kelvins, and the pressure is in Giga Pascals.

### 4.2.2. Average $D_C$ for core-forming magma oceans of terrestrial planets

The experimental constraints and the predictive model for $D_{\text{metal/silicate}}$ developed here allow us to constrain the applicable $D_{\text{metal/silicate}}$ value for metallic alloy liquid-silicate liquid equilibrium at the base of the magma ocean estimated for various terrestrial planets. Table 6 gives the average conditions of base of the magma ocean or the final depth and conditions of metal-silicate equilibria for Earth, Mars, and the Moon based on non-volatile siderophile element partitioning experiments (Rai and Van Westrenen, 2012; Righter, 2011; Righter and Chabot, 2011). We note that the depth of the base of the magma ocean as estimated for Earth vary widely from one study to another and estimates range from pressure as low as ~25 GPa to as high as 60 GPa (e.g., Kegler et al., 2008; Li and Agee, 1996; Righter, 2011; Rubie et al., 2011; Siebert et al., 2012). We do not prefer one literature estimate over the other for Earth. The main purpose is to illustrate the difference in predicted $D_{\text{metal/silicate}}$ value as the depth of the magma ocean varies from very deep (Earth) to very shallow (the Moon) through intermediate depth (Mars); no matter
which literature estimate is chosen, the terrestrial magma ocean is predicted to be deeper compared to those of other terrestrial planetary bodies. Using the $P$, $T$, $fO_2$, and silicate melt composition (NBO/T) for different MOs, we estimate $D_{C^{metal/silicate}}$ applicable for terrestrial MO to be $\sim 10^5$, for martian MO to be $\sim 10^4$, and for lunar MO to be $\sim 10^2-10^3$ (Table 6).
Table 6. The conditions at the base of the magma ocean and the predicted $D_{\text{metal/silicate}}$ for terrestrial planets

<table>
<thead>
<tr>
<th></th>
<th>$T$(K)</th>
<th>$P$(GPa)</th>
<th>log $f_{O_2}$</th>
<th>NBO/T</th>
<th>Reference</th>
<th>$D_{\text{metal/silicate}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Earth</td>
<td>3300-3600</td>
<td>27-33</td>
<td>IW-1-IW-2</td>
<td>2.74</td>
<td>Righter (2011)</td>
<td>$(1.12\pm0.91)\times10^5$</td>
</tr>
<tr>
<td>The Moon</td>
<td>2100-2200</td>
<td>3.5-4</td>
<td>IW-1.5</td>
<td>2.8</td>
<td>Rai and van Westrenen (2012)</td>
<td>$(9.03\pm0.05) \times10^2$</td>
</tr>
<tr>
<td>Mars</td>
<td>1900-2300</td>
<td>11-17</td>
<td>IW-1.5</td>
<td>2.55</td>
<td>Righter and Chabot (2011)</td>
<td>$(4.25\pm1.46) \times10^4$</td>
</tr>
</tbody>
</table>
4.3. Partitioning of carbon between core and mantle in magma oceans of various terrestrial planets

4.3.1. Equilibration with metal:silicate ratio similar to the respective core:mantle mass ratio – implications for mantle and core carbon budget

The predicted, average values of $D_{\text{metal/silicate}}^C$ for MOs of Earth, Mars, and the Moon have important implications for the origin and evolution of carbon geochemistry in these three planetary bodies.

*Earth:* The high $D_{\text{metal/silicate}}^C$ value for deep MO of Earth suggests that for a similar metal:silicate ratio relevant for early differentiation and for similar degree of metal-silicate equilibration, carbon would be most efficiently sequestered in the core of Earth compared to those for Mars or the Moon. In other words, for a similar bulk carbon content and metal:silicate ratio of equilibration, Earth’s mantle would be most depleted in carbon after core formation, followed by the mantle of Mars, and then the mantle of the Moon.
Figure 11: Measured $\ln[D_{\text{metal/silicate}}]$ values versus calculated $\ln[D_{\text{metal/silicate}}]$ values based on the parameterization developed in this study. The solid line is the 1:1 line and the dashed lines mark the 5% error bounds. The experimental $D_{\text{metal/silicate}}$ data are from Dasgupta et al. (2013a) and this study. To minimize uncertainty in the parameterization, experiments with only glassy melt pool are taken from the study of Dasgupta et al. (2013a).

Figure 11 shows that for a perfect equilibration between the segregating metallic liquid and magma ocean silicate liquid and for metal:silicate ratio of the equilibrium similar to the present-day core:mantle mass ratio, Earth’s bulk silicate might have become virtually carbon-free after core formation. This is especially true, if bulk Earth
carbon content during core formation was \(\leq 1000\) ppm (Marty, 2012; McDonough, 2003). This prediction is in agreement with the recent suggestions on the nature of core-mantle carbon fractionation, although the extent of mantle carbon depletion predicted based on \(D_C^{\text{metal/silicate}}\) predicted for deep MO is even more extreme than that shown in previous literature based on experimental data solely at moderate pressures (Dasgupta, 2013; Dasgupta et al., 2013a). For the bulk Earth carbon content of 730 ppm (McDonough, 2003), equilibrium partitioning of carbon between whole mantle and core leaves the mantle with only 0.06±0.06 ppm, which is at least 2-3 orders of magnitude lower than the present-day estimate of the mid-ocean ridge basalt source regions (Cartigny et al., 2008; Dasgupta and Hirschmann, 2010; Saal et al., 2002). Because the bulk Earth carbon content during core formation is largely unknown the extent of deficit cannot be pinned down with certainty. However, our predicted \(D_C^{\text{metal/silicate}}\) value suggests that even with CI-chondritic content of carbon in the whole mantle MO (3.5 wt.% C) with core:mantle mass ration of equilibration results in far less carbon than what is in the present-day terrestrial mantle.

**Mars:** Because the estimated depth of the martian MO is shallower than that of Earth (Rai and van Westrenen, 2013; Righter and Chabot, 2011), the predicted \(D_C^{\text{metal/silicate}}\) value is less extreme (Table 6). Hence after equilibrium between alloy melt and silicate melt in mass ratio similar to the core:mantle mass ratio of Mars, post-core-formation martian mantle would contain 0.09 ± 0.04 ppm C, if the bulk Mars carbon content is also assumed to be similar to that of Earth, i.e., 730 ppm. Bulk Mars carbon budget is highly uncertain and estimate varies from value as low as ~16 ppm (Morgan and Anders, 1979) to as high
as 2960 ppm (Lodders and Fegley, 1997). If 16 ppm carbon participated in core-mantle equilibration in a magma ocean, then the mantle of Mars after core formation would have had ~0.001 ppm C whereas if the bulk Mars carbon that participated in the magma ocean fractionation was ~2960 ppm, then the Martian mantle would attain carbon content of 0.36 ± 0.17 ppm. We note that even this latest concentration is 1-2 orders of magnitude lower than the similar estimate for the depleted upper mantle of the Earth (7-30 ppm C; Saal et al., 2002; Cartigny et al., 2008; Hirschmann and Dasgupta, 2009). The carbon content of the martian mantle is not particularly constrained and the available carbon content data for martian meteorites (shergottites and Chassigny) are widely variable, i.e., 1-100 ppm (Grady et al., 2004; Grady and Wright, 2006). Extrapolating carbon concentration from meteorites to martian mantle remains problematic because most meteorites contain variable extent of cumulate minerals and thus bulk carbon content does not represent magmatic liquid concentration. However, given the abundance of water and carbon in the Earth’s mantle are not too dissimilar with CO₂:H₂O mass ratio of 0.55 ± 0.20 (Hirschmann and Dasgupta, 2009), one may gain some insight into the possible range of martian mantle carbon abundance from estimates of martian mantle water contents.

Earlier estimates, based on mineral and bulk rock analyses suggested that martian interior is water-poor (e.g. Leshin et al., 1996; Wänke and Dreibus, 1994). However, more recently, McCubbin et al. (2012), from hydroxyl content of apatites, estimated that the mantle source region of depleted shergottite QUE 94201 contains 73-210 ppm H₂O and that of enriched shergottite shergotty contains 160-290 ppm H₂O. These values are also only slightly higher than the water content estimates for the mantle source of
shergottite NWA 6324 (Gross et al., in press) and similar to the mantle source of
Chassigny meteorite (140-250 ppm H\(_2\)O) (McCubbin et al., 2010a). Thus if one assumes
that CO\(_2\):H\(_2\)O ratios of the terrestrial and martian mantle are similar, the C content of the
martian mantle becomes 10-44 ppm. This carbon budget remains significantly higher
compared to the carbon budget that could be derived from the whole mantle MO alloy-
silicate equilibration.

The Moon: Lunar MO was the shallowest among all the planetary bodies considered
here (Table 6) and high temperature, low-pressure condition of the base of the lunar
magma ocean as estimated in literature (Rai and van Westrenen, 2012) suggests that
carbon behaves only as a moderately siderophile element at these conditions (Table 6).
With 5% by mass of metallic core melt equilibrating with the mantle, the lunar mantle is
estimated to retain as much as 15.8 ± 0.1 ppm C, if 730 ppm C participated in the core-
mantle fractionation. Even if the bulk Moon had only 100 ppm C during early
differentiation, mantle would retain ~2.2 ppm C after core segregation. Therefore, our
prediction of moderately siderophile nature of carbon in the lunar magma ocean leads to
the suggestion that even a relatively volatile-poor bulk Moon can result in a lunar mantle
with carbon budget similar or close to that of the modern terrestrial mantle. Carbon
budget of the present-day lunar mantle is poorly constrained; however, we can adopt a
similar approach as discussed for Mars to use the H\(_2\)O estimate of the lunar mantle to
gain a possible insight into the carbon budget.

The water content estimate for the mantle of the Moon varies from as low as 64 ppb
– 5 ppm (McCubbin et al., 2010b) to as high as 79-409 ppm H\(_2\)O (Hauri et al., 2011). The
combination of the low-end of H₂O content with CO₂:H₂O ratio of 0.55 yields C abundance of ~10 ppb to 0.75 ppm. Whereas the use of the higher-end of the H₂O abundance yields C abundance of 12-61 ppm. Our estimate of $D_{C_{\text{metal/silicate}}}$ relevant for the Moon suggests that low to intermediate values of this carbon content range, i.e., 1-5 ppm C in the lunar mantle, would require $\leq 100$ ppm C in the bulk Moon. Therefore we suggest that one way the lunar mantle might have achieved its carbon budget is through less extreme partitioning of carbon into the segregating metallic core over the molten silicate although the bulk Moon might have been significantly depleted in carbon over that of the bulk Earth.
**Figure 12:** The effect of equilibrium partitioning of carbon between metallic and silicate melt in a MO on the inventory of mantle and core carbon of (a) Earth, (b) Mars, and (c) the Moon. The calculation assumes that the inventory of carbon in the planetary bulk silicate and the planetary bulk metallic core reflects perfect equilibration of the present-day mass of the core with the mass of silicate. Carbon concentration of the planetary reservoirs (core: black line with dark grey error envelope and mantle: solid black line with light grey error envelope) are plotted as a function of bulk carbon that participated in the core-mantle fractionation event. The mantle and core concentrations for Earth, Mars, and the Moon are plotted for $D_{\text{metal/silicate}}$ values that are obtained for the estimated conditions of the base of the MO for these planetary bodies (Table 4). The shaded error bands in core and mantle C content derive from the range of metal-silicate equilibration conditions for each planetary body as given in Table 4. Plotted for comparison, in all the panels, are the estimated range of modern Earth mantle carbon contents [depleted mantle similar to the source regions of mid-ocean ridge basalts: ~50-200 ppm CO$_2$ (Cartigny et al., 2008; Marty and Tolstikhin, 1998; Saal et al., 2002); enriched mantle similar to the source regions of intraplate ocean island basalt or off-axis seamounts: up to 4000 ppm CO$_2$; (Pineau et al., 2004)], primarily based on volcanic CO$_2$ flux and the estimate of BSE carbon content of 120 ppm (McDonough and Sun, 1995) and ~765 ppm (Marty, 2012). Also plotted for reference are the carbon abundance in CI chondrite of ~3.5 wt% (Anders and Grevesse, 1989; Lodders, 2003), estimated bulk Earth carbon content of 730 ppm (McDonough, 2003), and carbon solubility limit for Fe-rich alloy melt at high temperature and low pressure (Chipman, 1972; Dasgupta et al., 2013a; Dasgupta and Walker, 2008; Nakajima et al., 2009; Siebert et al., 2011; Wood, 1993). The panel (b) also includes the bulk Mars carbon content estimates from two different sources (Lodders and Fegley, 1997; Morgan and Anders, 1979).
4.3.2. Equilibration with metal:silicate ratio different than the respective core:mantle mass ratio

The mantle and the core budget of carbon for planetary bodies can be affected if the mass ratio of alloy and silicate melt differed from the mass ratio similar to the present-day core and mantle mass ratio. In particular, if carbon was delivered towards the end of the accretion process and into a large molten but metal-free MO – as has been argued for terrestrial accretion (Wood et al., 2013) – it may be possible that the metal:silicate ratio relevant for carbon fractionation was lower compared to the core:mantle mass ratio. Alloy:silicate ratio lower than the core:mantle mass ratio can also be realized with a fraction of the core formation being a disequilibrium process, perhaps direct merging of the cores of some of the differentiated impactor (Dahl and Stevenson, 2010; Rudge et al., 2010). To evaluate the effect of variable alloy:silicate ratio during equilibration in a magma ocean on carbon budget of the equilibrated alloy fraction and the mantle of the Earth, Mars, and the Moon, in Figure 12 we plot the estimated mantle and core carbon content as a function of alloy:silicate ratio. Figure 10 covers the range of $D_{\text{metal/silicate}}^c$ relevant for the planetary bodies such as Earth, Mars, and the Moon. It can be observed that very low alloy:silicate ratio during magma ocean equilibration could have elevated the residual molten silicate carbon budget. However, for Earth, in order to attain the present-day depleted mantle budget of carbon, metal:silicate ratio during equilibration needed to be $<1.2\%$. In order for the segregating metallic liquid to reach carbon saturation, thus promoting flotation of diamond in a magma ocean, alloy:silicate ration also requires to be $<1.5\%$ for Earth and Mars. For the Moon, however, owing to much lower predicted $D_{\text{metal/silicate}}^c$ value, even a small batch of alloy liquid could not have
reached carbon saturation. Therefore, if exsolution of carbon (diamond/graphite) from segregating core liquid has to be a major mechanism for acquiring early mantle carbon budget (Hirschmann, 2012), the bulk carbon budget has to be significantly greater; this is predicted not only for Earth but for other terrestrial planets such as Mars and the Moon.

One possibility of realizing a higher carbon budget during alloy:silicate equilibration in early Earth is to accrete volatile-rich material not evenly throughout the accretion history but rather within a restricted period. Wood et al. (2013), based on the work of Schönbächler et al. (2010), which showed that terrestrial Ag was acquired during the last 13% of the accretion, argued that elements of similar volatility such as carbon must have also been added during the late stage of accretion. If this is correct, and if we assume that the bulk Earth carbon content of 730 ppm was achieved by this late-stage addition, then the final 13% of accreting material contained 0.56 wt.% carbon. Therefore a maximum of 0.56 wt.% C could have participated in a late-stage, core-mantle fractionation. The reason that this is an absolute maximum is the fact that molten silicate from already accreted proto Earth would have made the bulk carbon content relevant for metal-silicate fractionation to be lower than this limit. In other words, bulk carbon content of 0.56 wt.% during metal-silicate fractionation would only be realized if the previously accreted silicates are already completely solidified. Yet, to put a limit on the alloy:silicate ratio at which diamond exsolution can occur and silicate carbon budget, In Figure 13, we also present estimated carbon contents of core and mantle of various planetary bodies using 0.56 wt.% as the initial bulk carbon content. It can be seen that for Earth, even the final 13% of accreted material cannot force the late accreting silicates to achieve carbon content similar to the present-day depleted mantle. The residual molten
silicate, if equilibrated with the metal melt in core:mantle mass ratio, then the final 13% of mantle silicates will have ≤2-3 ppm C. Much lower alloy:silicate ratio would be necessary to elevate residual mantle carbon budget to the present-day level. Even with high bulk carbon content of 0.56 wt.%, alloy:silicate ratio needs to be <8% in order to force segregating alloy liquid to diamond saturation and to elevate the mantle carbon budget to the level of present-day mantle or BSE. However, we note that for ~0.56 wt.% C to participate in a low (<8%) alloy:silicate mass ratio magma ocean (a possibility if a chondritic accreting mass mixes in with metal-free, molten silicate with the latter having no carbon) requires carbon content of the final accreting mass to be non-chondritic. For Mars, however, if the bulk carbon content of 2960 ppm C of Lodders and Fegley (1997) is reasonable, then late accretion of volatile-rich material may force the low alloy:silicate mass ratio to be realized and hence the Martian mantle may not only retain significant carbon dissolved in post-core formation magma ocean, but also may force late stage, small mass of core liquid to exsolve and supply diamond to the mantle carbon budget.
Figure 13: Estimated carbon contents of the planetary mantle (A and C) and core (B and D) as a function of metal alloy:silicate mass ratio. Model curves are forSpanning the range estimated for the base of the MO for Earth, Mars, and the Moon. All calculations in (A) and (B) assume that the bulk carbon content that participated in the alloy-silicate partitioning is 730 ppm, i.e., bulk Earth carbon content proposed by McDonough (2003) whereas calculations in (C) and (D) assume a carbon content of 5600 ppm (final 13% of accreting mass bringing in all the terrestrial carbon). Also plotted for reference, are the predicted core and mantle carbon contents for Earth, Mars, and the Moon for metal-silicate equilibration at their respective core:mantle mass ratio, the depleted mantle carbon content estimate in (A) and (C) (green horizontal band), and the expected solubility of carbon in metallic alloy melt in (B) and (D) (grey horizontal band; see the caption of Figure 9 for the references). In (A) it can be observed that for the
$D_{\text{metal/silicate}}$ value applicable for Earth, alloy:silicate ratio <1-2% is needed for molten silicate to achieve carbon content as much as the present-day depleted mantle and for segregating alloy liquid to saturate in carbon and exsolved diamond. In (C), it can be seen that if the final 13% of accretion of Earth brings in all the terrestrial carbon, higher carbon content can be retained in the mantle. However, achieving a higher mantle carbon budget by exsolution of diamond from alloy liquid still requires alloy:silicate ratio of >8%.

4.3.3 Implications for the origin of relative abundance of carbon and nitrogen in the Earth’s depleted mantle

The data and model developed for $D_{\text{metal/silicate}}$ of Earth has implications for the origin of relative volatile budget of the Earth’s present-day mantle. Marty (2012) showed that the nitrogen abundance of the Earth’s depleted mantle relative to chondrite is one order of magnitude less compared to that of carbon. Marty (2012) argued that such nitrogen depletion of the mantle relative to chondrite may be a consequence of core formation, with nitrogen behaving as a siderophile element. A more recent study of Roskosz et al. also argued, based on experimentally measured partition coefficients of nitrogen between Fe-rich alloy melt and silicate melt, that because nitrogen is a siderophile element, its low abundance in the mantle-atmosphere system can result from equilibrium partitioning between segregating core liquid and MO. However, the experimental $D_{\text{metal/silicate}}$ values determined at 4-18 GPa are only in the order of ~5-20 (Kadik et al., 2013; Roskosz et al., 2013) and pressure appears to have a negative effect on $D_{\text{metal/silicate}}$. Therefore, nitrogen is only mildly siderophile at terrestrial MO conditions, in contrast to our estimate of carbon being highly siderophile, with $D_{\text{metal/silicate}}$ value of
deep MO as high as $10^4$-$10^5$, i.e., 3-4 orders of magnitude higher than $D_{N_{\text{metal/silicate}}}$. Hence we argue that even though the nitrogen concentration of the BSE may be influenced by partitioning in the core, C/N ratio of the BSE cannot be explained by core formation. The measurements and model of $D_{C_{\text{metal/silicate}}}$ presented here suggests that equilibrium fractionation of C and N between alloy and silicate in MO should lead to depletion of carbon relative nitrogen, not the other way. Therefore the present-day, chondrite-normalized C/N ratio of the depleted mantle or mantle-atmosphere system was likely shaped by post-core formation addition of carbon to the Earth and preferential subduction of carbon relative to nitrogen over the last 1.5 Ga (Dasgupta, 2013). It cannot be ruled out, however, that a significant amount of nitrogen is stored in nominally N-free silicates in deep, reduced domains of the mantle (Li et al., 2013); although in that case, such N-rich reduced domains would have to escape decompression-induced oxidation and partial melting over long-time period of the Earth’s history.
5. CONCLUDING REMARKS

Our experimental $d_{c_{\text{metal/silicate}}}$ values and parameterization appear applicable to a range of carbon speciation conditions, from carbon being chiefly dissolved as carbonates, to being dissolved significantly as hydrogenated (alkyne and methane) or carbonyl species. The depth of MO appears to be the key variable for alloy-silicate fractionation of carbon, with very deep MO such as that of Earth observing most of existing carbon being partitioned into the core whereas very shallow lunar MO causing a significant carbon to be retained in the molten silicates. Martian MO with intermediate depth might have kept somewhat more carbon in the mantle than that of Earth but in the absence of any other mechanism of late carbon addition, bulk silicate Mars might have ended up being fairly carbon poor. Our study suggests, small planetary bodies with shallow MO alloy-silicate equilibration, would retain significant quantity of carbon in the post-core segregation MO, i.e., mantles of small planetary bodies may have significant carbon budget even without addition of late volatile-rich veneer. Larger terrestrial planets such as Earth (likely Venus as well), which likely had deep MO although saw initial stripping of its silicate carbon to the segregating core, might have had the opportunity to regain volatiles by prolonged addition of volatile-rich material and ingassing from thick atmosphere (e.g. Albarede et al., 2013; Dasgupta et al., 2013a). If Mars is a planetary embryo and lacked the late and protracted addition of volatile-rich material (Dauphas and Pourmand, 2011), then its mantle may have ended up being the most carbon starved among terrestrial planets. Future experiments with wider range of alloy composition (e.g., the presence of
other light elements), $f_{O_2}$, pressure, and capturing speciation specific partition coefficient measurement will be required to refine our prediction of carbon partitioning in MO of variable depth and conditions. Finally, comparison of the current data on alloy-silicate partitioning of carbon (this study; Dasgupta et al., 2013) versus nitrogen (Kadik et al., 2013; Roskosz et al., 2013) suggests that equilibrium core formation would have created a strong depletion of carbon relative to nitrogen in the silicate reservoir of the Earth. Therefore the estimate of high C/N ratio of the present-day depleted mantle or mantle-atmosphere system must be shaped by later addition and preferential subduction of carbon relative to nitrogen.


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