**Speciation and solubility of reduced C-O-H-N volatiles in mafic melt:
Implications for volcanism, atmospheric evolution, and deep volatile cycles in
the terrestrial planets**

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Abstract

Using vibrational spectroscopy and SIMS, we determined the solubility and speciation of C-O-H-N dissolved volatiles in mafic glasses quenched from high pressure under reduced conditions, with f_{O_2} from -3.65 to +1.46 relative to the iron-wüstite buffer (IW). Experiments were performed on martian and terrestrial basalts at 1.2 GPa and 1400 °C in graphite containers with variable availability of H₂O, and in the presence of FePt alloys or Fe-C liquids. The dominant C-O-H-N species varies systematically with f_{O_2} and H₂O content: the carbonate ion prevails above IW+1, but for dry conditions between IW-2 and IW+1, C≡O species are most important. Below IW, reduced NH-bearing species are present. At the most reducing and hydrous (~0.5 wt.% H₂O) conditions, small amounts of CH₄ are present. Concentrations of C diminish as conditions become more reduced, amounting to 10s to ~100 ppm in the interval ~IW-2 to IW+1 where C≡O species dominate, and as little as 1-3 ppm at more reduced conditions. Concentrations of non-carbonate carbon, dominated by C≡O species, correlate with CO fugacities

along a trend implying that the species stoichiometry has just one $\text{C}\equiv\text{O}$ group and suggesting that carbonyl complexes (transition metals with multiple carbon monoxide ligands) are not important species under these conditions. C partition coefficients between Fe-C liquid and silicate melt increase with decreasing f_{O_2} , becoming as great as 10^4 for the most reducing conditions investigated. The low solubility of C in silicate liquids under reducing conditions means that most C during the magma ocean stage of planetary differentiation is either segregated to the core or in the overlying atmosphere. Precipitation of C-rich phases in a carbon-saturated magma ocean is also possible, and is one mechanism by which some C can be retained in the mantle of a planet. The predominant magmatic carbonaceous species for both martian and lunar volcanism is likely $\text{C}\equiv\text{O}$.

Keywords:

C-O-H-N volatiles, reduced carbon, reduced nitrogen, deep carbon, vibrational spectroscopy, volatile speciation, planetary volcanism, magma ocean, early atmospheres

1. Introduction

C-O-H-N volatile partitioning between metallic cores, silicate mantles, and proto-atmospheres during terrestrial planet formation is critical for the evolution of these reservoirs and in the establishment of deep volatile cycles (Williams and Hemley, 2001; Dasgupta and Hirschmann, 2010). Furthermore, C-O-H-N volatiles affect both surface environments and interior dynamics of terrestrial planets (Hirth and Kohlstedt, 1995, 1996; Sleep and Zahnle, 2001; Jakosky and Phillips, 2001; Hayes and Waldbauer, 2006; Hirschmann, 2006; Dasgupta and Hirschmann, 2010). On planetary surfaces, C-O-H-N species modulate climate and supply nutrients necessary for equable conditions and life (Green, 1990; Kasting et al., 1993). In the interior, C-O-H species facilitate melting at depth, mediate mass transfer and internal differentiation, and determine the nature of volcanic eruptions (Cashman, 2004; Dasgupta and Hirschmann, 2010). Silicate melts, when present, are the

principal carrier of dissolved volatiles at elevated temperatures and pressures. As a result, magmatic volatile solubility and partitioning govern the distribution of C, O, H, and N within planetary mantles and between different planetary reservoirs. Volatile solubility in magmas depends on pressure, temperature, melt composition, and importantly oxygen fugacity (f_{O_2}), which also affects the speciation of C-O-H-N complexes in melts and fluids (Eggler and Baker, 1982; Pan et al., 1991; Holloway et al., 1992; Holloway and Blank, 1994; Brooker et al., 2001; Libourel et al., 2003; Kadik et al., 2004, Morizet et al., 2010; Mysen et al., 2011; Wetzal et al., 2013; Dasgupta et al., 2013; Ardia et al., 2013; Stanley et al., 2014; Chi et al., 2014).

C-O-H-N behavior in magmas at low f_{O_2} is key to several critical processes during planetary differentiation, when magma oceans in contact with core-forming metal experienced conditions with f_{O_2} below the iron-wustite (IW) buffer (Righter and Drake, 1996; Frost et al., 2008). These include: (1) Retention of volatiles in the interior versus degassing to the proto-atmosphere, which depends on volatile solubilities in molten and crystalline phases. (2) Magma ocean degassing, in which volatiles are transferred from the interior to the overlying atmosphere. Depending on f_{O_2} and volatile speciation in a magma ocean, early planetary atmospheres could be rich in H_2O and CO_2 (oxidized) or in reduced species such as H_2 , CH_4 , NH_3 , and H_2O (Hirschmann, 2012). Early atmospheric composition on Earth impacted prebiotic chemistry, the conditions that led to planetary habitability, and the origin of life (Kasting et al., 1993; Mather et al., 2004). (3) The establishment of atmospheric pressures great enough to stabilize liquid water on planetary surfaces— from the formation of the Earth’s oceans to the presence of liquid water early in Mars’ history (Rubey, 1951; Miller and Urey, 1959; Pollack et al., 1987; Abe and Matsui, 1988; Pepin, 1994; Carr, 1999; Delano, 2001; Zahnle et al., 2007; Elkins-Tanton, 2008; Hamano et al., 2013). (4) The formation of organics (such as abiotic macromolecular carbon found in martian igneous rocks) whose origin has been proposed to involve reduced

magmatic volatiles (Steele et al., 2012).

The shallow terrestrial mantle was oxidized to its present state as early as 3.8 Ga (Canil, 1997; Delano, 2001) or possibly earlier (Trail et al., 2013), limiting the effects of reduced volatile species at shallow mantle depths to Earth's earliest history when more reduced conditions could have prevailed. However, the modern mantle becomes more reduced with depth such that at pressures of ≥ 7 -8 GPa, f_{O_2} may be as or more reduced than the IW buffer (Rohrbach et al., 2007; Frost and McCammon, 2008; Stagno et al., 2013). In this case, melts and fluids in the deep upper mantle and below will contain reduced C-O-H-N species, which will impose a control on melting and metasomatic processes in the deep mantle (Roskosz et al., 2006; Mysen et al., 2009; Litasov et al., 2014). Reduced magmatic volatiles are also relevant to Mars and the Moon, as their mantles have f_{O_2} ranging from IW-1 to IW+1 and IW-2 to IW, respectively (Karner et al., 2006; Wadhwa, 2008). Evidence for surface volcanism on the terrestrial planets and on the Moon (Greeley, 1987; Rutherford and Papale, 2009; Zolotov, 2011; Ivanov and Head, 2013) suggests that for all of these bodies, C-O-H-N volatiles were exchanged between interior and surface reservoirs even following early magma ocean-related differentiation, and played a role in mantle melting, eruptive processes, and magmatic degassing.

Under oxidizing conditions, the chief magmatic species for H, C, and N are, respectively, OH^- and H_2O , CO_3^{2-} and CO_2 , and N_2 , and solubility laws are reasonably well-understood (Pan et al., 1991; Holloway and Blank, 1994; Jambon, 1994; Dixon et al., 1995; Libourel et al., 2003; Miyazaki et al. 2004, Mysen et al., 2008). However, as conditions become more reduced, both the identities and the quantitative solubilities of volatile magmatic species are less well-established. Hydrogen-bearing species OH^- and H_2O persist to modestly reduced conditions, though concentrations diminish and molecular H_2 becomes increasingly important at highly reduced conditions (Schmidt,

1998; Hirschmann et al., 2012). For carbon-bearing species, the solubility of CO_3^{2-} diminishes proportionally to f_{O_2} below the C-CO- CO_2 buffer (Holloway et al., 1992; Pawley et al., 1992; Hirschmann and Withers, 2008; Stanley et al., 2014), and CO_3^{2-} is replaced by one or more reduced entities. These could include species with C-H or $\text{C}\equiv\text{O}$ bonds (Kadik et al., 2004, 2006; Mysen et al., 2009, 2011; Wetzel et al., 2013; Dasgupta et al., 2013; Stanley et al., 2014; Chi et al., 2014). Recent studies disagree regarding the species that may predominate. For example, several studies found CH_4 and possibly other CH-bearing molecules such as alkynes ($\text{C}_n\text{H}_{2n-2}$) to be the chief species in mafic and ultramafic melts in equilibrium with Fe-carbide liquids (Kadik et al., 2006; Dasgupta et al., 2013; Chi et al., 2014). While Mysen et al. (2009) found appreciable dissolved CH_4 in Na_2O - SiO_2 liquids, quantitative solubility determinations in haplobasaltic liquid implied very low dissolved methane concentrations except at very high fugacities of H_2 (Ardia et al., 2013). Wetzel et al. (2013) and Stanley et al. (2014) suggested that Fe-carbonyl complexes, including possibly $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_6^{2+}$, are found in reduced lunar and martian basalts. Additional species that have been identified include $\text{C}\equiv\text{O}$ (Brooker et al., 1999), and other CO and Si-C complexes (Kadik et al., 2004, 2006). Together, these studies present a confusing and somewhat contradictory set of observations, in which the identity and relative concentrations of reduced C species are poorly defined.

Dissolution of N species at reduced conditions and high pressure are dominated by N-H complexes, including possibly NH_4^+ (Kadik et al. 2013), NH_2^{2-} and NH_3 (Mysen et al., 2008; Mysen, 2013; Mysen et al., 2014; Kadik et al., 2011, 2013). Some evidence also exists for more complex amine or amide species (Stanley et al., 2014). Clarification of the influence of intensive variables and melt composition on the relative stabilities of these diverse species is a prerequisite for a quantitative understanding of solubilities and behavior of C-O-H-N species in reduced planetary magmas.

Here we determine systematic changes in C-O-H-N volatile speciation and

solubility in mafic melts over conditions spanning 3 orders of magnitude of H₂O concentrations (~0.01-1 wt%) and 5 orders of magnitude of f_{O_2} (> IW-3.5 to IW+1.5). Our results reconcile many of the discrepancies between previous studies and provide a framework for understanding the behavior of reduced volatile species at conditions applicable to the terrestrial planets and the Moon.

2. Methods

2.1 Experimental and analytical techniques

Experiments on synthetic martian and mid-ocean ridge basalts were performed at high pressure and temperature under graphite-saturated and volatile-undersaturated conditions in a piston cylinder apparatus at 1.2 GPa and 1400 °C, with varying water contents and f_{O_2} .

2.1.1 Starting materials

The martian basalt starting materials HB-ox and HB-gl (Table 1) are based on the Adirondack-class Humphrey basalts (Gellert et al., 2006; McSween et al., 2006) from Gusev Crater, Mars, and are nearly identical to the starting material used by Stanley et al. (2014). The terrestrial basalt GMORB-ox (Table 1) is a synthetic mid-ocean ridge basalt modelled after sample 4973 from the Galapagos spreading ridge, reported in Melson et al. (2002). Starting materials were prepared mainly from high-purity oxides and carbonates that were dried as described in Stanley et al. (2014) prior to weighing. After weighing, iron-free mixes were ground in ethanol in an agate mortar for 30 minutes. The mixes were subsequently decarbonated at 400-1000 °C for 24 hours, reground, and decarbonated again to ensure full CO₂ loss. After decarbonation, iron was added to oxide mixes as FeO, because under the reducing conditions of the experiments, all iron in the melt should be present in the ferrous state. In the case of starting material HB-gl, after preparation of the Fe-free oxide mix, a glass was fused in a Pt crucible at 1 atm, then

crushed and ground with FeO. The purpose of this additional starting material was to see if lower water concentrations could be achieved with a glass starting material, but better results were obtained with the HB-ox mixture using the drying procedures described in the following section.

2.1.2 Water concentrations

Experiments conducted without any special drying procedure resulted in quenched glasses with ~0.5 wt% H₂O, as measured by FTIR (details below), but we were able to generate a range of water-poor of melts by loading the starting materials into capsules and then drying at 400-500 °C for 24-48 hours followed by welding the capsules immediately after removal from the oven. Drying time was modulated to produce melts with varying water concentrations, with the driest melts containing <100 ppm H₂O. We note that water can never be fully eliminated in experiments in high pressure, high temperature solid-media devices and so all comparatively H₂O-poor experiments must be considered to be only nominally anhydrous (e.g. (Holloway, 1998; Robinson et al., 1998; Médard et al. 2008). A single experiment was conducted at more hydrous conditions, A1143, which had deionized water added using a microsyringe. All experiments were vapor undersaturated.

2.1.3 Experimental oxygen fugacity

Imposition and monitoring of a range of oxygen fugacities was facilitated by addition to the basaltic starting materials of varying amounts of powdered Pt, Fe, and/or Si. This resulted in run products consisting of an Fe-rich metallic phase coexisting with the quenched mafic melt, and the compositions of these phases allowed calculation of oxygen fugacity as detailed in section 2.2 below. For comparatively oxidized experiments, the silicate starting mixtures were combined with 4 wt % Fe metal and 5 wt % Pt black. At experimental conditions, the two metals alloyed. Experiments with the same starting composition but varying water concentrations exhibited a range of oxygen

fugacities because the addition of water to graphite saturated systems lowers the f_{O_2} below the CCO buffer owing to the dilution of C-O species' fugacities (e.g. Spear, 1995, Schmidt et al., 2014).

To generate more reducing conditions, Fe metal was added without Pt, and this reacted with the graphite capsule to form an iron carbide melt. Powdered Fe metal oxidized when the capsule was dried in the oven prior to welding, resulting in a silicate melt highly enriched in FeO and lacking any coexisting metallic alloy, so experiments that required pre-drying had Fe added as 1-2 pieces of high-purity 2 mm Fe wire. Even more reducing conditions were achieved by adding variable amounts of high purity, powdered, Si metal together with Fe. The silicon reduced some FeO in the starting material during the experiments, resulting in more Si-rich, Fe-poor melts coexisting with iron carbide at a lower f_{O_2} . In experiment A1229, Si_3N_4 was added rather than Si metal. Metal-free mixes were stored in a vacuum oven at 120 °C, whereas Fe- and FePt-bearing mixes were stored in a desiccator to inhibit oxidation of iron metal.

2.1.4 Piston cylinder experiments

Experiments were carried out in half-inch piston cylinder assemblies which consisted of CaF_2 sleeves surrounding a graphite furnace, MgO cell parts, and a type S thermocouple. The Pt-C capsule was placed in a consistent location in the assembly so that the temperature difference between the top of the sample and the tip of the thermocouple was 12 °C based on previous calibrations (Xirouchakis et al., 2001). No correction for friction was included in the reported experimental pressures and a hot piston in technique was used to reach the desired pressure and temperature. Run duration once at temperature was six hours, previously determined to be long enough for basaltic melt and coexisting FePt alloy or Fe-carbide to reach equilibrium (Stanley et al., 2014). The experiments were temperature-quenched by cutting off the power to the furnace. Recovered capsules were cut in half

longitudinally using a wire saw, revealing crystal-free glass coexisting with a metallic alloy or carbide. One half of each charge was polished on diamond-impregnated polishing paper, carbon-coated, and analyzed on the electron microprobe to determine the phase compositions. The other half of each charge was double-polished to 50-700 μm thickness to allow a clear path through the glass for analysis by Fourier transform infrared (FTIR) spectroscopy. Raman spectroscopy and secondary ion mass spectrometry were also conducted on each sample.

2.1.5 Electron microprobe analyses

Electron microprobe analyses were performed at the University of Minnesota using a JEOL JXA8900R electron microprobe analyzer (EMPA). For glasses, analytical conditions were 20 kV and 10 nA with a 5 μm beam. Silicate minerals and basaltic glasses were employed as standards and a ZAF correction method was used to process the data. Count times were 20 seconds on peak and 10 seconds on background for all elements except for Na, for which 10 seconds on peak and 5 seconds on background was used. Analyses of FePt alloy grains were challenging owing to their morphology (spheres or interconnected blobs commonly a few microns or less in diameter). Standards used were Fe and Pt metal, and it was found that the best analytical conditions employed a focused beam at either 15 kV and 5 nA for larger grains, or 8 kV and 3.5 nA for smaller grains. Count times were 35 seconds on peak and 15 seconds on background for 15 kV, and 70 seconds on peak and 35 seconds on background for 8 kV. Si metal was also included in the analyses to test for contamination from the surrounding glass. Iron carbides were analyzed at 15 kV and 5 nA. The carbon content of carbides was estimated by difference between measured Fe concentrations and 100 percent. In some cases, Si metal concentrations were also measured in the carbides.

2.1.6 FTIR Spectroscopy

Volatile species in quenched glasses were analyzed by Fourier Transform

Infrared Spectroscopy (FTIR). A Bruker Tensor 37 spectrometer with a Hyperion 2000 microscope was used to collect unpolarised spectra of clean glassy regions exposed in double-polished samples, allowing determination of volatile concentrations and speciation. Depending on sample characteristics, rectangular areas with side dimensions of 30-500 μm were analysed in the 1000-4500 cm^{-1} range with 256 scans per spectrum and a spectral sampling of 4 cm^{-1} . A KBr beamsplitter and mid-IR source were used.

H_2O and CO_2 concentrations were calculated on the basis of OH^- and CO_3^{2-} absorptions in the infrared, using the Beer-Lambert law. Because the Si- and Fe-concentrations in the glasses varied, glass density was calculated as a function of composition using the empirical model of Fluegel (2007). The molar absorption coefficient (ϵ) used for OH stretching is from Jendrzejewski et al. (1996) ($78 \pm 1 \text{ L mol}^{-1} \text{ cm}^{-1}$). The integrated molar absorptivity (ϵ^*) used for the carbonate doublet in experiments on martian basalt is the value determined for Humphrey basalt by Stanley et al. (2011) ($81,500 \pm 1500 \text{ L mol}^{-1} \text{ cm}^{-2}$). For experiments on MORB, ϵ^* of $69,500 \pm 3000 \text{ L mol}^{-1} \text{ cm}^{-2}$ from Fine and Stolper (1985) determined for natural terrestrial basalts was used. Unless otherwise noted, all subsequent H_2O and CO_2 concentrations are derived from FTIR measurements. Because there were additional C-bearing species, the amount of C in carbonate does not represent the total C concentration of the glasses. Measurements of total C in glasses are described in section 2.1.8.

2.1.7 Raman Spectroscopy

Raman spectra were collected using a 458 nm, diode-pumped, solid-state laser (Melles Griot 85-BLS-601). A neutral density filter was used to reduce the 250 mW output of the laser to 10-13 mW at the focal spot on the sample, which was chosen to be below the damage threshold for this suite of glasses. Raman spectra were collected through an objective lens with 0.80 numerical

aperture (Mitutoyo LWD M Plan FL 100x) mounted on an Olympus BX optical microscope. Transmitted and reflected light microscopy was used to ensure that Raman spectra were recorded on polished surfaces at spots free of crystalline inclusions, graphite, or carbides. The optical path included a beam expander and confocal aperture before the sample, resulting in a focal spot size of approximately 1-2 μm . Raman spectra were collected through a secondary confocal aperture and focused into a 0.3 m focal length Andor Shamrock-303 spectrograph using a 1200 lines per mm diffraction grating giving about 1.5 cm^{-1} frequency shift resolution. Spectra were recorded from 0-4500 cm^{-1} on an Andor Newton DU970 CCD camera, calibrated using the emission lines from a xenon lamp. All spectra were recorded using full binning of the vertical channels with 60 second acquisition times, averaged over 5 times, i.e. 300 seconds total acquisition time.

2.1.8. Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry was performed at Arizona State University, with the primary aim of determining the total carbon concentrations in glasses and metallic phases. Polished samples were prepared and pressed into indium mounts alongside standards and blanks as described in detail by Aubaud et al. (2007), then gold-coated. For carbon measurement in glasses, four experimentally-synthesized, CO_2 -bearing martian basaltic glasses previously described by Stanley et al. (2011) were used as standards. Four natural, water-bearing basaltic glasses described by Aubaud et al. (2007) were used as standards for hydrogen in experimental glasses. Humphrey basalt glass fused at 1 atm by Stanley et al. (2014) and containing no detectable CO_2 or H_2O on the basis of FTIR measurements was used as a blank for both carbon and hydrogen. For C in iron carbides, an Fe_3C standard synthesized by Hastings (2012) and described by Stanley et al. (2014) was employed.

A Cameca 6f mass spectrometer with a Cs^+ primary ion source was used for the measurements, as described by Stanley et al. (2014). Each analysis comprised a 300 second pre-sputter followed by a 300 second measurement,

and three different analyses were collected for each unknown. For mafic glasses, counts were collected for ^{12}C , ^{16}OH , ^{18}O , ^{19}F , and ^{30}Si , whereas for iron carbides, ^{12}C , ^{26}CN , ^{28}Si , ^{31}P , and ^{56}Fe were measured. For glasses, ^{19}F was not quantified but rather used as an indicator for contamination, as was ^{28}Si for carbides. ^{26}CN and ^{31}P were measured for carbides in order to provide qualitative information about N and P concentrations after the detection of these elements in the carbides by EDS on the microprobe. Standards were analyzed at the beginning of each session, and blanks were analyzed multiple times throughout each session.

For each session, a linear relationship between C or H_2O concentration and the $^{12}\text{C}/^{30}\text{Si}$ or $^{16}\text{OH}/^{30}\text{Si}$ count ratio was observed, allowing a calibration to be constructed for C and H_2O concentrations in the glasses (Table S1, Fig. S1). The background for carbon was 1-2 ppm C, and the background for water varied from 235-247 ppm H_2O . Due to the high background for water, H_2O concentrations referenced in this study are from FTIR measurements unless otherwise noted. For carbides, the C/Fe ratio and average count rates on the stoichiometric Fe_3C standard allowed the unknown C concentrations to be determined from $^{12}\text{C}/^{56}\text{Fe}$ count ratio (Stanley et al., 2014).

2.2 Fugacity calculations

The methods used for determining oxygen fugacity are described in detail in Stanley et al. (2014) and summarized here. Oxygen fugacities were calculated from the Fe-content of the metal alloy or carbide and FeO-content of the coexisting melt (Grove, 1981; Médard et al., 2008) using the reaction

For experiments containing FePt alloy, f_{O_2} was calculated using the method of Médard et al. (2008),

$$\log f_{O_2} = \frac{2}{\ln(10)} \left[\ln \left(\frac{X_{FeO}^{melt}}{X_{Fe}^{alloy}} \right) + \ln(B_{Fe}^{melt}) - 2 \ln(B_{Fe}^{alloy}) - 2 \ln K \right] \quad (2)$$

where X_{FeO}^{melt} and X_{Fe}^{alloy} are the mole fractions of FeO and Fe in the melt or alloy, respectively. K is the equilibrium constant and the activity coefficient of FeO in the melt and Fe in the alloy are B_{FeO}^{melt} and B_{Fe}^{alloy} , respectively (Kessel et al., 2001).

For experiments containing iron carbide, f_{O_2} was calculated from

$$\log f_{O_2} = \frac{2}{\ln(10)} \left[\ln(X_{FeO}^{melt}) + \ln(B_{FeO}^{melt}) - 2 \ln(a_{Fe}^{Fe-C}) - 2 \ln K \right] \quad (3)$$

where a_{Fe}^{Fe-C} is the activity of Fe in the iron carbide. The method of Wang et al. (1991), modified by Stanley et al. (2014), was used to calculate a_{Fe}^{Fe-C} .

Carbon monoxide fugacity (f_{CO}) for each experiment was calculated from the reaction

using the relationship:

$$f_{CO} = K \cdot f_{O_2}^{1/2} \cdot a_C \quad (5)$$

where K is the equilibrium constant calculated from Zhang and Duan (2009) and a_C is the activity of carbon, which is unity for the graphite-saturated conditions investigated here.

3. Results

3.1 Run products and phase compositions

All experimental charges (Table 2) contain graphite-saturated mafic melt coexisting with minor amounts of a metallic phase (Fig. 1). Experiments that contained platinum produced a phase assemblage of melt + FePt alloy, while Pt-free experiments produced melt + iron carbide. Some experiments also contain graphite crystals or carbon nanotubes (Ardia et al., 2013). Silicate melts quenched to chemically uniform glasses that in most cases include large (hundreds of microns) metal-free regions. No bubbles were observed, and so we infer no evidence of a vapor phase in the run products. FePt alloys within each experiment are compositionally homogeneous on the basis of backscattered electron imaging, and are present as beads or blobs with a maximum dimension of $\leq 20 \mu\text{m}$ (Fig. 1c-d). Iron carbides were liquids at experimental conditions based on their morphology and textures, occurring in recovered charges as droplets with diameters of tens to hundred of microns (Fig. 1a), with quench textures of two intergrown metallic phases as well as minor graphite (Fig. 1b). When measured, Si metal in the carbides was below the detection limit of the EMPA. Qualitative EDS and SIMS analyses indicate that the carbides also contain small amounts of N (in all cases) and P (if in the starting material), but these elements were not measured quantitatively.

Melt compositions determined by EMPA are given in Table 3. As f_{O_2} diminishes, melts become more Si-rich and Fe-poor relative to the starting compositions owing to oxidation of added Si and reduction of FeO of the melt, with the most reducing melts containing $< 3 \text{ wt } \% \text{ FeO}$. FePt alloys have 17-43 wt % Fe (43-72 mole percent), depending on the f_{O_2} at which they formed (Table 4). Carbon concentrations in FePt alloys were not measured, but based on EMPA totals of 99-101 weight percent for Fe and Pt metal, any C present was at a level of less than one weight percent. Si was near or below the EMPA detection limit for most FePt alloys (Table 4), with higher

numbers more likely to indicate trace contamination from the surrounding silicate glass rather than Si dissolved in the alloy. Iron carbides contain 91-94 wt % Fe (71-77 mole percent; Table 5), and 0.03 wt % or less Si in the cases it was measured. Higher standard errors for carbide compositions relative to FePt alloy and glasses reflect the heterogeneous nature of quenched carbide liquids.

3.2 Oxygen and carbon monoxide fugacity determinations

Calculated oxygen fugacities (Table 2) span 5 orders of magnitude, ranging from 3.65 log units below the iron-wustite (IW) buffer to 1.46 log units above it (5.6 to 0.5 log units below the carbon-CO-CO₂ buffer, or CCO). For experiments with the same bulk composition, higher dissolved H₂O concentrations result in lower f_{O_2} . Calculated carbon monoxide fugacities range from log f_{CO} of 1.80 to 4.35 (Table 2).

3.3 Total C and H concentrations in glasses and carbides

Total C and H concentrations of the glasses were determined by SIMS (Table 7; Fig. 2). Carbon concentrations in the glasses vary from 1–864 ppm and diminish as conditions become more reduced. Carbides contain 6.17–7.65 wt % C according to SIMS analyses and 5.8-8.2% based on Fe weight deficits by EMPA (Table 5). The two techniques show reasonable agreement within the relatively large uncertainties (averaging 0.75%) of the analyses, but the SIMS results are presumed to be more accurate. SIMS-determined C concentrations were used in f_{O_2} calculations, except for experiments B597 and A1217, which lack SIMS analyses and EMPA analyses were employed. Total H concentrations in the glasses determined by SIMS are 0–0.17 wt %, corresponding to 0–1.5 wt % H₂O if all of the H is contained in OH⁻. However, Raman spectroscopy indicates that in addition to water dissolved as OH⁻, many samples contain reduced hydrogen in the form of H₂ and other species. Thus, converting total H concentrations from SIMS directly to H₂O overestimates the water concentrations for most experiments.

3.4 CO₂ and H₂O concentrations in glasses

CO₂ and H₂O concentrations in glasses were determined from FTIR spectra as described in section 2.1.6. H₂O was present in all glasses at concentrations of 0.006 -1.069 wt % (Table 6). Glasses with $f_{O_2} \geq \text{IW-1}$ contain up to 688 ppm CO₂ (Table 6). Subtracting the concentration of C in CO₂ (determined by FTIR) from the total C in the glass (determined by SIMS) gives the ‘non-carbonate C’ or ‘reduced C’ (Stanley et al., 2014; Fig. 2d).

3.5 Volatile speciation in glasses

Volatile speciation in quenched melts was determined by vibrational spectroscopy. Representative spectra of glasses spanning a range of f_{O_2} are shown in Figs. 3 and 4. A summary of species present in individual experiments is given in Table 7 and shown visually as a function of f_{O_2} and H₂O in Fig. 5. In addition to samples from this study, experiments from Stanley et al. (2014) were re-analyzed using a more sensitive Raman system than available in the original study. New bands were discovered that were not originally reported and these updated findings are included in Table 7 and in Fig. 5. The following sections describe the speciation results from the present study as well as the new results on samples from Stanley et al. (2014).

At all conditions investigated, H₂O is dissolved in melts as the hydroxyl ion, OH⁻, as evidenced by a broad asymmetrical band in both FTIR and Raman spectra with the peak at 3550-3580 cm⁻¹. The H-O-H bending vibration of molecular water at 1630 cm⁻¹ is detectable in the infrared only in experiment A1143. There is no evidence of molecular hydrogen (4105-4140 cm⁻¹, Hirschmann et al. (2012)) in FTIR spectra (Fig. 3). In Raman spectra (Fig. 4), a vibration at 4115-4130 cm⁻¹ attributable to H₂ (Luth et al., 1987; Hirschmann et al., 2012) is present in all glasses with more than 0.5 wt % H₂O, and in most glasses with 0.2-0.5 wt % H₂O and f_{O_2} of less than IW-1 (Table 7, Fig. 5c).

Glasses with $f_{O_2} \geq IW-1$ contain CO_2 dissolved as carbonate, CO_3^{2-} , as shown by characteristic IR absorptions at 1430 and 1520 cm^{-1} (Fig. 3). The carbonate doublet is not evident in more reduced experiments, even though all were examined initially as thick (≥ 0.5 mm) glass chips. The molecular CO_2 band at 2350 cm^{-1} was not detected in FTIR spectra.

In glasses with intermediate f_{O_2} ($> IW-1$ to $IW+1.5$), bands with frequencies in the > 2100 -2200 cm^{-1} range were observed (Table 7, Fig. 3-4 and 5b). Over this entire f_{O_2} range, an absorption at 2205 cm^{-1} , previously reported by Stanley et al. (2014), was present in FTIR spectra but never in Raman spectra. Over a more limited range of f_{O_2} ($IW-1$ to $IW+1$), a band at 2110-2120 cm^{-1} was observed in most Raman and in a few FTIR spectra. This band was first described in silicate glasses by Wetzel et al. (2013), who observed it in both FTIR and Raman spectra of quenched lunar basaltic melts at f_{O_2} below $IW-0.55$. Bands at > 2100 -2200 cm^{-1} were not observed in glasses quenched from experiments more reduced than $IW-1$. CH_4 bands near 2900 cm^{-1} were observed in Raman but not FTIR, only at the most reducing conditions for the most water-rich glasses (Table 7, Fig. 5c).

Absorptions at 1615 and 3370 cm^{-1} are found in FTIR spectra of the more reduced samples (Table 7). As observed by Stanley et al. (2014), the two bands are typically evident in the same glass. In experiment A1217 with a particularly intense band at 3370 cm^{-1} , an additional band is present at 3280 cm^{-1} . Raman spectra are consistent with FTIR results, with many glasses exhibiting bands centered at 1615-1620 cm^{-1} , 3280 cm^{-1} , and 3360-3370 cm^{-1} . Because Stanley et al. (2014) speculated that some of these absorptions could be related to N-bearing species, experiment A1229 had 4.5 weight percent Si_3N_4 added to Fe-, Pt-bearing HB-ox starting material. The resulting spectra are shown in the lowermost portions of Fig. 3-4. In the N-doped experiment, the normalized intensities of the 1615, 3280, and 3370 cm^{-1} bands were

greatly enhanced in both Raman and the infrared compared to glasses that did not contain added nitrogen, and an additional band near 3180 cm^{-1} became visible in the FTIR spectrum.

4. Discussion

4.1 C-bearing species in reduced silicate melts

Studies on natural and simple melt compositions yield a complex picture of C solubility under reduced conditions involving an array of C-H and C-O species (Kadik et al., 2004, 2006; Mysen et al., 2009; Wetzel et al., 2013; Dasgupta et al., 2013; Stanley et al., 2014; Chi et al., 2014). Fig. 6 provides a rational map for the predominant species as a function of f_{O_2} and H_2O -content consistent with this and most previous studies. Key features include the shift with diminishing f_{O_2} , from carbonate to $\text{C}\equiv\text{O}$ complexes, with C-H species important only under hydrous conditions. Previous work on C-O-H volatiles in quenched silicate melts at f_{O_2} of IW+0.5 and higher found no evidence of CO or CH_4 (Pawley et al., 1992, Morizet et al., 2010). Our results are consistent with these observations in the case of CH_4 , and nearly so in the case of CO, which is seen in our experiments at f_{O_2} of roughly IW+1 and below. C solubility decreases with f_{O_2} , such that there are in effectively 3 regimes-oxidized (above $\text{IW}+1$), where carbonate solubility is high, intermediate (IW-1 to IW+1), where the remnants of carbonate + $\text{C}\equiv\text{O}$ yield small (10s to >100 ppm), but finite solubilities, and reduced (below $\text{IW}-1$), where solubility is so low that no well-defined C-bearing feature is evident in vibrational spectra, except at hydrous conditions (>2000 ppm H_2O) where CH_4 is important. We note that our glasses produced under highly reduced conditions are Fe-poor, as FeO is removed from the melt as Fe alloy when the activity of FeO must be low. The influence on C solubility of melt FeO concentrations that are independent of f_{O_2} changes remains poorly constrained and warrants future study.

Experiments on graphite-saturated basaltic melts show that the solubility of both CO_3^{2-} (Pawley et al., 1992; Thibault and Holloway, 1994; Stanley et al., 2011) and, under water-poor conditions, of reduced carbon species (Wetzel et al., 2013; Stanley et al., 2014) diminish as a function of f_{O_2} . Methane exhibits the opposite behavior but is present in appreciable quantities only at high $f\text{H}_2$ (Ardia et al., 2013; Chi et al. 2014). CO_3^{2-} concentration ($X_{\text{CO}_3^{2-}}$) is proportional to f_{O_2} (Holloway et al., 1992; Holloway, 1998), and Stanley et al. (2011) determined the thermodynamic parameters needed to calculate $X_{\text{CO}_3^{2-}}$ in graphite-saturated martian basalts at different oxygen fugacities. Compared to experimental data, the predictions of Stanley et al. (2011) underestimate the amount of C dissolved at f_{O_2} of IW+1 and below, and this is presumably owing to the contributions of $\text{C}\equiv\text{O}$ species.

Our results suggest a gradual change in the proportions of $\text{C}\equiv\text{O}$ and carbonate species (Fig. 2e) with the crossover of predominating species at f_{O_2} of $\sim$ IW+1. This contrasts with the sharp transition in C-O speciation at f_{O_2} of IW-0.55 observed from lunar basalts at 0.036-1 GPa, by Wetzel et al. (2013). Such a discontinuous transition is not expected thermodynamically (Mallmann and O'Neill, 2009). At conditions more reducing than IW-1.5, C solubility in mafic melts becomes very low, below 3 ppm in our experiments (Fig. 2c). This may reflect an f_{O_2} -driven change in reduced C speciation as suggested by vibrational spectra.

4.2 Reduced carbon speciation in silicate melts

It was previously proposed that the main C-bearing species in reduced melts contain $\text{C}\equiv\text{O}$ groups, with absorptions at 2205 and 2110 cm^{-1} provisionally attributed to iron carbonyls $\text{Fe}(\text{CO})_5$ and $[\text{Fe}(\text{CO})_6]^{2+}$, respectively (Wetzel et al., 2013; Stanley et al., 2014). Although the 2205 and 2110 cm^{-1} bands observed in FTIR and Raman spectra match certain features characteristic of iron carbonyls, some important bands are lacking. For example, two

prominent Raman bands characteristic of Fe-hexacarbonyl (ν_1 at 2241 cm^{-1} and ν_3 at 2220 cm^{-1} ; Bley et al., 1997; Bernhardt et al., 1999) are not observed in this or previous studies (Wetzel et al., 2013; Stanley et al., 2014). Similarly, the most prominent infrared bands related to $\text{Fe}(\text{CO})_5$ (ν_2 at 2030 cm^{-1} , ν_6 at 2002 cm^{-1} , and ν_{10} at 1939-1982 cm^{-1} ; Bigorgne, 1970; Cataliotti et al., 1971) are not observed here or by prior workers (Wetzel et al., 2013; Stanley et al., 2014), nor are the most prominent Raman bands (ν_2 and ν_{10} at the same positions as in the infrared; Bigorgne, 1970; Cataliotti et al., 1971). The 2110 cm^{-1} band seen in quenched mafic melts is one of the weaker bands expected for $\text{Fe}(\text{CO})_5$ (ν_1 ; Bigorgne, 1970), and so it would be surprising if dissolved Fe-pentacarbonyl could produce a band at 2110 cm^{-1} but not at 2030, 2002, or 1939-1982 cm^{-1} . However, in a very recent study by Yoshioka et al. (2015), the Raman spectrum of pure $\text{Fe}(\text{CO})_5$ fluid showed only two dominant bands, the strongest at 2014 cm^{-1} and the second strongest at 2108 cm^{-1} . In the same study, graphite-saturated silicate glasses synthesized at 1 GPa and -1 log units below IW exhibited the 2110 cm^{-1} Raman band in both Fe-bearing and Fe-free samples, indicating that 2110 cm^{-1} is not due to iron-carbonyl.

Our interpretation of the bands at 2205 and 2110 cm^{-1} is that they arise chiefly from isolated $\text{C}\equiv\text{O}$ groups, but perhaps also as part of more complex carbonaceous or organometallic clusters. Brooker et al. (1999) observed molecular carbon monoxide in Fe-free silicate melts with a band at 2150-2175 cm^{-1} , and it is feasible that compositional effects shift the frequency of the $\text{C}\equiv\text{O}$ band to 2205 cm^{-1} . Other species that could potentially produce these bands include $\text{C}\equiv\text{C}$ stretching vibrations in alkynes, $\text{C}\equiv\text{N}$ stretching vibrations in nitriles and cyanoamides, CN^- or CNO^- groups, or as vibrations in NH^+ groups and Si-H groups (Socrates, 2001). However, we consider these less likely because the solubility of these species should increase with $f\text{H}_2$ (and consequently, as f_{CO} and f_{O_2} decrease).

4.3 Concentrations and stoichiometry of C≡O species in dry reduced melts

The spectroscopic evidence from reduced glasses indicates that reduced carbon is largely in complexes associated with C≡O bonding, but the exact speciation is not clear. The magnitude of the C≡O IR absorption does not correlate with calculated f_{CO} , perhaps because the areas of the comparatively weak absorption bands above background are subject to high uncertainties. However, concentrations of reduced C (Fig. 7) can be related to f_{CO} , which facilitates both empirical modeling of expected concentrations as a function of intensive variables and exploration of the mechanism of C≡O dissolution.

The concentration of a C≡O complex with unknown stoichiometry dissolved in silicate melt can be considered as $[\text{CO}]_x$, where x denotes the stoichiometric coefficient. If the amount of the complex dissolved in the melt is small, then its concentration $C_{[\text{CO}]_x}$ can be approximated as a linear function of its mole fraction:

$$C_{[\text{CO}]_x} = qX_{[\text{CO}]_x} \quad (6)$$

where q is a coefficient that relates mole fraction, X , to mass concentration, C , and q is linearly related to the stoichiometric coefficient, x . At a given f_{CO} , the equilibrium constant K is given by:

$$K = X_{[\text{CO}]_x} / f_{\text{CO}}^{(x)} \quad (7)$$

and so

$$C_{[\text{CO}]_x} = qKf_{\text{CO}}^{(x)} \quad (8)$$

and

$$\log C_{[\text{CO}]_x} = \log q + \log K + x \log f_{\text{CO}} \quad (9)$$

Eq. 9 shows that the slope of the $\log C_{[\text{CO}]_x}$ versus $\log f_{\text{CO}}$ trend constrains the stoichiometric coefficient x . The 1-1.2 GPa data from this study and Stanley

et al. (2014) plot along a trend with a slope close to unity, indicating that the dissolved species may be similar to $C\equiv O$ (Fig. 7). Based on spectroscopy, there may actually be several $C\equiv O$ species present, and we infer that the mean stoichiometric unit is similar to a single $C\equiv O$. But importantly, the data do not support the predominance of pentacarbonyl or hexacarbonyl species, which would produce steep trends in Fig. 7 with slopes of 5 or 6. This supports the interpretation in the previous section, that the IR observations near 2205 and 2110 cm^{-1} are owing to isolated $C\equiv O$ species, rather than to pentacarbonyl or hexacarbonyl complexes.

Regression of the non-carbonate C concentrations determined from this study and Stanley et al. (2014) based on Eq. 9 yields the following empirical relationship:

$$\log C_{[CO]_x} = A + B \log f_{CO} + C P \quad (10)$$

for C concentrations in ppm and $\log f_{CO}$ and P in bars. The coefficients are $A=-0.738$, $B=0.876$, and $C=-5.44 \times 10^{-5}$. Importantly, the correlation between excess reduced carbon and f_{CO} predicts that graphite (or otherwise C-buffered) magmas have a maximum concentration of $C\equiv O$ species at comparatively oxidizing conditions (Fig. 7). This is because f_{CO} is at a maximum when f_{O_2} is greatest but still compatible with high C activity, owing to Eq. 1. This analysis is consistent with observations in this study and that of Stanley et al. (2014) indicating that non-carbonate carbon is greatest at comparatively oxidizing conditions close to the CCO buffer (Fig. 2e), affirming that the principle non-carbonate species in these glasses is indeed $C\equiv O$ related. In contrast, C-H related species should be most abundant at low f_{O_2} , where f_{H_2} is high. We note that Dasgupta et al. (2013) and Chi et al. (2014) infer that reduced carbon in their experiments is present chiefly as C-H species, but observe greater reduced (non-carbonate) carbon at intermediate oxygen fugacities, suggesting that $C\equiv O$ species are an undetected component in their

glasses. Indeed, Chi et al. (2014) mention possible molecular CO in some of their more oxidized samples.

In contrast to the relations evident from the present study and that of Stanley et al. (2014), the trend of $\log C_{[\text{CO}]_x}$ versus $\log f_{\text{CO}}$ from the study of Wetzel et al. (2013) has a slope of approximately 2.5 (Fig. 7). However, this data set does not include experiments with a range of f_{CO} at fixed pressures- the greater CO fugacities derive from experiments at higher pressure. Therefore, the trend implied by these data could be steeper than that evident in Fig. 7, and is not necessarily inconsistent with pentacarbonyl stoichiometry. It is unclear why the data of Wetzel et al. (2013) suggest such a different trend from those from the present study and Stanley et al. (2014), but the convolution of pressure, f_{CO} and melt composition (with high-pressure melts much more depolymerized than those from low pressure) in the study of Wetzel et al. (2013) means that the trend of that data in Fig. 7 need not be related to a specific C $\equiv$ O stoichiometry. For similar reasons, the experimental data of Dasgupta et al. (2013) and Chi et al. (2014) also cannot be subject to this kind of analysis, owing to the wide variety of melt compositions, temperatures, and pressures employed in those studies and because the glasses apparently have significant but poorly quantified concentrations of C-H and CO₂ species.

4.4 Reduced N-bearing species dissolved in silicate melts

Bands observed in FTIR and Raman spectra of reduced mafic glasses at 3180, 3280, and 3370 cm⁻¹ are consistent with N-H stretching vibrations, some of which have been previously observed in studies on reduced, N-bearing silicate melts (Mysen et al., 2008; Kadik et al., 2011, 2013). With one exception, nitrogen was not intentionally added to our experiments, but was likely an incidental contaminant owing to small amounts of air trapped in pore space during loading of sample powders in capsules or to organic contaminants in graphite. Addition of nitrogen to experiment A1229 resulted

in an increase in absorbance for the postulated N-related bands compared to nominally N-free experiments, consistent with the interpretation that N-H complexes are responsible for these spectroscopic features. The surprising appearance of marked N-H features in FTIR and Raman spectra of nominally N-free experiments suggests that at highly reducing conditions, the N-H species are either highly stable, highly absorbing, or both. Features at similar wavenumbers in silicate glasses from reduced, C-O-H-rich environments have in some cases been interpreted as related to alkyne bands (Dasgupta et al., 2013; Chi et al., 2014) but may instead be owing to N-H complexes. An unassigned FTIR band at 3370 cm^{-1} observed by Wetzel et al. (2013) in their most reduced basaltic glasses can also be explained by N-H stretching. Until recently, most studies on volatile speciation in magmas at high pressure have been carried out at more oxidized conditions at which N-H species solubility is expected to be low, perhaps explaining why N-related spectroscopic features have not previously been observed in nominally N-free experiments from much earlier studies.

The 3370 cm^{-1} band in FTIR spectra is generally accompanied by a corresponding band at 1615 cm^{-1} , which led Stanley et al. (2014) to suggest that the two may originate from a common, N-bearing species. Species that may account for both absorptions include amides (Stanley et al., 2014), amines, and metal-ammine complexes (Socrates, 2001). In all cases, the 3370 cm^{-1} band is owing to N-H stretching. The 1615 cm^{-1} band would be due to N-H or NH_3 deformation in amines or metal-ammine complexes (Socrates, 2001), but in an amide it would be owing to $\text{C}\equiv\text{O}$ stretching in a carbonyl group. The additional bands observed in some samples at 3180 and 3280 cm^{-1} fall within the N-H stretching region but cannot be explained by a single molecule that also produces the 3370 and 1615 cm^{-1} bands (Socrates, 2001). Because they appear in the samples with the most intense 3370 and 1615 cm^{-1} bands, we attribute them to additional N-H species dissolved in the melt. It is not presently possible to determine whether the 1615 and 3370 cm^{-1} bands

originate from a common species or from different N-H volatiles. Note that the possible coexistence of N-H and C≡O bonds in a common molecule such as an amide would mean that under reduced conditions the solution of C could be modulated in part by the amount of available nitrogen.

4.5 C partitioning between reduced silicate melt and molten Fe alloy

During terrestrial planet differentiation, the degree to which C is partitioned into core-forming alloys versus silicate magma is key for determining the carbon budgets of mantles and cores (Kuramoto and Matsui, 1996; Dasgupta and Walker, 2008; Hirschmann, 2012). Carbon is strongly siderophile, as all measured values of partition coefficient between silicate melts and iron-rich liquids, $D_C^{\text{metal/melt}}$, are orders of magnitude greater than unity, but the values applicable to core segregation are not yet well-established. Melt structure can be described by NBO/T, the ratio of non-bridging oxygens to tetrahedrally coordinated cations (Mysen et al., 1982), with larger values of NBO/T indicating more depolymerized melts. Previous studies showed significant dependence of $D_C^{\text{metal/melt}}$ on silicate melt composition as indexed by NBO/T (Dasgupta et al., 2013; Chi et al., 2014), but spanned a relatively small range of f_{O_2} (> 1.5 log units). Within this f_{O_2} range, increases in NBO/T led to smaller values of $D_C^{\text{metal/melt}}$ (Dasgupta et al., 2013; Chi et al., 2014). In contrast, the present experiments have a limited range of NBO/T (Fig. 8; calculated by the method of Brooker et al., 2001) but span a wider f_{O_2} range and extend to more reducing conditions than in previous studies. The effect of lowering the f_{O_2} without dramatic changes in NBO/T is an increase in $D_C^{\text{metal/melt}}$ (Fig. 8). This effect is just as expected, as f_{O_2} has little influence on C stability in alloy melts, but greatly affects solution of C in silicate (Fig. 2c). Any reduction in $D_C^{\text{metal/melt}}$ due to the slight increase in melt depolymerization at the most reduced conditions is apparently overshadowed by the effect of f_{O_2} . Chi et al. (2014) regressed a predictive model for $D_C^{\text{metal/melt}}$ as a function of pressure, temperature, NBO/T, f_{O_2} , and Ni content of the metal. The model predictions for $D_C^{\text{metal/melt}}$ are compared to our measured values in Fig. 8, and

match our data reasonably well considering that the model was calibrated over a narrow range of f_{O_2} (> 1.5 log units).

Given that magmas relevant to metal/silicate partitioning in the early Earth were ultramafic with high NBO/T and that redox conditions may have evolved from highly reducing (IW-4.5) during the earliest stages of core formation to more oxidized (IW-1.5) during later stages (Frost et al., 2008; Rubie et al., 2011), experimental determinations of $D_C^{metal/melt}$ do not as yet span the actual likely conditions and compositions most relevant to core formation on the terrestrial planets. Still, Fig. 8 suggests that appropriate values of $D_C^{metal/melt}$ for terrestrial core formation were likely on the order of 10^3 and may have evolved to somewhat lower values as core formation progressed. If most volatiles were delivered during the later stages of Earth accretion (Morbidelli et al., 2000) when conditions were more oxidized (Frost et al., 2008; Rubie et al., 2011), then it is the smaller values that were likely most relevant to Earth's large scale carbon distribution. Chi et al. (2014) inferred much larger ($> 5 \times 10^4$) values applicable to terrestrial core formation based on an extrapolation to 50 GPa that remains poorly constrained by experiment.

4.6 Reduced volatiles in magma oceans

Most modern models of Earth's early formation consider that material accreted to the growing Earth evolved from reduced and volatile-poor to more oxidized and volatile-enriched (Morbidelli et al., 2000; Raymond et al., 2006, 2007). Early in this process, when prevailing conditions were similar to IW-4 (Frost et al., 2008; Rubie et al., 2011), carbon concentrations in molten silicate were $\leq 1-3$ ppm (Fig. 2c). If any appreciable C was present at the pressures and temperatures investigated, much of it was likely incorporated into the growing core, with values of D_C near 10^4 (Fig. 8). Silicate magma C concentrations near 1 ppm limit the CO fugacity of any overlying atmosphere to > 0.1 MPa (Fig. 7). Thus, a thick C-rich atmosphere could not have been

sustained during the earlier stages of planetary accretion.

As accretion progressed, the growing mantle/magma ocean became more oxidized, eventually reaching IW-2 to IW-1 (Frost et al., 2008) and the fraction of volatiles delivered increased (Morbidelli et al., 2000; Raymond et al., 2006, 2007). The proportion of metal available to equilibrate with the silicate mantle during later stages of accretion is not well-constrained, in part because a significant amount of core formation likely occurred prior to delivery of appreciable volatiles and in part because metal/silicate equilibration depends on the size distribution of accreting bodies, the efficiency of metal/silicate reaction during transit through the mantle, and the extent of metal-silicate equilibration in the accreting planetesimals and embryos prior to accretion (e.g. Dahl and Stevenson, 2010; Wacheul et al 2014). Consequently the available metal could have been small compared to the mass of silicate (Hirschmann, 2012). With more oxidizing conditions ($\gg$ IW-1.5 log), metal/silicate partitioning of C becomes less extreme ($D_C^{metal/melt} \Rightarrow 10^3$) meaning concentrations of C in the magma ocean could potentially be as great as 10s of ppm. Under these conditions, much more C enters the core than remains in the mantle, but also a significant C-rich atmosphere will develop as the greater dissolved magmatic C would impose a fugacity of CO amounting to $\gg$ 10 MPa (Fig. 7)- a pressure similar to the present massive (CO₂) atmosphere of Venus. Formation of this massive atmosphere can limit sequestration of accreted C to the core and should be included in inventories of core/bulk silicate earth partitioning of carbon (Kuramoto and Matsui, 1996; Hirschmann, 2012). For a whole mantle terrestrial magma ocean with 20 ppm C overlain by an atmosphere with 10 MPa CO pressure, 80% of the C not in the core will be in the atmosphere and 20% will be in the mantle. We emphasize, however, that this calculation should be approached with caution because (a) it is based in large part on the large pressure dependence of Eq. 10, which is based on very few data and (b) it is inconsistent with the experimental results of Wetzal et al. (2013).

Once metal is effectively segregated to the core, interactions between the remaining silicate magma ocean and overlying massive C-rich atmosphere continue. Because of the pressure dependence of CO solubility (Fig. 7), the C dissolved in the near-surface portion of the magma ocean imposes higher f_{CO} on parcels of magma as they convect to greater depths and pressures. Upon magma ocean cooling, this may cause precipitation of a C-rich phase (graphite, diamond, carbide), thereby drawing down significant C from the atmosphere and creating a non-negligible inventory of C in the first-solidified mantle. This carbon pump, first proposed by Hirschmann (2012) and Dasgupta et al. (2013), could be enhanced or impeded by vertical gradients in f_{O_2} in the magma ocean (Hirschmann, 2012), but the sign and magnitude of such gradients in a deep magma ocean are as yet poorly constrained. Finally, gradual oxidation of a terrestrial magma ocean as a result of Fe-disproportionation in bridgmanite (Wade and Wood, 2005) has the overall effect of increasing C-solubility at a given pressure because of increased solubility of CO_2 and $\text{C}\equiv\text{O}$ species above IW-2. If such processes occurred during (rather than after) the magma ocean stage, greater magmatic solubility would force some of the atmosphere to redissolve in the magma ocean.

4.7 Applications to lunar volcanism

Recently, Wetzel et al. (2014) identified small amounts (up to 5.7 ppm) of indigenous C in lunar volcanic glasses. It has long been thought that magmatic C could be a principal propellant for lunar fire-fountain eruptions (Sato, 1976; Fogel and Rutherford, 1995), but questions of concentrations, sources, and origin are poorly resolved. Magmatic C requires a source in the lunar interior, which, given reduced conditions (IW-2 – IW; Wadhwa, 2008), could be graphite, carbide, or if concentrations are low, silicate minerals (Shcheka et al., 2006; Sen et al., 2013; Rosenthal et al., 2015). The maximum possible magmatic concentration would be accompanied by graphite saturation and dissolved C would be very low at IW-2 (≤ 3 ppm), and greater

at IW (>100 ppm). Among lunar samples, the pyroclastic beads are comparatively reduced, averaging IW-1.6 (Sutton et al., 2005). If this reflects source f_{O_2} rather than reduction during syn-eruptive degassing (Fogel & Rutherford, 1995), then the parent magmas of lunar pyroclastics must have been very C-poor with not much more than 15 ppm C (35 ppm $C\equiv O$) (Fig. 2c). Therefore it seems likely that additional components (e.g., hydrogen, sulfur, halides; e.g. Goldberg et al., 1976; Carusi et al., 1972; Saal et al., 2008; Rutherford and Papale, 2009) were needed to propel lunar pyroclastic eruptions.

As lunar basalts are comparatively dry (Saal et al. 2008, Hauri et al., 2011, Hauri et al., 2015), the principal C-bearing species are $C\equiv O$ related complexes, and, if conditions are sufficiently oxidizing, carbonate. Wetzel et al. (2013) found that carbonate species have negligible concentrations below IW-0.55, but our results suggest a more gradual transition. Consequently, carbonate makes a non-negligible contribution to C solution in more oxidized (IW-1 to IW) lunar basaltic-andesitic composition magmas, with total C concentrations on the order of 25-100 ppm C (Fig. 2). On the other hand, more reduced lunar magmas $<IW-1$ could have only very low concentrations of dissolved C, as even $C\equiv O$ related species diminish to small concentrations. N-related C species, though highly stable under reduced conditions, are likely of restricted importance on the Moon, as the few available measurements on volcanic glasses indicate that N concentrations $\leq 1-2$ ppm (Mathew and Marti, 2001). Similarly, methane stability is likely negligible for low-H lunar magmas (Ardia et al., 2013).

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Tables

Table 1. Starting compositions (weight percent).

Composition	HB-ox ^a	HB-gl ^b	GMORB-ox ^c
SiO ₂	46.91	47.09	48.72
TiO ₂	0.48	0.53	0.85
Al ₂ O ₃	10.59	10.56	16.17
FeO	19.5	20.07	8.51
MnO	0.37	0.38	--
MgO	11.27	10.83	9.76
CaO	8.03	8.01	12.9
Na ₂ O	2.82	2.41	2.04
K ₂ O	0.09	0.11	0.06
P ₂ O ₅	--	--	0.09
Total	100.00	100.00	99.10

^aHumphrey basalt oxide mix

^bHumphrey basalt Fe-free glass + FeO

^cGalapagos MORB oxide mix

Table 2. Experimental starting compositions and redox conditions.

Name	Composition ^a	Fe ^b	Pt ^b	Si ^b	H ₂ O added ^b	log f_{O_2} ! 1W ^c	log f_{CO} ^d
B547	HB-ox	4.0	5.0	0.0	0.0	1.46	4.35
B530	HB-ox	4.0	5.0	0.0	0.0	1.06	4.15
B533	HB-ox	4.0	5.0	0.0	0.0	1.04	4.14
A1100	HB-gl	4.0	5.0	0.0	0.0	1.02	4.13
A1090	HB-ox	4.0	5.0	0.0	0.0	1.00	4.12
B529	HB-ox	4.0	5.0	0.0	0.0	0.97	4.11
B528	HB-ox	4.0	5.0	0.0	0.0	0.92	4.08
A1085	HB-ox	4.0	5.0	0.0	0.0	0.87	4.06
B540	HB-gl	4.0	5.0	0.0	0.0	0.78	4.01
A1143	HB-ox	4.0	5.0	0.0	1.0	0.78	4.01
A1086	HB-ox	4.0	5.0	0.0	0.0	0.74	3.99
A1082	HB-ox	4.0	5.0	0.0	0.0	-0.16	3.54
B585	HB-ox	4.0	5.0	0.0	0.0	-0.54	3.35
B548	HB-ox	4.0	5.0	0.0	0.0	-0.60	3.32
A1124	HB-ox	4.0	5.0	0.0	0.0	-0.63	3.31
B597	HB-ox	9.9	0.0	0.0	0.0	-0.67	3.29
B527	HB-ox	4.0	5.0	0.0	0.0	-0.70	3.27
B595	HB-ox	8.0	0.0	0.0	0.0	-0.71	3.27
B639	GMORB-ox	14.4	0.0	0.0	0.0	-0.74	3.25
B619	HB-ox	8.9	0.0	1.6	0.0	-0.76	3.24
A1174	HB-ox	11.0	0.0	0.0	0.0	-1.01	3.12
A1211	GMORB-ox	14.5	0.0	0.0	0.0	-1.40	2.97
A1216	GMORB-ox	8.5	0.0	1.4	0.0	-1.65	2.80
A1229	HB-ox	7.6	0.0	4.5 ^e	0.0	-1.83	2.71
A1212	GMORB-ox	10.4	0.0	1.8	0.0	-2.64	2.30
A1213	GMORB-ox	12.0	0.0	4.5	0.0	-2.93	2.16
A1217	GMORB-ox	7.9	0.0	2.6	0.0	-3.65	1.80

^aHB-ox = Humphrey basalt oxide mix, HB-gl = Humphrey basalt Fe-free glass + FeO, GMORB-ox = Galapagos MORB oxide mix. ^bValues in weight percent.

^cCalculated from metal-silicate equilibria.

^dCalculated from graphite-CO-O equilibria. ^eValue listed is for Si₃N₄.

Table 3. Glass compositions as determined by EMPA (weight percent).

Exp. #	<i>n</i>	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
B547	25	46.20(23)	0.61(2)	10.59(11)	22.60(14)	0.38(2)	9.79(9)	7.54(6)	2.36(8)	0.09(1)	n.a.	100.15
B530	16	46.18(14)	0.53(3)	10.81(7)	23.16(17)	0.38(2)	9.74(19)	7.37(21)	2.32(6)	0.10(2)	n.a.	100.59
B533	18	46.04(12)	0.52(2)	10.69(8)	23.54(14)	0.37(3)	9.68(6)	7.41(11)	2.33(7)	0.10(1)	n.a.	100.69
A1100	11	44.16(14)	0.48(1)	10.01(4)	24.76(7)	0.38(1)	10.33(4)	7.66(3)	2.16(2)	0.11(0)	0.47(2)	100.51
A1090	20	44.53(29)	0.54(3)	10.80(7)	23.44(15)	0.39(3)	9.58(15)	7.86(19)	2.37(5)	0.09(1)	n.a.	99.59
B529	18	45.99(23)	0.54(2)	10.76(7)	23.12(12)	0.37(2)	9.63(15)	7.37(16)	2.32(7)	0.11(1)	n.a.	100.21
B528	19	46.39(15)	0.53(2)	10.87(5)	22.60(13)	0.37(3)	9.72(17)	7.44(17)	2.39(5)	0.10(2)	n.a.	100.41
A1085	18	46.03(27)	0.54(3)	11.15(5)	22.03(15)	0.38(2)	10.00(06)	7.85(11)	2.35(6)	0.10(2)	n.a.	100.43
B540	15	46.91(4)	0.48(1)	10.46(6)	20.47(9)	0.38(1)	10.64(5)	7.71(3)	2.54(4)	0.12(1)	n.a.	100.16
A1143 ^a	18	44.86(19)	0.51(1)	10.05(6)	22.02(3)	0.38(1)	10.34(4)	7.88(3)	2.16(1)	0.10(0)	n.a.	98.32
A1086	11	44.73(41)	0.52(3)	10.90(6)	23.40(13)	0.39(3)	9.99(3)	7.80(19)	2.40(7)	0.09(1)	n.a.	100.22
A1082	19	46.45(33)	0.52(3)	11.24(5)	21.37(10)	0.39(2)	10.18(6)	7.93(12)	2.42(8)	0.10(1)	n.a.	100.59
B585	19	46.10(9)	0.53(1)	10.48(4)	20.90(5)	0.39(1)	10.71(3)	8.14(2)	2.22(1)	0.10(0)	0.01(1)	99.61
B548	20	47.66(32)	0.61(3)	10.71(10)	20.54(15)	0.38(3)	10.03(7)	7.70(8)	2.42(8)	0.09(1)	n.a.	100.15
A1124	25	47.48(25)	0.62(2)	11.03(8)	20.28(19)	0.37(3)	9.95(8)	7.63(9)	2.43(6)	0.09(1)	n.a.	99.89
B597	14	42.86(11)	0.48(1)	9.84(4)	26.87(5)	0.38(1)	10.24(2)	7.57(3)	2.15(2)	0.09(1)	0.02(1)	100.48
B527	13	47.06(25)	0.56(2)	11.10(8)	20.67(13)	0.39(3)	9.94(10)	7.42(19)	2.39(4)	0.10(1)	n.a.	99.64
B595	11	47.55(12)	0.50(2)	10.65(3)	19.79(8)	0.38(1)	11.02(5)	8.01(6)	2.75(3)	0.10(1)	0.01(1)	100.75
B639	15	46.23(7)	0.74(1)	14.94(3)	16.12(6)	0.01(1)	8.72(2)	11.12(5)	2.10(4)	0.06(1)	0.06(1)	100.09
B619	9	46.87(8)	0.48(1)	10.14(3)	22.35(8)	0.36(1)	10.47(5)	7.55(4)	2.42(3)	0.10(1)	0.00(1)	100.76
A1174	9	44.02(4)	0.47(3)	9.92(4)	26.02(9)	0.34(2)	10.19(3)	7.37(3)	2.37(7)	0.09(1)	0.00(1)	100.78
A1211	25	48.87(6)	0.76(1)	15.43(3)	12.35(4)	0.00(1)	8.95(3)	11.67(4)	2.17(2)	0.06(0)	0.04(1)	100.31
A1216	15	51.42(10)	0.76(2)	15.44(4)	9.34(3)	0.00(2)	8.84(2)	11.56(6)	2.13(4)	0.06(1)	0.06(2)	99.61
A1229	19	59.85(14)	0.58(1)	11.56(3)	4.53(3)	0.43(1)	11.80(3)	8.68(3)	2.70(3)	0.13(0)	n.a.	100.26
A1212	25	56.46(5)	0.78(1)	16.38(3)	2.81(2)	0.00(1)	9.21(3)	12.66(4)	2.32(3)	0.07(1)	0.01(1)	100.70
A1213	14	58.97(55)	0.80(3)	15.93(11)	2.01(22)	0.01(1)	8.86(21)	11.66(19)	2.26(7)	0.07(1)	0.01(1)	100.57
A1217	25	62.27(13)	0.56(1)	12.01(4)	0.76(1)	0.45(1)	12.26(6)	9.23(4)	2.63(2)	0.11(0)	0.00(1)	100.29

^aHydrous glass; contains 1.07 wt % H₂O. n.a. = not analyzed.

Table 4. FePt alloy compositions as determined by EMPA (weight percent).

Exp. #	<i>n</i>	Fe	Pt	Total	XFe	Si
B547	7	17.76(30)	81.84(41)	99.60	0.43	n.d.
B530	9	20.43(16)	79.80(56)	100.23	0.47	0.01(1)
B533	11	20.66(23)	79.32(45)	99.97	0.48	0.01(1)
A1100	9	21.08(56)	78.84(54)	99.92	0.48	n.d.
A1090	10	20.86(52)	78.85(53)	99.70	0.48	n.d.
B529	9	21.11(18)	79.25(62)	100.35	0.48	0.01(1)
B528	11	21.27(16)	78.84(50)	100.11	0.49	n.d.
A1085	10	21.43(75)	78.72(77)	100.15	0.49	0.01(4)
B540	5	21.56(81)	78.30(61)	99.86	0.49	n.d.
A1143	6	22.25(51)	77.71(79)	99.97	0.50	n.d.
A1086	5	22.89(12)	77.35(68)	100.24	0.51	n.d.
A1082	6	31.95(25)	68.49(47)	100.44	0.62	0.02(1)
B585	5	38.69(86)	60.79(77)	99.55	0.69	0.06(7)
B548	4	41.17(42)	60.64(47)	100.81	0.70	0.04(1)
A1124	9	40.25(73)	59.31(58)	99.56	0.70	0.02(1)
B527	3	42.79(38)	57.03(4)	99.82	0.72	0.02(1)

n.d. = below detection limit

Table 5. Iron carbide compositions (weight percent).

Exp. #	<i>n</i>	Fe from EMPA	C from SIMS	C from EMPA	Si from EMPA
B595	22	91.76(39)	6.82(60)	8.24(39)	0.004(3)
B597	13	93.58(43)	n.a.	6.42(43)	0.03(1)
B639	15	92.11(1.76)	7.35(93)	7.89(1.76)	n.a.
A1174	39	94.14(68)	6.18(1.20)	5.86(68)	n.a.
B619	40	92.99(50)	7.11(18)	7.01(50)	0.00(0)
A1216	65	94.03(76)	6.18(1.04)	5.97(76)	n.a.
A1211	53	93.92(94)	7.01(8)	6.08(94)	n.a.
A1229	35	93.83(13)	n.a.	6.17(13)	n.a.
A1212	33	92.63(26)	6.72(91)	7.37(26)	0.004(2)
A1213	15	94.19(1.41)	6.74(90)	5.81(1.41)	n.a.
A1217	28	92.35(1.09)	7.65(1.09)	7.65(1.09)	0.03(1)

n.a. = not analyzed. C from SIMS used in f_{O_2} calculations when available.**Table 6.** Volatile concentrations measured in quenched glasses.

Name	$\log f_{O_2}$! IW	SIMS Total C (ppm)	FTIR CO ₂ (ppm) ^a	FTIR C in CO ₂ (ppm)	FTIR H ₂ O (wt %) ^a
B547	1.46	864 (151)	n.a.	n.a.	0.018
B530	1.06	299 (3)	294	80	0.025
B533	1.04	317 (1)	557	152	0.027
A1100	1.02	490 (20)	0 ^b	0 ^b	0.053
A1090	1.00	221 (6)	378	103	0.035
B529	0.97	241 (17)	300	82	0.052
B528	0.92	286 (11)	441	120	0.061
A1085	0.87	286 (2)	494	135	0.058
B540	0.78	357 (15)	688	188	0.062
A1143	0.78	194 (12)	145	40	1.069
A1086	0.74	171 (15)	356	97	0.063
A1082	-0.16	92 (3)	40	11	0.088

B585	-0.54	57 (6)	33	9	0.353
B548	-0.60	n.a.	35	9	0.345
A1124	-0.63	83 (3)	26	7	0.211
B597	-0.67	26 (6)	13	3	0.075
B527	-0.70	60 (2)	48	13	0.457
B595	-0.71	26 (1)	12	3	0.140
B639	-0.74	8 (1)	0	0	0.034
B619	-0.76	34 (1)	3	1	0.012
A1174	-1.01	69 (1)	26	7	0.009
A1211	-1.40	21 (11)	0	0	0.572
A1216	-1.65	16 (3)	0	0	0.008
A1229	-1.83	n.a.	0	0	0.157
A1212	-2.64	3 (2)	0	0	0.320
A1213	-2.93	1 (0.8)	0	0	0.006
A1217	-3.65	2 (0.5)	0	0	0.082

^aError for FTIR measurements estimated to be 10 % (Stanley et al., 2014).

^bSample likely contains CO₂ but was polished too thin for detection.

n.a. = not analyzed.

Table 7. Volatile speciation in quenched basaltic glasses from this study and in reanalysed samples from (Stanley et al., 2014) (marked with asterisk). Check marks indicate the presence of a species while horizontal dashes indicate the absence. F indicates that sample fluorescence prevented measurements in the wavenumber range of interest, and ‘n.a.’ indicates that no measurement was made. IR = observed in FTIR spectra, R = observed in Raman spectra, IR+R = observed in both FTIR and Raman spectra, IR/R = observed in FTIR and/or Raman spectra.

Name	$\log f_{\text{O}_2}$! IW	IR + R OH ⁻	R H ₂	R CH ₄	IR CO ₃ ²⁻	2205 cm ⁻¹ IR C≡O	2110 cm ⁻¹ R C≡O	1615 cm ⁻¹ R/IR N-H	3280 cm ⁻¹ R/IR N-H	3370 cm ⁻¹ R/IR N-H
B547	1.46	✓	n.a.	n.a.	✓	✓	n.a.	--	--	--
B530	1.06	✓	--	--	✓	✓	--	--	--	--
B533	1.04	✓	--	--	✓	✓	--	--	--	--
A1100	1.02	✓	--	--	-- ^a	✓	--	--	--	--
A1090	1.00	✓	--	--	✓	✓	--	--	--	--
B529	0.97	✓	--	--	✓	✓	--	--	--	--
B528	0.92	✓	--	--	✓	✓	--	--	--	--
A1085	0.87	✓	--	--	✓	✓	✓	--	--	--
B540	0.78	✓	--	--	✓	✓	--	--	--	--
A1143	0.78	✓	✓	--	✓	✓	--	--	--	--
A1086	0.74	✓	--	--	✓	✓	--	--	--	--
A1082	-0.16	✓	--	--	✓	✓	✓	--	--	--
B585	-0.54	✓	✓	--	✓	--	--	✓(IR+R))	✓(R)	✓(IR+R))
B548	-0.60	✓	n.a.	n.a.	✓	✓	n.a.	--	--	--
A1124	-0.63	✓	✓	--	✓	✓	✓	✓(IR)	✓(R)	✓(IR+R)

										)
B597	-0.67	✓	--	--	✓	✓	--	--	--	--
B527	-0.70	✓	✓	--	✓	--	--	✓(IR)	--	✓(IR)
B595	-0.71	✓	✓	--	✓	✓	✓	✓(IR)	✓(R)	✓(R)
B639	-0.74	✓	--	--	--	✓	--	--	--	--
B619	-0.76	✓	--	--	✓	✓	--	--	--	--
A1174	-1.01	✓	--	--	✓	✓	✓	--	--	--
A1211	-1.40	✓	✓	✓	--	--	--	--	✓(R)	✓(R)
A1216	-1.65	✓	--	--	--	--	✓	✓(R)	--	✓(IR)
A1229	-1.83	✓	--	✓	--	✓	✓	✓	✓	✓
								✓(IR+R		✓(IR+R
A1212	-2.64	✓	✓	✓	--	--	--	)	✓(R)	)
A1213	-2.93	✓	F	F	--	--	F	✓(IR)	--	--
A1217	-3.65	✓	F	F	--	--	F	✓(IR)	✓(IR)	✓(IR)
A877*	2.0	✓	✓	--	✓	--	--	--	--	--
B347*	2.1	✓	--	--	✓	--	--	--	--	--
B349*	2.3	✓	✓	--	✓	--	--	--	--	--
B361*	2.2	✓	✓	--	✓	--	--	--	--	--
B372*	1.9	✓	✓	--	✓	--	--	--	--	--
B379*	1.9	✓	✓	--	✓	--	--	--	--	--
B412*	2.2	✓	--	--	✓	--	--	--	--	--
B420*	1.1	✓	✓	--	✓	--	--	--	--	--
B441*	1.7	✓	✓	--	✓	✓	--	✓(R)	--	✓(R)
B442*	2.2	✓	--	--	✓	--	--	--	--	--
B465*	1.0	✓	--	--	✓	✓	--	✓(R)	--	✓(IR)
										✓(IR+R
B466*	-0.7	✓	✓	--	✓	✓	✓	✓(IR)	--	)
B477*	0.0	✓	✓	--	✓	✓	--	✓(IR)	✓(R)	✓(IR)

B485*	0.4	✓	✓	--	✓	✓	--	--	--	✓(R)
B486*	1.0	✓	✓	--	✓	✓	--	--	--	--
B489*	-0.8	✓	✓	--	✓	✓	✓	✓(IR)	--	✓(IR+R)
B490*	-0.8	✓	--	--	✓	✓	✓	✓(IR+R)	--	✓(IR+R)
B491*	-0.8	✓	--	--	✓	✓	--	✓(IR)	✓(R)	✓(IR+R)
B492*	-0.8	✓	✓	--	✓	✓	--	✓(IR)	--	✓(IR+R)
B493*	-0.8	✓	✓	--	✓	✓	✓	✓(IR)	--	✓(IR+R)
B494*	-0.8	✓	✓	--	✓	✓	✓	✓(IR)	--	✓(IR+R)
B495*	-0.8	✓	✓	✓	✓	✓	--	✓(IR+R)	--	✓(IR+R)
B497*	-0.8	✓	✓	--	✓	✓	--	✓(IR)	--	✓(IR+R)

^aCO₃²⁻ not observed but likely present as sample was polished too thin prior to FTIR analysis.

Figure Captions

Figure 1. Backscattered electron images of experimental run products. A) Basaltic glass and coexisting iron carbide (B585). B) Quench crystals in carbide from A1211. C) Basaltic glass with FePt alloy (B529). D) FePt alloy and glass in experiment B547.

Figure 2. Concentrations of different carbon species in basaltic glasses. A) Total carbon measured by SIMS and FTIR. FTIR measurements only detect carbon dissolved as carbonate, resulting in an underestimation of total carbon content due to additional reduced carbon species, or ‘non-carbonate C’. B) Total CO₂ concentrations measured by FTIR. C) Total C concentrations measured by SIMS. D) Non-carbonate carbon concentrations, or the difference between total C and C in CO₂. E) Percentage of carbon present as non-carbonate carbon.

Figure 3. FTIR spectra of quenched glasses. Spectra are offset from one another on the y-axis.

Figure 4. Raman spectra of quenched glasses. Spectra are offset from one another on the y-axis.

Figure 5. Volatile speciation as a function of H₂O concentration in the glass (as determined by FTIR) and f_{O_2} . All samples contain OH. Data points show all experiments from this study and Stanley et al. (2014). Large colored symbols surrounding experiment markers indicate the presence of a specific volatile species in that experiment. Volatile species detected are a) CO₂, dissolved as the carbonate ion and measured by FTIR, b) C≡O-bearing species with vibrations at 2205 and 2110 cm⁻¹ in FTIR and Raman, respectively, c) H₂ and CH₄, detected in Raman, and d) N-bearing species with vibrations at 1615, 3280, and/or 3370 cm⁻¹ in FTIR and/or Raman.

Figure 6. Volatile speciation map. Colored fields mark regions where a particular volatile species is dissolved in basaltic melt at 1.0-3.2 GPa and 1340-1617 °C. The map is based on data

in Fig. 5 from this study and from Stanley et al. (2014). The line at the top of the N-H field is dashed because its extension to high H_2O concentrations is not constrained at f_{O_2} below IW.

Figure 7. Solubility of reduced carbon at different f_{CO} . Solid lines show best fit for different pressures using the slope of the fit for 1-1.2 GPa data from this study and from Stanley et al. (2014), using Eq. 10 and the coefficients given in the text. Oxygen fugacity errors are estimated to be ± 0.1 log units. Dashed line is best fit to data from Wetzel et al. (2013) – note that for the data from that study, the experiments at low f_{CO} are at low pressure (~ 40 MPa) and those at high f_{CO} are at high pressure (800-1000 MPa). S14: Stanley et al. (2014), W13: Wetzel et al. (2013).

Figure 8. Carbide-melt partition coefficients for carbon, shaded as a function of melt NBO/T. All NBO/T values were calculated using the method of Brooker et al. (2001) even if that method was not used in the original publications. Black curve is the best-fit to the data from this study and from Stanley et al. (2014). The dashed curve is the best-fit to the predictions for $D_C^{carbide/melt}$ from the model of Chi et al. (2014) using the experimental conditions from this study and from Stanley et al. (2014). For melt compositions and expected conditions of core formation, beginning at more reduced conditions and becoming more oxidized with time (as described in text), these trends suggest values of $D_C^{carbide/melt}$ near 10^3 , though data are lacking for ultramafic (high NBO/T) magmas under highly reducing conditions.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8