

CARBON CYCLING IN SHALLOW MAGMA OCEANS OF TERRESTRIAL PLANETS CONSTRAINED BY HIGH P-T EXPERIMENTS. Rajdeep Dasgupta^{1*}, Han Chi¹, Nobumichi Shimizu², Antonio Buono³, and David Walker³, ¹Department of Earth Science, Rice University, Houston, TX, USA (*Rajdeep.Dasgupta@rice.edu), ²Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA, USA, ³Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, USA

Introduction: Deep carbon cycle have critical influence on planetary geodynamics, chemical differentiation, long-term climate, and habitability. Although a number of studies have considered the deep carbon cycle in the plate-tectonic framework of the modern Earth [e.g., 1], little is known about carbon's behavior, abundance, and distribution during planetary accretion and early planetary differentiation. In particular, the fate of carbon during magma ocean processes, such as storage capacity and fractionation between metal and silicate during core formation and distribution between various reservoirs i.e., metals, silicates, and atmosphere, are largely unconstrained. Key questions include whether the Earth and planets poses the volatiles and achieve their present distribution between the exosphere and the interior at the time of birth (accretion and early planetary differentiation), or is the present day budget (including ocean and atmosphere) shaped by later processes, such as late bombardment of volatile-rich materials (e.g., meteorites, comets)? Also, why do different terrestrial planets have drastically different atmosphere? Is this owing to accretion from vastly different compositions, or is this owing to the difference in conditions of early evolution (thermal and oxidation state and depth of core-mantle separation) that caused very different fractionation of fluids between the interior and the exosphere? To gain insight into the questions posed above, here we investigate the solubility, partitioning, and speciation of carbon-rich volatile species in a shallow magma ocean environment relevant for terrestrial planets, i.e., in equilibrium with metallic and silicate melts.

Methods: A series of high pressure-temperature experiments using piston cylinder (at Rice University) and multi-anvil apparatus (at Columbia University) were performed at 1-7 GPa, 1500-2100 °C on mixtures of silicates (tholeiitic basalts/ komatiite/ fertile peridotite) and Fe-Ni-C±S mix contained in graphite or MgO capsules. Major element compositions of the resulting phases and the carbon content of metallic melts [2] were analyzed by EPMA at NASA-JSC. Carbon and hydrogen concentrations of basaltic glasses and carbon content of non-glassy quenched silicate melt were determined using Cameca IMS 1280 SIMS at WHOI and speciation of dissolved volatiles in experiments with silicate glasses was constrained using FTIR and Raman spectroscopy at Rice University. Based on the

equilibria - FeO (silicate melt) = Fe (metal alloy melt) + 1/2O₂, we estimate the oxygen fugacity of our experiments within a narrow range of IW-1 to IW-2. Carbon concentrations in the silicate melts including those at graphite saturation (CCGS) were measured using SIMS ¹²C/³⁰Si intensity ratio as the proxy and 4-5 basaltic glasses with CO₂ content in the range of 50-3000 ppm as standards for developing the calibration curve. C content of metallic melts were also determined using SIMS ¹³C/⁵⁶Fe as the proxy and laboratory synthesized Fe-carbides as standards.

Results: The experiments with basaltic compositions (NBO/T<0.8-1.0) and contained in graphite capsules produced glassy silicate melt pool (Fig. 1) whereas experiments with more depolymerized melts (NBO/T>1.8) or experiments in MgO capsules produced quenched silicate melts with a network of olivine dendrites and interstitial glassy patches. All the experiments had equilibrium quenched metal melt composed of dendrites of cohenite and kamacite.

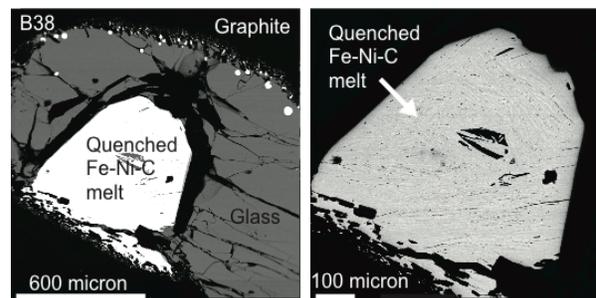


Fig. 1. Typical run products of basaltic silicate melt quenched to a glass at 1 and 2 GPa. Metallic melt quenches to a dendritic aggregate of cohenite, kamacite, and taenite

FTIR analysis on doubly polished basaltic glass chips suggests that the concentrations of dissolved CO₃²⁻ or molecular CO₂ are negligible in graphite and metal saturated reduced conditions, whereas the presence of dissolved OH⁻ is evident from the asymmetric peak at 3600 cm⁻¹. Collected Raman spectra of basaltic glasses in the frequency range of 200-4200 cm⁻¹ suggest that hydrogen is present both as dissolved OH⁻ species (band at 3600 cm⁻¹) and as molecular H₂ (band near 4150 cm⁻¹) for all of our experiments that produced glassy silicates. Small but definite peaks near 2915 cm⁻¹ suggest that possible carbon species in our reduced

glasses are likely minor CH_4 or other methyl groups and is consistent with the recent solubility studies at reduced conditions [3-6]. Fitted peak heights of CH_4 spikes show an increasing trend with increasing temperature but decreases with increasing pressure.

Carbon concentrations at graphite saturation (CCGS) at 1-3 GPa and 1500-2000 °C in our reduced basaltic glasses (NBO/T~0.8-1.0) vary between 8 and ~120 ppm C and increases with increasing temperature and oxygen fugacity and decreases with increasing pressure. In contrast to the low dissolved carbon concentration in the basaltic silicate melts, carbon solubility in metallic melts varies in the range of 4-9 wt.% with lower C content measured at lower T, P, and melt with higher Ni contents, broadly consistent with the thermodynamic prediction of C-solubility in Fe-rich metallic melt [7]. Thus at graphite saturation, the equilibrium partition coefficient of carbon between metallic Fe-Ni alloy melt and basaltic silicate melt, D_C (metal/silicate) varies from ~5500 to ~500, with lower D_C (metal/silicate) applicable for higher temperatures, lower pressures, and higher oxygen fugacity (Fig. 2).

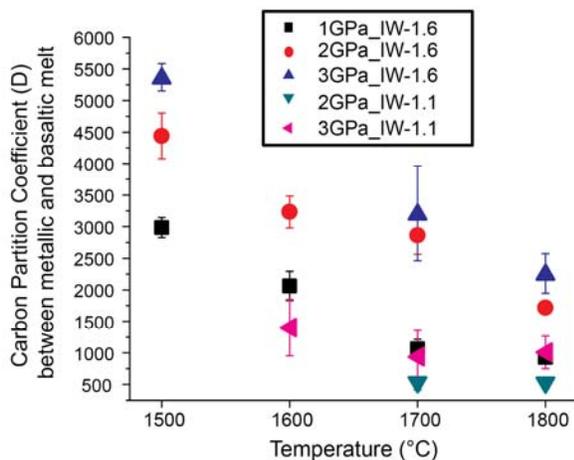


Fig. 2. D_C (metal/silicate) relevant for glassy Fe-Ni alloy melt and basaltic melt for a subset of our experiments using piston cylinder device.

The effect of more depolymerized silicate melt. While CCGS for glassy basaltic melt shows low values, the same obtained for komatiitic and peridotitic melt compositions, which quenched to dendritic aggregates, shows values as high as 700 ppm C thus suggesting the importance of melt composition on metal/silicate partitioning of carbon. However, owing to non-glassy nature of these quenched melts, spectroscopic verification of the nature of dissolved C was not possible. Thus in order to verify that high CCGS and somewhat lower D_C obtained for peridotitic and komatiitic melts are not analytical artifacts, further metal-silicate experiments with more depolymerized basaltic

melts of variable compositions are underway and will be presented.

Discussion: Our experimental data indicate that the solubility of carbon in reduced basaltic melts relevant for early magma conditions may be several orders of magnitude lower compared to the solubility of carbon in modern terrestrial basalts and the dominant C-species of interest may be hydrogenated rather than carbonated. This coupled with significant solubility of carbon in Fe-Ni metallic melt suggests that most of magma ocean carbon was likely partitioned into deep metallic melts. Because D_C (metal/silicate) increases with increasing pressure, variation in the depth of magma ocean between different terrestrial planets (e.g., deeper for Earth and shallower for Mars) may have caused the silicate mantles to inherit different amount of carbon post core segregation (Mars C-rich, Earth C-poor).

Our measured values of carbon partition coefficient, D_C (metal/silicate), suggest that the Earth's residual molten mantle after core segregation likely was depleted in carbon compared to the concentration estimated for the present-day basalt source regions. This then poses the question – how did the Earth's mantle manage to acquire the present-day budget of the carbon. A plausible process of later gain of carbon of course includes addition of chondritic late-veener. Alternatively, reduced magma oceans of terrestrial planets may have gained carbon from a C-rich atmosphere, facilitated by the pressure dependent C-solubility in reduced basalts. In this scenario, convection in a magma ocean will dissolve C from the early atmosphere at low pressures and deposit it in the form of graphite (or other reduced species) at deeper depths where the CCGS is lower. Finally, C-bearing metallic alloy melt may not drain completely to the core and may get partially trapped in the solid silicate matrix of the lower mantle. Convective overturn of these lower mantle materials (with interstitial carbide or alloy) may thus also have supplied a sizeable portion of the initial carbon budget of the mantle.

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