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 fractionation in a magma ocean in particular might be key because of carbon’s role in building a habitable planet. A difference in carbon partitioning behavior in magma ocean stage of various terrestrial planets might have forced Earth to evolve differently than other terrestrial planets such as Mars [1]. Partition coefficient of carbon between Fe-rich, metallic alloy melt and silicate melt, $D_{C\text{metal/silicate}}$ is a key quantity that must have had influence on the carbon budget of the silicate fraction of the terrestrial planets versus the metallic core [2-4]. However, no quantitative framework yet exists that allow prediction of $D_{C\text{metal/silicate}}$ as a function of key variables of relevant for core-mantle equilibration at a magma ocean condition. Recent studies with vastly different approaches and assumptions produced disparate estimates of metal/silicate $D_{C\text{metal/silicate}}$ relevant for terrestrial magma ocean with value as low as ~9 [5] and as high as $10^4$-$10^6$ [6] and experimental constraints on $D_{C\text{metal/silicate}}$ remain limited [3]. To build on the recent experiments [3], here we present results from 25 new high pressure experiments on the solubility of carbon in coexisting Fe-Ni metallic alloy melt and basaltic silicate melt in order to quantify the effect of pressure ($P$), temperature ($T$), oxygen fugacity ($f_{O2}$), silicate melt composition, and silicate melt hydration on $D_{C\text{metal/silicate}}$.

Methods: Experiments were conducted using an end-loaded piston cylinder device between 1 and 3 GPa and 1500-1800 °C using graphite capsules. Four different 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 0.810 to 1.544 were studied. Major element composition of alloy melts along with concentration of carbon in the alloy melt were determined using electron microprobe whereas carbon content of quenched basaltic glasses was determined using secondary ionization mass spectrometry (SIMS). Identification of carbon and hydrogen-bearing species in silicate glasses were performed using Raman and Fourier-transformed infrared (FTIR) spectroscopy. FTIR spectroscopy was also employed to quantify the dissolved CO$_2$ and H$_2$O. Details of the analytical protocols for SIMS and Raman are given in ref. [3].

Results: Experiments with all starting materials generated pools of silicate glasses, in which discrete Fe-Ni-rich metal alloy blobs are embedded. Metallic melt domains were composed of aggregates of blades of cohenite with interstitial Fe-Ni alloy. Carbon in our experimental, metallic alloy melt varies between 4.39 and 7.43 wt.% and increases with increasing temperature, modestly with increasing pressure, and decreases with increasing Ni content, similar to the observation of ref. [3]. 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, melt NBO/T, oxygen fugacity and water content of the silicate melts. Oxygen fugacity of the experiments, estimated based on Fe (in metallic alloy melt)-FeO (in silicate melt) equilibrium, varied from IW-0.37 and IW-1.02, where IW refers to the oxygen fugacity imposed by the coexistence of iron and wüstite.

Discussion: Our experiments and analyses constrain both the carbon solubility and speciation at shal-
low magma ocean conditions as well as allow us to parameterize $D_{^2\text{C}_{\text{silicate}}}$ as a function of key variables.

**Carbon speciation in silicate glasses.** Comparison of bulk CCGS with the expected solubility of carbon in the form of CO$_2$ at graphite saturation based on the thermodynamic model of ref. [7] and those measured using FTIR suggests that our experimental basalts contain excess carbon. Dissolved carbonates contribute to $\sim$80% of the total carbon for oxidized (~IW-0.5) tholeiitic basalts, $\sim$45% of the total carbon for reduced (~IW-1) tholeiitic basalts, $\sim$38% for the hydrated alkali basalts (~IW-0.75), and $\sim$15% for the water-poor alkali basalts (Fig. 1). Raman spectroscopy suggests that this excess carbon is contributed at least in part by dissolved CH$_4$ or –CH$_3$ (bonded to silicate network), and alkyne (C≡C-H) groups, and by only minor, if any, carbonyl groups.

Parameterization of $D_{^2\text{C}_{\text{silicate}}}$ Our experimental $D_{^2\text{C}_{\text{silicate}}}$ varies from $510 \pm 53$ to 5369 $\pm 217$ and also increases as a function of increasing $P$ and decreases as a function of increasing $T$, $f_O^2$, silicate melt water content, the composition of the silicate melt (expressed as NBO/T).

Fig. 2: $D_{^2\text{C}_{\text{silicate}}}$ values for experiments with water-poor, alkali basalt (Knippa; [3]) and hydrated alkali basalt (Knippa-H; [3]) as a function of temperature at three different pressures.

Using the data from this study and 10 more experimental $D_{^2\text{C}_{\text{silicate}}}$ values from glassy sample-bearing experiments of ref. [3], a preliminary, empirical parameterization was derived of the form: $\ln (D_{^2\text{C}_{\text{silicate}}}) = a/T + b \times P/T + c \times \ln f_O^2 + d \times (\text{NBO}/T) + e \times X_{^2\text{silicate}_H \text{O}_2} + f \times \ln (1 - X_{^8\text{metal}_\text{H}_2\text{O}}) + g$, where $a$, $b$, $c$, $d$, $e$, $f$, and $g$ are all constants derived from data regression and $T$ is in Kelvin and $P$ in Gigapascal. The use of the above parameterization, in conjunction with the estimated conditions of the base of the single-stage magma ocean for Earth ($P = 30$ GPa, $T = 3450$ K, $f_O^2 = \text{IW-1}$, $X_{^8\text{metal}} = 0.032$, $X_{^2\text{silicate}_H \text{O}_2} = 0.000143$, NBO/T = 2.74; [8-10]), and Mars ($P = 14$ GPa, $T = 2100$ K, $f_O^2 = \text{IW-1.5}$, $X_{^8\text{metal}} = 0.16$, $X_{^2\text{silicate}_H \text{O}_2} = 0.000143$, NBO/T = 2.55; [11]) yields $D_{^2\text{C}_{\text{silicate}}}$ value of $\sim$1500 and $\sim$100 for the base of the terrestrial and martian magma oceans, respectively. Thus metal-silicate fractionation may cause a difference in the abundance of carbon in the post-core formation magma ocean between various terrestrial planets such as Earth and Mars; post-core-formation magma ocean of Earth would be even more depleted compared to that of Mars. For Earth, equilibrium core formation with molten alloy: molten silicate ratio similar to the present-day core and mantle masses would lead to effectively carbon-free mantle [3, 4]. Thus for both Earth and less for Mars, other post-core-formation processes need to be considered to deliver carbon (and possibly other volatiles) to the silicate fractions of the planets. Much shallower magma ocean of the Moon on the other hand, likely retained much more carbon after a similar core-mantle fractionation. However, additional experiments at higher pressures and with more complex alloy melt chemistry (e.g., more S-rich and Si-rich) are necessary to validate these predictions on comparative volatile fractionation during early differentiation of terrestrial planets.