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**Introduction:** Partition coefficient of carbon between Fe-rich alloy melt and silicate melt, $D_c^{metal/silicate}$, at conditions similar to a magma ocean (MO) is a key quantity that needs to be determined in order to constrain the origin and initial distribution of carbon between planetary silicate fraction and metallic core [1, 2]. So far only [2, 3, 4] have experimentally measured $D_c^{metal/silicate}$ (100-5000) as a function of temperature ($T$: 1350-2100 °C), pressure ($P$: 1-5 GPa), $f_{O_2}$ (~IW-0.4 to IW-1), silicate melt composition (NBO/T = 0.8-3.6), and alloy melt composition (Fe/Ni ratio). However, all of these studies constructed alloy melt compositions that either had carbon as the only light element or had only a minor presence of sulfur. Nevertheless, about 5-12% light elements mainly including carbon, sulfur, and silicon may be present in the Earth’s outer core [e.g., 5]. Furthermore, these experiments did not extend to very reducing conditions (<1W-1.5) that may be relevant for early accretion of terrestrial planets such as Earth [e.g., 6].

On the other hand, understanding the solution mechanism of carbon in silicate melt is also of great importance in understanding carbon solubility in silicate melt and thus magma’s storage and transport capacities of carbon [1-3, 7]. The species of C-H-O volatiles in silicate, which are mainly a multi-function of fugacities of H$_2$O, H$_2$, and O$_2$, have been studied at $f_{O_2}$ around FMQ±2, and it was found that the dominant carbon species are carbonate complexes [1, 8]. However, both the solubility and speciation of C-H-O remain unclear in reduced silicate melt, resulting in the carbon species degassed from reduced MOs, and reduced, solid planetary mantles such as those of Mars and the Moon remaining unclear and debated [1, 4, 9].

We therefore performed an experimental study investigating systematically the effects of $T$, $P$, sulfur and/or silicon in Fe-rich alloy melt, water in silicate melt, and $f_{O_2}$ ranging from ~IW-1 to IW-5 on carbon solubility and partitioning in Fe-rich alloy and silicate melt systems.

**Experiments:** The starting silicate powder was a natural, alkalic Knippa basalt. To obtain a large range of $f_{O_2}$, about 30-40 wt% metal powder of Fe-Ni-S, Fe-Ni-Si, or Fe-Ni-S-Si mixture was mixed with the starting silicate powder. Three sets of experiments were conducted: The first set was conducted in the Knippa-Fe-Ni-S system at 3-6 GPa and 1600-1800 °C, the second set conducted in the Knippa-Fe-Ni-Si system at 3-8 GPa and 1600-2200 °C, and the third set conducted in the Knippa-Fe-Ni-S-Si system at 3-8 GPa and 1600-2200 °C. The silicate powder was dehydrated at 1000 °C and $f_{O_2}$ of ~FMQ-2 in order to obtain a relatively low water content. All the experiments at 3 GPa and 1600-1800 °C were conducted in graphite capsules, using an end-loaded piston cylinder device, while all the experiments at 4-8 GPa and 1800-2200 °C were conducted in graphite capsules, using a Walker-style multi-anvil device.

Electron microprobe was used for determining the major and minor element compositions of silicate melt and the alloy melt. A Cameca IMS 1280 ion microprobe was used for determining the bulk carbon and water contents in silicate glasses, and Raman and FTIR spectroscopy were used for determining and quantifying the possible C-H-O species in the silicate glasses.

Following previous studies [2, 3], the $f_{O_2}$ prevailing during the experiments was calculated from the equilibrium of Fe-rich alloy melt and FeO-bearing silicate melt. Our experiments covered $f_{O_2}$ range of IW-0.6 to IW-5.3.

**Results:** C solubility in Si-free alloy melt is around 5.5 wt%, and is affected little by $P$-$T$, or the presence of 0-5 wt% S in the alloy melt. C solubility in Si-bearing alloy melt, however, decreases significantly with increasing Si content in alloy melt (Fig. 1), although at a given Si content in alloy melt it is again little affected by $P$ and $T$.

![Fig. 1. C solubility in Fe-rich alloy melt as a function of Si content in alloy melt. The literature data at 1 bar are taken from [10].](image-url)

C solubility in silicate melt is affected strongly by $f_{O_2}$ and the bulk water content, rather than $P$ and $T$ in particular at $f_{O_2}$<IW-1.5 (Fig. 2). At $f_{O_2}$ from IW-0.6
to IW-1.5, there is a drop in C-solubility. However, at fO2<IW-1.5, C solubility increases significantly with decreasing fO2, and at a given fO2 the C solubility in silicate melt with a high water content is a few ten times higher than those in silicate with a low water content. Raman and FTIR spectra show that the silicate melts with fO2 around IW-0.6 contained ~10 ppm carbon as carbonate; however, at fO2<IW-1.5 only methane was detected. At 3 GPa and 1600 °C, a positive correlation between non-hydroxyl hydrogen and non-carbonate carbon has been observed, regardless of fO2, consistent with the Raman and FTIR observations that the main carbon species in reduced silicate melt is methane.

**Discussion and Implications:** At graphite-saturation, the dissolution of carbonate and/or methane in silicate melt is controlled by the fugacities of H2O, H2, and O2. A high fH2 would favor the dissolution of carbon as methane, while a high fO2 would favor the dissolution of carbon as carbonate. At a given fO2, a high fH2O would lead to a high fH2. The observed drop in C-solubility at fO2 from IW-0.6 to IW-1.5 (Fig. 2) is mainly due to the decreased carbonate content with decreasing fO2. However, the observed increase in C-solubility with decreasing fO2 is mainly caused by the increased fH2, and the observed low C-solubility in silicate melt with low water contents at a given fO2 is due to the low fH2O and thus fH2.

Our results demonstrate that fO2 and bulk water contents in silicate melt play an important role in determining the dissolution, partitioning, and thus fractionation of carbon in planetary MOs. A dry MO (<0.15 wt% H2O) would have lost its entire carbon into the core, and if delivery of bulk Earth carbon predominantly occurred after >90% of accretion, i.e., in a relatively oxidized MO (IW-2 to IW-1), then with applicable Dmetalsilicate >1000, most early Earth carbon would also enter the segregating core. A reduced, hydrous MO may have the potential to lead to a considerable fraction of carbon retained in the silicate mantle; however this requires that the fO2 of the MO may have to be <IW-3 and the water content of the MO may have to be > 0.75 wt.%, the maximum value investigated in this study.

The predominance of methane in reduced silicate melt at fO2<1W-1 also indicates that degassing of a hydrous, solidifying MO, as well as the reduced silicate mantles of Mars and the Moon may have released a certain amount of methane, creating a reduced atmosphere, which in turn may play an important role in the thermal evolution of the post-differentiation MO and the climate change of Mars.