THE ROLE OF CARBON IN CORE FORMATION UNDER HIGHLY REDUCING CONDITIONS WITH IMPLICATIONS FOR THE PLANET MERCURY. Kathleen E. Vander Kaaden[1,2], Francis M. McCubbin[2], D. Kent Ross[2, 3, 4], and David S. Draper[2]. [1]Lunar and Planetary Institute, 3600 Bay Area Boulevard Houston, TX 77058, [2]NASA Johnson Space Center, Mail Code XI, 2101 NASA Parkway, Houston, TX 77058, [3]Jacobs JETS, NASA Johnson Space Center, 2101 NASA Parkway, Houston TX 77058, [4]University of Texas at El Paso-CASSMAR (kathleen.e.vanderkaaden@nasa.gov).

Introduction: Results from the MErcury Surface, Space ENvironment, GEochemistry and Ranging (MESSENGER) spacecraft have shown elevated abundances of carbon on the surface of Mercury [1-3]. Furthermore, the X-Ray Spectrometer on board MESSENGER measured elevated abundances of sulfur and low abundances of iron [4, 5], suggesting the planet's oxygen fugacity (fO_2) is several $\log_{10}$ units below the Iron-Wüstite (IW) buffer [6, 7]. Similar to the role of other volatiles (e.g. sulfur) on highly reducing planetary bodies, carbon is expected to behave differently than it would under higher fO_2. As discussed by Nittler et al. [4] and Hauck et al. [8], under such highly reducing conditions, the majority of the iron partitions into the core. On Mercury, this resulted in a relatively large core and a thin mantle [8, 9].

Using a composition similar to the largest volcanic field on the planet (the northern volcanic plains), Vander Kaaden and McCubbin [10] conducted sink-float experiments to determine the density of melts and minerals on Mercury. They showed that graphite would be the only buoyant mineral in a mercurian magma ocean. Therefore, Vander Kaaden and McCubbin [10] proposed a possible primary flotation crust on the planet composed of graphite. Concurrently, Peplowski et al. [3] used GRS data from MESSENGER to show an average northern hemisphere abundance of C on the planet of 1.4 ± 0.9 wt%. However, as this result was only at the one-sigma detection limit, possible carbon abundances at the three-sigma detection limit for Mercury range from 0 to 4.1 wt% carbon. Additionally, Murchie et al. [1] investigated the possible darkening agent on Mercury and concluded that coarse-grained graphite could darken high reflectance plains to the low reflectance material. To further test the possibility of elevated abundances of carbon in Mercury's crust, Peplowski et al. [2] used the low-altitude MESSENGER data to show that carbon is the only material consistent with both the visible to near-infrared spectra and the neutron measurements of low reflectance material on Mercury, confirming that C is the primary darkening agent on Mercury. Confirmation of carbon on the planet prompts many questions regarding the role of carbon during the differentiation and evolution of Mercury. Given the elevated abundances of both S and C on Mercury's surface, it begs the question, what is the core composition of the planet? This study seeks to understand the impact of C as a light element on potential core compositions on Mercury.

Methods: With the exception of the 1300 °C experiments, conducted at UNM using procedures outlined in Vander Kaaden and McCubbin [11], all experiments were conducted in the high pressure laboratory at Johnson Space Center (JSC). Each experiment began by packing one of the Si-Fe metal mixtures (Table 1) into a graphite capsule using a Teflon coated spatula and wooden tamper to minimize Fe-loss due to magnetization with the spatula/tamper. The main difference between the UNM setup and the JSC setup is the pressure medium used and how the temperature is measured and monitored throughout an experiment. For the experiments conducted at JSC, loaded graphite capsules were placed within barium carbonate ($BaCO_3$) cells, which were used as a pressure medium, with crushable MgO parts and a graphite furnace. A hard fired alumina disk was placed between the top of the thermocouple wire and the graphite capsule to ensure no contact during the run that could result in oxidation or corrosion of the thermocouple wire. A Type C ($W_5Re_{95}/W_{26}Re_{74}$) thermocouple was used to monitor temperature throughout the run and was controlled by a Love controller throughout the duration of each run. Experiments were quenched by shutting off power to the furnace and slowly decompressing. Experiments were run at 1.0 GPa in the temperature range of 1300 °C – 1700 °C, with run durations of 8–24 hours.

Table 1. Composition of the metal starting materials used in this study. All values are in wt%.

	Low Si	Intermediate Si	High Si
Si	5	10	22
Fe	95	90	78
Total	100	100	100

All run products were polished using hexagonal boron nitride powder instead of water to ensure no carbon was lost from experimental charges [12]. All phases were analyzed using a JEOL 8530F microprobe at NASA's JSC. Samples were painted with colloidal silver slurry from the capsule to the edge to ensure electrical contact with the sample holder. Since each experiment only contained metal, there was no need to coat the samples with a conductive material. All analyses were conducted at 15 keV and 30 nA while using the cold finger on the microprobe to minimize carbon contamination. Si, Fe, and C were analyzed in each experiment. Carbon was analyzed with the LDE2 synthetic multi-layer crystal and was standardized using a synthetic cohenite (Fe_3C) standard made in the piston cylinder apparatus at JSC and verified by selected area

electron diffraction in a transmission electron microscope. Due to the wide peaks on the LDE2 spectrometer crystal as well as an interference between the backgrounds of C and Si, an optimal background was chosen to ensure this overlap was avoided. All data was corrected using the phi-rho-z matrix correction method, which is preferred when analyzing light elements.

Results: Each run product consisted of a metallic portion hosted by a graphite capsule. The metallic portion of each run typically quenched to a dendritic texture of Si-Fe rich, C-poor dendrites surrounded by C-rich, Fe-Si interstitial phases indicative of a quench texture. Consequently, we inferred that the metallic portion of each experimental charge was a single molten metallic phase during the run. Given that graphite was present at the end of each run, we also assume that the metallic liquid was saturated in C at the P and T conditions of the experiment. According to the 1-bar Fe-Si phase diagram, the runs at 1300 °C in the Si_5Fe_{95} should have remained solid. However, C addition into the Fe-Si system must have depressed the liquidus of the Fe-Si alloys as evidenced by the quenched dendritic texture exhibited by the run products. The ability of C to depress the liquidus apparently out-competed the effect of P to raise the liquidus temperatures, indicating that C has a strong effect on liquidus depression on the Fe-Si system.

We conducted broad beam analyses (15–20 µm) to determine the bulk compositions of the metallic melts at P and T. The Fe-Si alloy composition we investigated were similar to our target compositions in Table 1 with ~4.5–22.6 wt% Si and ~79.1–92.8 wt% Fe. The entire range of compositions we investigated exhibited a range in C abundances from 0.6 to 4.1 wt%, and we observed a strong positive correlation with C abundance and Fe abundance (Figure 1). We did not observe a strong T effect on the solubility of C in Fe-Si alloys.

Discussion: Given the surface composition of Mercury, it is likely that the planet formed under highly reducing conditions [6, 7]. The geochemical behavior of elements under these highly reducing conditions will differ from what is generally seen in more oxidizing conditions, like Earth [11]. At conditions as reducing as IW-3 to IW-7, Si partitions into the core of the planet [13]. Based on the experimental results in the present study, as Fe-rich cores become more Si-rich, the C solubility of that core composition will decrease.

Our experiments indicate that if Mercury has a Si-rich core (having more than ~5 wt% silicon), it would have saturated in carbon at low C abundances. If Mercury's volatile-rich nature [e.g., 14, 15] holds true for carbon, a substantial proportion of the carbon in Mercury would have been excluded from the metallic portion of the planet. Additionally, carbon solubility in silicate melts is exceptionally low under highly reducing conditions, so it would have been excluded from the silicate portion of the planet as well [16]. These two factors would have led to the early saturation in graphite within a mercurian magma ocean at 4–7 GPa. Following the results of Vander Kaaden and McCubbin [10], this

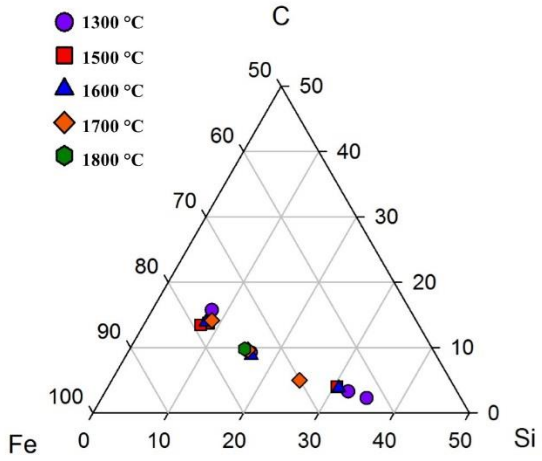

Figure 1. Fe-C-Si ternary diagram (atom %). Each symbol represents an average for all broad beam analyses within a given experiment.

graphite would have been less dense than the surrounding melt and would have floated toward the surface, possibly forming a primary graphite flotation crust. The presence of this flotation crust is consistent with observations from the MESSENGER spacecraft of darkened low-reflectance materials on the surface [1-3].

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