EXPLORING THE INFLUENCE OF OXYGEN ON PARTITIONING IN THE FE-S-O SYSTEM. Nancy L. Chabot[1] and Munir Humayun[2], [1]Johns Hopkins University Applied Physics Laboratory, 11100 Johns Hopkins Rd, Laurel, MD, 20723, USA. Nancy.Chabot@jhuapl.edu. [2]Department of Earth, Ocean, and Atmospheric Science, & National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, 32310, USA.

Motivation: The presence of non-metals, or "light elements," in metallic systems can have important effects on the partitioning behaviors of elements. Previous work has demonstrated this influence for S, P, C, and Si [e.g. 1-6]. Oxygen is another important light element in planetary processes, and considered a possible component of Earth's core [7], but experimental data examining the effect of O on partitioning behavior are lacking.

Data for the influence of O are lacking because the standard experimental approach used to examine the effects of S, P, and C can not be applied to examine the effect of O; solid metal-liquid metal experiments can't simply be run in the Fe-O binary system, as has been done in the Fe-S, Fe-P, and Fe-C systems. Experiments that involve O-bearing metallic liquids and silicate phases are difficult to interpret, as the O content of the liquid metal is tied to the oxygen fugacity of the system, which is a strong influence on element partitioning behavior.

Here, we present the first results from a study to determine the effect of O on partitioning behavior by conducting experiments in the Fe-S-O system. The approach is similar to a recent study published in the Fe-S-Si system to examine the effect of Si [6]. By leveraging the well-determined effect of S from numerous experiments in the Fe-S system [e.g. 3], experiments in the Fe-S-O system can be used to explore the effect of O on partitioning behavior.

Experimental and Analytical Methods: Experiments were conducted at 1 atm in evacuated silica tubes in a Deltech vertical tube furnace at the Applied Physics Laboratory, using similar techniques to previous studies in this lab [3, 6]. Starting materials consisted of commercially purchased powders of Fe, FeS, and FeO, doped with >20 trace elements at hundreds of ppm each, and starting mixtures were contained within hard alumina crucibles.

Experiments were run at 1400°C for 1 day. Run products consisted of solid metal coexisting with liquid metal, as shown in Fig. 1. Runs were first analyzed for the major elements of Fe, S, and O using the JEOL 8900L electron microprobe at the Carnegie Institution of Washington. Trace element concentrations were measured by laser ablation ICP-MS microanalysis at Florida State University.

First Results: To date, three experiments have been successfully conducted and analyzed. Running experiments in the Fe-S-O system is new to our lab

and proving to be more challenging than experiments previously conducted in other metallic systems. Laser ablation ICP-MS measurements indicated that in these three experiments, the highly siderophile elements of Pt, Ru, Ir, Re, and Os did not reach equilibrium. Future experiments and revisions to our experimental approach are planned to yield equilibrium partitioning values for these elements.

All three experiments were conducted at 1400°C and produced metallic liquids with ~20 wt% S. However, the liquid of #O1 was relatively O-poor, with ~3 wt% O, while the liquids of #O5 and #O9 were O-rich, with ~10-12 wt% O. Figure 1 illustrates the clearly visible difference between the O-poor and O-rich metallic liquids; the liquid in the O-poor run #O1 quenches to Fe dendrites surrounded by largely FeS, while the liquid in the O-rich run #O5 (and #O9) quenches to FeO dendrites surrounded by largely FeS.

Figure 2 summarizes the partitioning results of the three experiments. The measured solid metal/liquid metal partition coefficients (D) for the O-poor run #O1 are shown as black circles. One would expect the partitioning results of #O1 to be generally consistent with previous experiments in the Fe-S system, the results of which have been parameterized using an approach based on the domains present in the metallic liquid [3, 6, 8]. We consider the metallic liquid as being composed of FeS, FeO, and Fe domains. By this method, for run #O1 the fraction of domains in the liquid are roughly: Fe, 0.4 (40% of the liquid domains), FeS, 0.5, and FeO, 0.1. Using these liquid domains values, we calculate the D values predicted based on parameterizations of results from the Fe-S system. Overall, there is good general agreement between the measured D values for run #O1 (black circles) and the predicted D values (black line), as shown in Fig. 2.

The D results for the O-rich runs #O5 and #O9 are plotted on Fig. 2 as red circles and squares, respectively. Applying the same liquid domains calculation to the O-rich runs of #O5 and #O9, these liquids are composed of about 50% FeS domains, 50% FeO domains, and 0% Fe domains. The parameterizations of D from the Fe-S system are undefined at zero Fe domains, so we used a very small fraction of Fe domains of 0.05 (5%) to calculate the comparison D values, shown as a red line on Fig. 2. Thus, these predicted values from the Fe-S system are an extrapolation near the undefined portion of the parameterizations, sug-

gesting that confidence shouldn't be placed in the exact D values but rather in the generally predicted behavior.

The majority of elements show higher D values in runs #O5 and #O9 than in run #O1. This is consistent with the behavior predicted in the Fe-S system for elements that exhibit non-metal avoidance. For the elements Sb, Sn, Pd, As, Ni, Au, Mo, Co, Ga, and Rh, the measured D values in #O5 and #O9 (red circle and square) are generally consistent with the predicted behavior in the Fe-S system (red line), as seen on Fig. 2. This suggests that these elements avoid O in a similar manner to their avoidance of S.

Our results include data for three elements with chalcophile behavior in the Fe-S system: Ag, Cu, and Zn. Chalcophile elements are parameterized based on FeS domains in the liquid. These parameterizations predict that the D values for the O-rich runs of #O5 and #O9 will be similar to the D values measured in the O-poor run #O1, and indeed that is what is seen for these three elements in our data, as shown on Fig. 2.

Two elements exhibit behavior distinctly different in the O-rich runs of #O5 and #O9 than run #O1: Ga and W. Both elements have lower D values in the O-rich system than in the O-poor system. This behavior is consistent with Ga and W partitioning into the FeO domains of the liquid rather than avoiding them. Thus, the presence of an O-bearing metallic liquid will create fractionations of Ga and W from other elements with siderophile behaviors. Gallium and W are easily oxidized and are depleted in the metal of bulk ordinary chondrites [9, 10], so their affinity for O in the Fe-S-O system can be considered consistent with their behaviors in other systems [11].

Further experiments, with a range of O contents, are planed and will provide more detailed insight into these interesting first results regarding the effect of O.
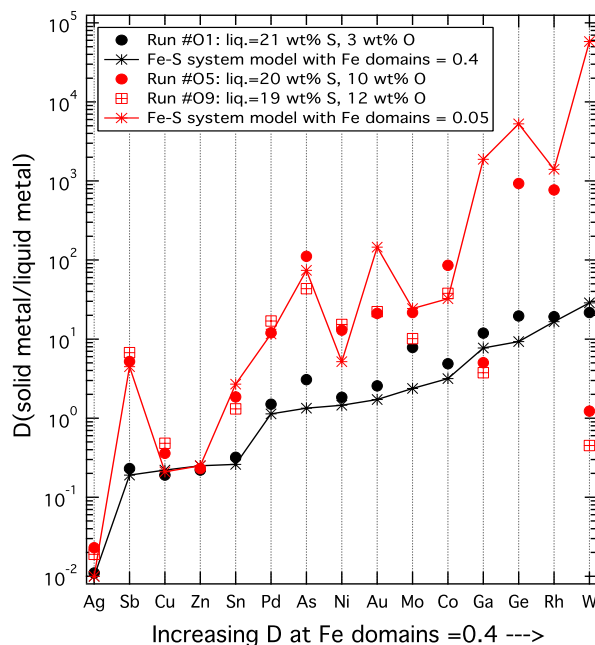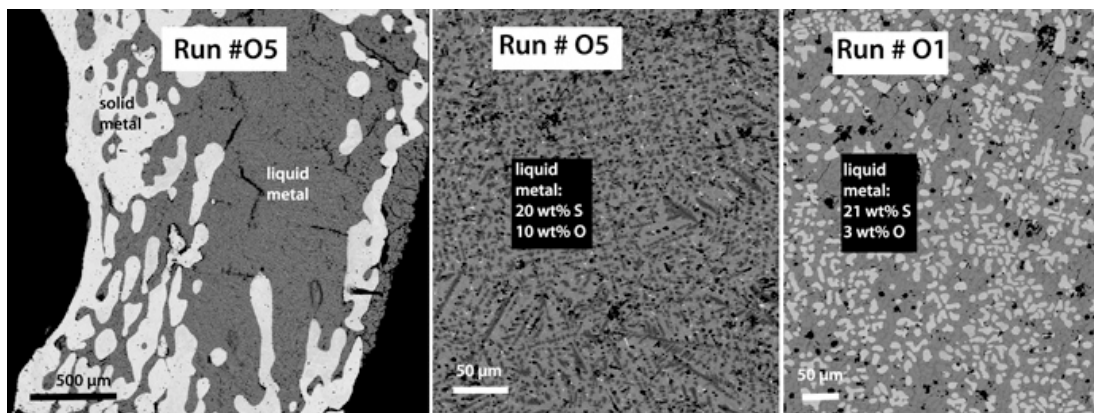
Fig. 1. (Above) Back-scattered electron images of runs.
Fig. 2. (Left) Partition coefficient results for experiments.

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