Introduction: Light elements (e.g., S, P, C) are known to have significant roles during the crystallization and cooling of asteroidal cores. During crystallization, these elements both influence partitioning of siderophile trace elements and form a variety of inclusions common in iron meteorites (e.g., sulfides, phosphides, carbides, graphite). During solidification, phosphorus, in particular, plays a significant role in the formation of the metallographic structure [1]. We have begun a series of solid metal-liquid metal partitioning experiments for a range of siderophile elements in the Fe-Ni-P system. Our interest stems from an ongoing project to link ungrouped irons to the established groups. As fractional crystallization of an asteroidal core reaches more evolved compositions, the P content of the core is also expected to increase dramatically. Yet, the effect of P on trace element partitioning behavior remains largely unknown.

Experimental methods: Fe-Ni-P experiments were conducted in 1 atmosphere Deltech vertical tube furnaces at the Smithsonian Institution and Johnson Space Center. All experiments were run using methods similar to those from previous studies [2]. Initial powders were mixtures of Fe and Ni (at 8-10 wt%), P (at varying wt % according to the Fe-P phase diagram seen in [3]) and a mixture of trace elements (at ~100 ppm each). Trace elements include Ag, As, Au, Bi, Co, Cr, Cu, Ge, Ir, Mb, Os, Pb, Pd, Pt, Re, Rh, Ru, Sb, Sn, Ta and W.

For each experiment, 0.300g of powder was placed into alumina crucibles and vacuum sealed into silica tubes. These silica tubes were hung in the furnaces for varying lengths of time (7 days to 14 hours, time decreasing with increasing temperature). Temperatures ranged from 1100ºC-1500ºC, increasing in 50ºC increments, with the addition of an 1125ºC run to better constrain the partitioning behavior at the low end of the temperature scale. Still-sealed silica tubes were immediately submerged in cold water upon removal from the furnace in order to quench the liquid metal.

Each successful experiment was sliced and made into a polished section. Each polished section was imaged (Fig. 1) and analyzed for major elements (Fe, Ni, P) using the electron microprobe. Solid metal regions were generally analyzed by point analyses, while liquid metal regions were measured using line scans with a defocused beam and averaged. Once runs were deemed successful, they were analyzed for trace elements on the LA-ICP-MS in the Department of Geology at the University of Maryland, College Park. Laser ablation measurements were made using line scans in a technique similar to that used in [4].

Results: The use of 8 wt.% Ni (chosen to match the average Ni concentration of a range of iron meteorite groups, including IVA) produced experiments at 1150ºC within the α-γ-liquid three-phase field and at 1100ºC likely in the α-liquid field. At higher temperatures, the 8 wt.% Ni experiments produced two-phases within the γ-liquid field. We observe a significant compositional difference between α and γ (including a factor of 2 difference in P), and consequently, only experiments showing the partitioning between γ and liquid are plotted in Fig. 2. In order to produce a comprehensive set of experiments which all lie in the γ-liquid field, we are re-running experiments at 1100-1200ºC with 10 wt.% Ni.

Ni and P exhibit essentially invariant partitioning between 1250º and 1450ºC, or 3.5 - 8.5 wt.% P in the metallic liquid, with $D_{Ni} = 0.89$ and $D_{P} = 0.11$.

Trace elements included in these experiments can be roughly placed into four groups:

1) Highly compatible elements include Os, Ir, Re, Pt and Ru.

2) Elements that have partition coefficients near unity at high-temperature and become highly-compatible at low-temperature, high-P concentrations include Ge, Rh, Co, W, Ga, Cu and Cr.
3) As and Au exhibit incompatible behavior at high-T, low-phosphorus and become compatible at low-T, high phosphorus.

4) Pd, Sb, Mo, Sn, Ag and Bi are all incompatible throughout the range of temperatures and phosphorus concentrations.

Overprinted on these groupings is the tendency for numerous elements (As, Au, Cu, Ge, Ga, Pt, Sb, and Sn) to become increasingly compatible at lower temperature and higher P concentration. No element was observed to exhibit P-loving behavior by having a partition coefficient that decreased as the P content of the metallic liquid increased.

Discussion. Although our work on partitioning in the Fe-Ni-P system is preliminary, several interesting implications can be drawn from this work. Phosphorous is strongly enriched in late-stage melts and, thus, in late-crystallizing irons. The enrichment of P in the liquid, combined with the likely incompatibility of oxygen in the Fe-Ni-P system and Fe-Ni-P-S system, suggests that late-stage phosphate formation, such as that observed in the high-Ni IVA iron EET 83230 [5,6] occurred in the liquid. This is consistent with the presence of euhedral phosphate surrounding rare FeS.

Further, our experiments suggest that the increase in D for a range of elements corresponds to an increasing P concentration. This same transition (to more P-rich melts) likely occurred during the crystallization of IVA irons, particularly if that group extends to high-Ni irons, such as EET 83230. Previous attempts to model the formation of these high-Ni irons (e.g., [7]) have been unsuccessful, postulating that changes in the partition coefficients for some elements at high S values might be the problem. Along with an evolved liquid having a high S content, it will also have a high P content, which must be accounted for in any attempt to understand the trace element fractionation patterns. Additionally, it is possible that liquid immiscibility in the Fe-Ni-S-P system was encountered in the latest stages of asteroidal cores [8] and to model the effects of this occurrence on trace elements requires knowledge of the effects of both S and P on partitioning values. Prior to this work, the effect of P on the behavior of trace elements was not well constrained. Using these data, these late stage processes can be modeled for the first time for many trace elements.