ANALYSIS OF MODERATELY SIDEROPHILE ELEMENTS IN ANGRITES: IMPLICATIONS FOR CORE FORMATION OF THE ANGRITE PARENT BODY. N. Shirai¹, M. Humayun¹, K. Righter² and A. J. Irving¹ ¹National High Magnetic Field Laboratory and Department of Geological Sciences, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, FL, 32310, USA (shirai@magnet.fsu.edu, humayun@magnet.fsu.edu), ²Astromaterials Research and Exploration Science, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, USA (kevin.righter-1@nasa.gov), ³Department of Earth & Space Sciences, University of Washington, Seattle, WA 98195, USA (irving@ess.washington.edu).

Introduction: Angrites are an enigmatic group of achondrites, that constitute the largest group of basalts not affiliated with the Moon, Mars or Vesta (HEDs). Chemically, angrites are exceptionally refractory element-enriched (e.g., Al, Ca) and volatile element-depleted (e.g., Na and K) achondrites [1]. Highly volatile siderophile and chalcophile elements (Zn, Ge and Se) may be less depleted than alkalis and Ga taken to imply a fractionation of plagiophile elements [1]. Core formation on the angrite parent body (APB) is not well understood due to the dearth of moderately siderophile element (Ga, Ge, Mo, Sb, W) data for angrites, with the exception of Ni and Co [2]. In particular, there are no data for Mo abundances of angrites, while Sb and W abundances are reported for only 3 angrites, and have not always been determined on the same sample [1, 3-7].

The recent increase in angrite numbers [13] has greatly increased our knowledge of the compositional diversity of the angrite parent body (APB). In this study, we report new Co, Ni, Ga, Mo, Sb and W abundances for angrites by laser ablation ICP-MS in order to place constraints on core formation of the APB.

Analytical methods: Determination of elemental abundances for D’Orbigny [8], Angra dos Reis, NWA 4801, NWA 4590 and NWA 4590 (fusion crust) were performed on a New Wave UP213 laser ablation system coupled to a Finnigan Element™ ICP-MS. A portion of the sample was rastered using a 100 µm beam spot, at 10µm/s, 20 Hz, 1.6 mJ laser energy on the UP 213. The peaks²³Na,²⁷Al,²⁹Si,⁴⁴Ca,⁴⁵Sc,⁴⁷Ti,⁵¹V,⁵²Cr,⁵⁵Mn,⁵⁶Fe,⁵⁹Co,⁶⁰Ni,⁶⁵Ga,⁷³Ge,⁷⁴Ge,⁹⁵Mo,⁹⁷Mo,¹²¹Sb,¹²³Sb,¹³⁹La,¹⁴⁴Nd,¹⁸⁵W and¹⁹⁳Ir were monitored in medium resolution mode (R = 4300). A detailed analytical procedure for fusion crust of NWA 4590 is reported separately [9]. Individual rasters on NWA 4801 and NWA 4590 exhibited a rather large degree of scatter, relative to data obtained from D’Orbigny, Angra dos Reis, and NWA 4590 fusion crust, so that not all ratios determined were used in the final averages reported here.

Results and Discussions: Co and Ni. Cobalt and Ni data are reported more often than other MSEs in the literature. Iron and Co abundances for angrites are shown in Fig. 1. There can be seen a positive correlation between Fe and Co abundances among angrites. However, a systematic deviation for Angra dos Reis to higher values of Co at a given value of Fe should be noted (indicated by open circles in Fig. 1). Based on spot analysis of pyroxene in Angra dos Reis, we found that Fe, Co and Ni abundances positively correlated with that of S, indicating that Fe, Co and Ni are affected by sulfide contribution. From these correlations, Fe, Co and Ni abundances for the silicate portion of Angra dos Reis were obtained. The elemental abundances for the parent magma of Angra dos Reis were calculated by using partition coefficients from [10]. The estimated Co/Fe and Ni/Mg ratios for parent magma of Angra dos Reis are then consistent with those for other angrites. As shown in Fig. 1, deviations of literature values from regression line is due to heterogeneous distribution of sulfide. CI-normalized Co/Fe and Ni/Mg ratios for APB are then obtained as 0.067± 20% and 0.0096± 55%, respectively.

Ga. Angrites have good correlations between Ga and Al abundances. The (Ga/Al)CI ratio obtained for the APB is 0.0055± 26%.

Mo. It is known that Mo and Nd have similar degrees of incompatibility during terrestrial igneous processes [11]. Our data for Mo/Nd ratios of angrites have a range of 0.015-0.043. The (Mo/Nd)CI ratios obtained in this study is 0.014 ± 48%.
Sb. Jochum and Hofmann [12] found that Sb/Pr ratios for MORB and OIB were constant, indicating that Sb behaves like the incompatible element Pr during terrestrial igneous processes. Neodymium abundances for angrites are plotted against their Sb abundances in Fig. 2, where literature values are also shown for comparison. For Angra dos Reis, our Sb values are in good agreement with literature values obtained by RNAA [1]. Angra dos Reis exhibits a Sb/Nd ratio identical to that of other angrites (Fig. 2), implying that incompatibility of Sb is similar to that of Nd during igneous processes in APB, as found for terrestrial rocks [12]. The (Sb/Nd)$_{IC}$ ratio obtained for APB is 0.017 ± 14%.

W. There is a considerable spread in W/La ratios among angrites due to variation of W abundances. This variation of W/La ratios for angrites is higher that of previous studies [2]. D’Orbigny and NWA 4590 have similar W/La ratios of 0.064 and 0.060, respectively, three times higher that of our Angra dos Reis value (0.023). As Angra dos Reis is a pyroxene-cumulate rock, its W/La ratio requires a correction for selective partitioning by pyroxene, for which suitable experimental data is not currently available.

Figure 2. Neodymium vs. Sb abundances for angrites. Solid and open symbols represent our data and literature values, respectively. The line represents a regression line for angrites, excluding LEW 87051.

Conditions of Metal-Silicate Equilibrium in the APB. MSE abundances of the APB mantle were calculated from the observed correlations with refractory lithophile elements, using estimates of the LREE content of the APB mantle. Our new data for Mo imply that the angrite parent body mantle contained ~ 40 ppb Mo. When this result is combined with new and existing data for Ni, Co, and W [2], depletions for all four elements can be estimated. Using these new estimates of APB mantle concentrations, the metal/silicate partition coefficient expressions of [13], and assuming a CV chondrite bulk composition of the APB [14], we can test whether the new Mo data is consistent with the presence of a small core in the APB, as suggested by [2]. Figure 3 compares the observed depletions with calculated depletions of MSE. Consideration of a simple model shows that if the core size is fixed at 8 mass%, the Ni, Co, Mo and W abundances can be explained by metal-silicate equilibrium between peridotite mantle and a FeNi metallic liquid core at 2073 K, 1 kb, and IW-1 (Fig. 3). This pressure is consistent with a core near the center of a body a few hundred km in radius. Since angrites record oxygen fugacity near IW+1 [10], angrite basalts would have to be oxidized upon degassing and eruption. This is consist with the presence of vesicles in several angrites [15] possibly indicating the presence of a C-bearing gas derived from carbon (graphite) in the APB mantle source that underwent oxidation during melting.

Figure 3 Comparison of observed (solid region) and calculated (solid circles) depletions of Ni, Co, Mo and W.