PRESSURE EFFECT ON PARTITIONING OF Ni, Co, S: IMPLICATIONS FOR MANTLE-CORE FORMATION, J. Li and C. B. Agee, Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, U.S.A.

Summary. Isothermal experiments up to 20 GPa show a dramatic influence of pressure on partitioning of Ni and S between molten Fe-alloy and silicate melt. Both Ni and Co become less siderophile with pressure. Pressure affects Ni much more than Co such that their decreasing partition coefficients (D alloy melt / silicate melt) reach values of 29 and 26 respectively at an extrapolated pressure of ~28 GPa. The observed abundances of Ni and Co and their near chondritic ratio can be explained by alloy-silicate chemical equilibrium at high pressure during core extraction in a magma ocean. The partitioning behavior of sulfur is the opposite of Ni and Co -- it becomes more siderophile with pressure. Sulfur's enhanced affinity for Fe-alloy with depth indicates that it is likely the dominant light element in the Earth's core.

Experimental and Analytical methods. Experiments were performed at pressures of 2, 5, 10, 12, 14, and 20 GPa, under isothermal conditions of 2000°C, with a Walker-style octahedral multi-anvil device. Details of the experimental design and technique can be found in Agee et al. [1]. Starting material was finely ground powder from a split of the Allende meteorite from The Smithsonian Institution. Sample capsules were fashioned from high purity MgO rod. All experiments contained coexisting immiscible liquids of silicate and Fe-rich alloy. Both silicate and alloy liquids, upon quenching, formed discrete, relatively large masses of crystals and glass. The average compositions of these domains were determined by multiple broad beam analyses using a Cameca electron microprobe.

Results. In the range 2 to 20 GPa the partition coefficient of Ni decreases more than five fold from 318 to 59 while that of Co only decreases by less than half from 45 to 27. Sulfur behaves in the opposite way. Its partitioning coefficient increases by several fold from 74 to 519 over the same pressure range. Oxygen fugacity was estimated to be near or slightly below the iron-wuestite buffer and varies only by one half log unit in the experiments. As the effect of oxygen fugacity on partitioning would cancel out, the observed variations in D_{Ni} to D_{Co} ratio are owing mainly to a pressure effect (Figure 1). Our results agree well with that of Thibault and Walter [2] who studied a sulfur-free system up to 12 GPa.

Discussion. The high pressure partitioning data can explain one of the most enigmatic aspects of the "excess siderophile problem", namely the near chondritic Ni/Co in the upper mantle. The results are consistent with molten Fe-alloy equilibrating at the base of a silicate magma ocean with depth 750-1100 km. The data do not favor a magma ocean that reached depth of ~2900 km (the present core-mantle boundary) because mantle Ni/Co would become strongly super-chondritic. Shallow magma oceans (<700 km) are also ruled out because of the sub-chondritic Ni/Co produced at lower pressures. The data can also be applied to a scenario in which core formation commenced when the Earth reached one tenth of its present mass or about half of its present radius. In this case, the upper and the lower mantles could have a similar Ni/Co signature. The fate of sulfur during accretion is more difficult to assess than Ni and Co due to its moderately volatile nature. It is generally agreed that the sulfur content of the upper mantle is two orders of magnitude lower than the concentration of sulfur in chondrites. Such large depletion can be partly explained by volatile loss to space during a high temperature stage of Earth accretion, or a significant fraction of sulfur may have entered the Earth's core. Our experimental results argue in favor of a sulfur-depleted mantle by alloy/silicate equilibria and in turn support the hypothesis that sulfur is the dominant light element in the molten outer core.

PRESSURE EFFECT ON Ni, Co, S PARTITONING: Li J. and Agee C. B.

References. [1]. Agee, C.B. et. al. (1995) *J. Geophys. Res.*, **100**, 17,725-17,740. [2]. Thibault, Y. and Walter, M.J., (1995) *Geochim. Cosmochim. Acta*, **59**, 991-1002.

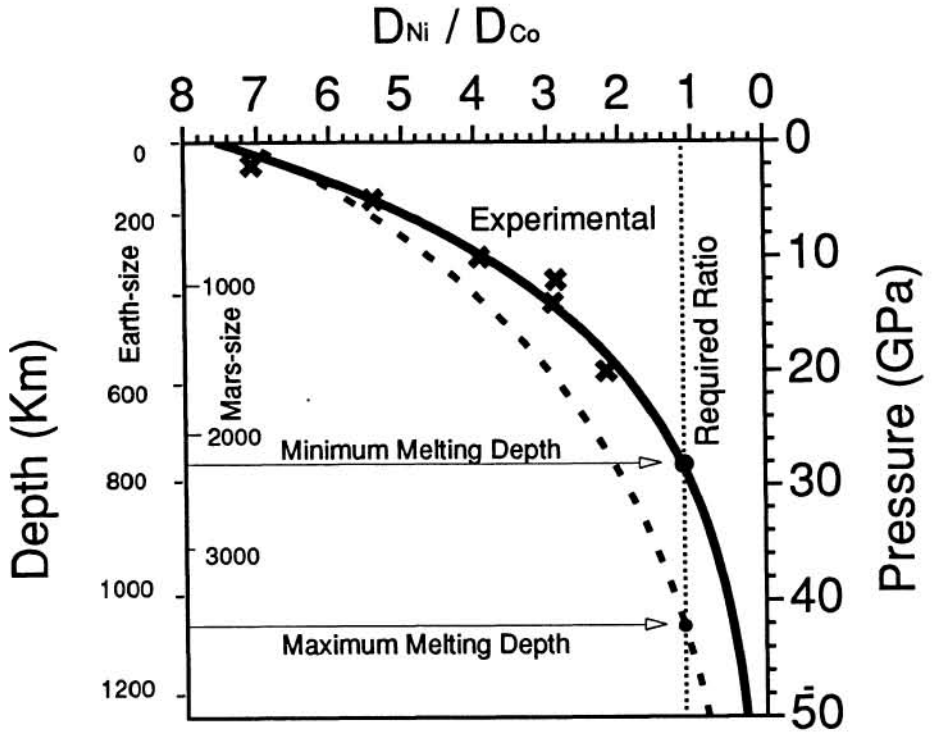

Figure 1. D_{Ni} / D_{Co} versus Pressure (P) diagram. The equivalent depths in the Earth and Mars are shown as references.

Solid curve is least-squares fit for the experimental data of the form D_{Ni} / D_{Co} = A*e^(B*P), where A and B are constants. Solid curve describes the changing D_{Ni} / D_{Co} with depth in a magma ocean. It intersects the required ratio line (D_{Ni} / D_{Co} = 1.1) at ~28 GPa. The pressure of 28 GPa can be interpreted as the base of the molten mantle (depth of ~750 km) where a well-mixed magma ocean equilibrates with ponded molten alloy.

Dashed curve is calculated from experimental data and represents the bulk effect of local equilibriums between a compositionally-zoned magma ocean and the core. It intersects the required ratio line at ~ 42 GPa or a depth of ~1100 km. The physical meaning of this "bulk value depth" can be envisaged as small immiscible alloy droplets dispersed throughout a poorly-mixed magma ocean. In contrast to the previous scenario, here convective mixing is inefficient -- the silicate melt column equilibrates with droplets at local pressures as they sink and develops a Ni/Co gradient that increases with depth.