SULFUR IN EARTH'S MANTLE AND ITS BEHAVIOR DURING CORE FORMATION. Nancy L. Chabot[1] and Kevin Righter[2], [1]Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel, MD, 20723, nancy.chabot@jhuapl.edu. [2]NASA JSC, Mail Code KT, Houston, TX, 77058, kevin.righter-1@nasa.gov.

Introduction: The density of Earth's outer core requires that about 5-10% of the outer core be composed of elements lighter than Fe-Ni; proposed choices for the "light element" component of Earth's core include H, C, O, Si, S, and combinations of these elements [e.g. 1]. Though samples of Earth's core are not available, mantle samples contain elemental signatures left behind from the formation of Earth's core. The abundances of siderophile (metal-loving) elements in Earth's mantle have been used to gain insight into the early accretion and differentiation history of Earth, the process by which the core and mantle formed, and the composition of the core [e.g. 2-4]. Similarly, the abundance of potential light elements in Earth's mantle could also provide constraints on Earth's evolution and core composition.

The S abundance in Earth's mantle is 250 (±50) ppm [5]. It has been suggested that 250 ppm S is too high to be due to equilibrium core formation in a high pressure, high temperature magma ocean on early Earth and that the addition of S to the mantle from the subsequent accretion of a late veneer is consequently required [6]. However, this earlier work of Li and Agee [6] did not parameterize the metal-silicate partitioning behavior of S as a function of thermodynamic variables, limiting the different pressure and temperature conditions during core formation that could be explored. Here, the question of explaining the mantle abundance of S is revisited, through parameterizing existing metal-silicate partitioning data for S and applying the parameterization to core formation in Earth.

Method: Li and Agee [6] conducted liquid metal-liquid silicate partitioning experiments using the CI Allende meteorite as the starting composition, and their results are in good general agreement with the experimental results of previous studies involving the solubility of S in magmas [7-9]. The experiments found that as the temperature increased, the liquid metal-liquid silicate partition coefficient for S, D(S), decreased. In contrast, increasing pressure resulted in an increase in D(S). However, without parameterizing these contrasting effects, it is difficult to quantitatively explore what the behavior of S would be like during core formation in a magma ocean, which involved both high temperatures and high pressures.

In addition to the effects of pressure and temperature, the metallic liquid composition can affect the partitioning behavior. Experimental studies [10, 11] suggest that D(S) does not obey Henry's Law over a wide range of S contents, and this effect must also be included in any parameterization.

Oxygen fugacity and silicate composition can also significantly affect D(S) [7-9, 12]. However, since the purpose of the parameterization is to examine Earth's core formation, silicate composition and oxygen fugacity conditions can be selected that are relevant to Earth and then the parameterization can be derived to be appropriate to these fixed conditions. The chosen form of the parameterization was based on thermodynamic relationships and is similar to the form used by other studies that have examined the distribution of siderophile elements during core formation [e.g. 13, 14]. The resulting parameterization of D(S) is:

$$\log[D(S)] = 90\frac{P}{T} + \frac{4900}{T} + 0.08(wt\%S) - 1.1 \quad \textbf{eq. 1}$$

where P is in GPa, T is in K, and the concentration of S in the metallic liquid is in wt%. It is important to remember the imposed limitations of the above parameterization. The parameterization was designed to be applicable only to a silicate composition similar to bulk silicate Earth, an oxygen fugacity about one to two log units below the iron-wüstite buffer, and with ≤ 10 wt% S in the metallic liquid. Though these are limitations, these are also the conditions that are generally relevant to core formation on Earth.

Application to Earth: Using a core with a S content of 2-10 wt% [e.g. 1] yields a required D(S) of about 80-400, respectively. A S content of ~10 wt% could account fully for the outer core density deficit, without a significant concentration of other light elements. However, such a high concentration of S may be above what is cosmochemically available for the bulk Earth, which Dreibus and Palme [15] estimate could provide a maximum of 1.7 wt% S to Earth's core. Regardless, for a given core S content, eq. 1 can be used to solve for combinations of pressure and temperature that produce the value of D(S) required to match the S abundance in Earth's mantle.

Figure 1 shades the pressure and temperature space where the parameterized value of D(S) is predicted to be within a factor of two of the value required to explain the mantle S abundance. The factor of two is used as a rough estimate of the uncertainty, consistent with that used by Chabot et al. [14] for a similar parameterization with similar 10-20% errors in the determined parameterization

constants. Interestingly, using a core S content of 2 versus 10 wt% yields almost identical pressure and temperature solution spaces. This is related to the fact that as the S content of the metal increases, both D(S) and the required D(S) to match the mantle S abundance increase, resulting in a general cancellation of the two effects.

As shown on Fig. 1, there are a number of pressure and temperature combinations that predict D(S) values that can explain Earth's mantle S concentration. There is also a sizable overlap in the D(S) solution space with the pressure and temperature solution space as determined from matching the Ni and Co depletions in Earth's mantle by core formation in a deep magma ocean [14]. Furthermore, the pressure range (~35-60 GPa) and temperature range (~2500-4000 K) suggested by the overlapping solutions from D(S), D(Ni),and D(Co) provide generally reasonable pressure and temperature combinations for having a liquid magma ocean overlaying a solid silicate mantle [16, 17]. This result suggests that simple metal-silicate equilibrium during core formation on Earth, such as that present in an early magma ocean, is consistent with the currently observed mantle abundance of S.

This work represents a rough estimate and parameterization of the behavior of S during core formation on Earth. The experimental data sets used to determine the behavior of S are limited, and the solution spaces are at much higher pressures and temperatures than covered by the experimental data, requiring extrapolations. However, even with these caveats, a rough estimate suggests that Earth's mantle S content can be matched by liquid metal-liquid silicate equilibrium in a magma ocean.

This result does not rule out the possibility of a late influx of material being added to Earth's mantle; the relative chondritic proportions of the highly siderophile elements, the near chondritic ratios of S, Se, C, and Te, and the similar relative abundances for all of these elements could be due to the addition of a late veneer [18, 19]. Our result simply indicates that a late veneer of material may not be necessary to explain the S abundance in Earth's mantle. However, if core formation did occur in an early magma ocean on Earth, the behavior of S during core formation combined with the observed S abundance of the mantle today places important constraints on the composition and amount of any late veneer material that was subsequently added to Earth.

References: **[1]** Hillgren V. J. et al. (2000) in: *Origin of the Earth and Moon*, Univ. AZ Press, 245-263. **[2]** Walter M. J. et al. (2000) in: *Origin of the Earth and Moon*, Univ. AZ Press, 265-289. **[3]** Rubie D. C. et al. (2003) *EPSL 205*, 239-255. **[4]** McDonough W. F. (2003) in: *Treatise on Geochemistry, Vol. 2*, Elsevier-Pergamon, 547-568. **[5]** McDonough W. F. and Sun S. -s. (1995) *Chem Geol. 120*, 223-253. **[6]** Li J. and Agee C. B. (2001) *GRL 28*, 81-84. **[7]** Haughton D. R. et al. (1974) *Econ. Geol. 69*, 451-467. **[8]** Wallace P. and Carmichael I. S. E. (1992) *GCA 56*, 1863-1874. **[9]** Mavrogenes J. A. and O'Neill H. St. C. (1999) *GCA 63*, 1173-1180. **[10]** Chabot N. L. and Drake M. J. (1999) *EPSL 172*, 323-335. **[11]** Chabot N. L. and Agee C. B. (2003) *GCA 67*, 2077-2091. **[12]** Kilburn M. R. and Wood B. J. (1997) *EPSL 152*, 139-148. **[13]** Righter K. et al. (1997) *PEPI 100*, 115-134. **[14]** Chabot N. L. et al. (2005) *GCA 69*, 2141-2151. **[15]** Dreibus G. and Palme H. (1996) *GCA 60*, 1125-1130. **[16]** Zhang J. and Herzberg C. (1994) *JGR 99*, 17729-17742. **[17]** Boehler R. (2000) *Rev. Geophys. 38(2)*, 221-245. **[18]** Yi W. et al. (2000) *JGR 105*, 18927-18948. **[19]** Morgan J. W. et al. (2001) *MaPS 36*, 1257-1275.
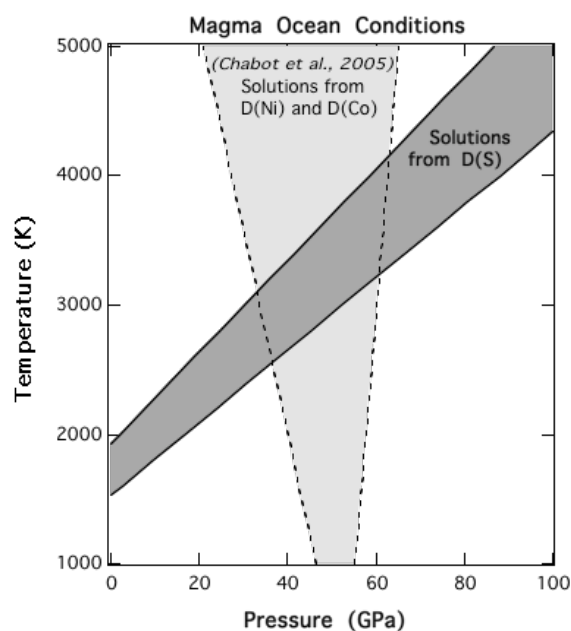

Fig. 1. Shaded areas represent the pressure and temperature conditions where Earth's mantle concentrations of Ni, Co, and S can be fit within a factor of two by equilibrium metal-silicate core formation in a magma ocean.