

CORE/MANTLE PARTITIONING OF CHLORINE AND A NEW ESTIMATE FOR THE HYDROGEN ABUNDANCE OF EARTH. Z.D. Sharp¹, D. S. Draper² and C. B. Agee^{1,2}, ¹Dept. Earth and Planetary Sciences, Northrop Hall, University of New Mexico, Albuquerque, NM 87131, zsharp@unm.edu, ²Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131.

Introduction: Chondrites have been used to ascertain the Earth abundances of all but the most volatile elements. Of these, H abundance has dramatic ramifications for the properties of the planet, including rheology and melting relations of the mantle and density and phase relations in the core, yet is poorly known. The very mechanisms of formation of Earth and degassing history depend on the amount of water originally accreted and ultimately lost. If the Earth's chlorine abundance were well known, it could be used to constrain its H content, because 1) Cl has a strong affinity for water – it is a hydrophilic element; 2) the H/Cl mass ratio of chondrites is relatively constant (Table 1), and 3) the ratios of volatile elements in Earth closely resemble chondritic abundances [1]. We have constrained the Cl abundance on Earth and are able to refine the H (water) estimate of Earth using a completely new method.

Table 1. Wt fraction and H/Cl ratio of chondrites. Average ratio is 25 if CO is excluded. Data from [13,14].

| | CI | CM | CV | CO | L | Avg. |
|----------|------|-----|------|------|-----|------|
| H (wt %) | 2.02 | 1.4 | 0.28 | 0.07 | 0.2 | 0.98 |
| Cl ppm | 700 | 430 | 250 | 280 | 76 | 364 |
| H/Cl | 29 | 33 | 11 | 3 | 26 | 20 |

The crustal abundance of H – mostly as water in the ocean – is well known. The ocean volume of $1.37 \times 10^9 \text{ km}^3$ corresponds to $\sim 1.5 \times 10^{23} \text{ g}$ of H_2 . The recognition that nominally anhydrous minerals in the mantle contain some hydroxyl adds another 85% to the H budget [2] and the deep mantle may “store about five times more H_2O than the oceans” [3]. Ohtani [4] estimated that the mantle contains six times the ocean hydrogen abundance. The recognition of hydrous high pressure phases [5-7] implies a larger water component in the deep mantle. The H content of the core is very poorly known; estimates range from 600 ppm or $1.2 \times 10^{24} \text{ g}$ [8], 0.6%, or $1.3 \times 10^{25} \text{ g}$ [9], to $1.7 \times 10^{26} \text{ g}$ [7].

Experiments: Most elements closely follow the ‘planetary volatility trend’ line. The halogens fall dramatically below this line (Fig. 1). McDonough [8] proposed that the deficiency may be explained if Cl is

strongly partitioned into the core, containing 200 ppm (8th most abundant element in core) compared to 17 ppm for the bulk silicate Earth. We tested this hypothesis by conducting high pressure Cl partitioning experiments using a Walker-style multianvil press (Table 2). Two experiments were run at 5 GPa and 1800°C in graphite capsules, one (A503) with equal proportions of primitive basalt (10.4 wt% MgO, Mg# 67) and pure Fe and excess FeCl_2 , and a second (A505) with equal proportions of basalt and $\text{Fe}_{95.5}\text{S}_{4.5}$. A third experiment (A516) was run at 1900°C and 15 GPa, also using $\text{Fe}_{95.5}\text{S}_{4.5}$ as a ‘core’ composition. All experiments produced homogeneous quenched silicate and metallic liquid (Fig. 2). Cl contents in metal were below detection (60 ppm) in A503 and A516 and in three of the six metal analyses in A505. The maximum metal-silicate D_{Cl} values are three orders of magnitude lower than required for significant sequestration of Cl in the core. Unless there are strong effects of pressure and/or silicate liquid composition on D_{Cl} , our experimental results imply that Cl does not reside in the core. This constrains the total Cl content of Earth to $1.1 \times 10^{23} \text{ g}$; ($6.9 \times 10^{22} \text{ g}$ in mantle; $3.9 \times 10^{22} \text{ g}$ in crust) [10], with an uncertainty of about a factor of two.

There are a number of mechanisms for H and Cl loss during Earth formation, however, it is difficult to envision a process by which Cl would be lost *preferentially* to H. Noble gas ratios argue against a primary (nebular) atmosphere, so that the vast majority of volatiles were delivered from solid bodies [11]. Some H_2 and H_2O can be lost by hydrodynamic escape. HCl could also be lost by this process, but to a lesser extent due to the higher mass than H_2O . Also, Cl will reside as an aqueous salt if liquid water is present unless the water was extremely acidic, a condition that could not be maintained for any appreciable length of time.

The vast majority of H on Earth comes from planetesimals – hydrogen contribution from the solar nebula and comets is minimal [12]. Using a H/Cl chondritic mass ratio of 25 ± 7 [13,14], the mass of H on Earth is $2.8 \pm 0.7 \times 10^{24} \text{ g}$, or less if there has been a

Table 2. Experimental results.

| Expt. # | Metal Comp. | FeCl_2 wt% starting material | P GPa | T (°C) | Cl wt% in silicate | Cl in metal (ppm) | D (metal/silicate) |
|---------|----------------------------------|---------------------------------------|-------|--------|--------------------|-------------------|--------------------|
| A503 | Fe | 0.22 | 5 | 1800 | 0.53 | <60 | <0.01 |
| A505 | $\text{Fe}_{95.5}\text{S}_{4.5}$ | 0.88 | 5 | 1800 | 1.05 | 78 | 0.007 |
| A516 | $\text{Fe}_{95.5}\text{S}_{4.5}$ | 0.88 | 15 | 1900 | 0.81 | <60 | <0.007 |

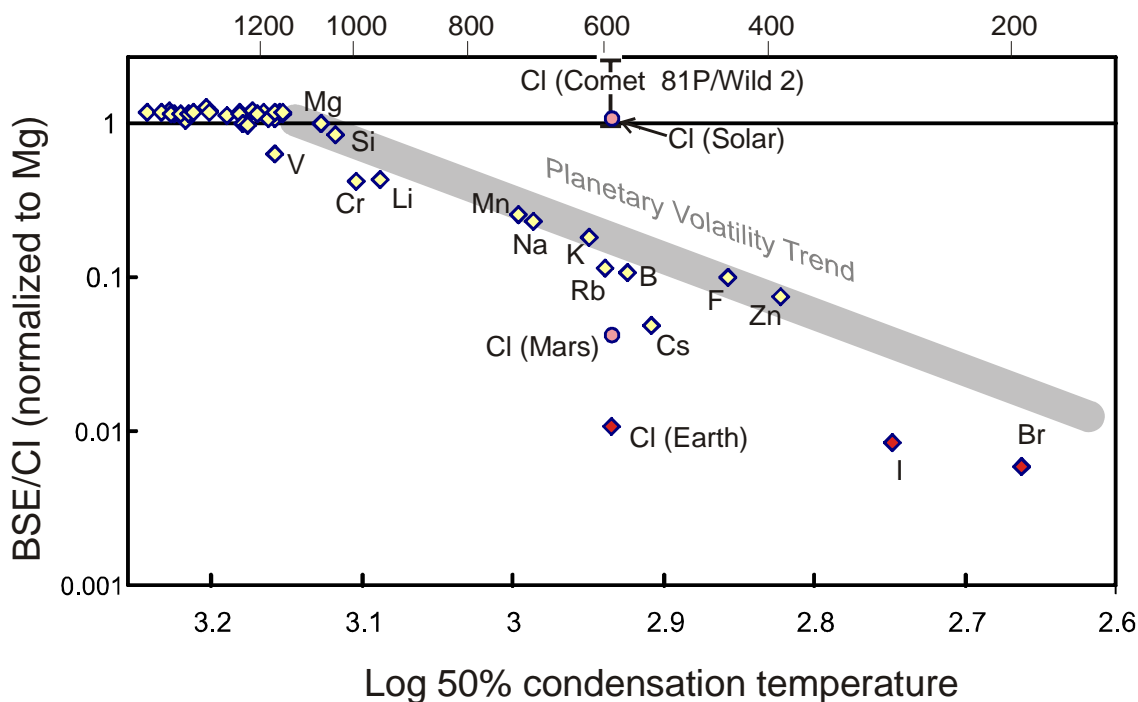


Fig. 1. Planetary volatility trend showing the 10× depletion of halogens on Earth. Data from the following sources: [8, 15-17].

preferential loss of hydrogen. These results significantly constrain the H core abundance. Regardless of whether the mantle has 5 or 10 times the crustal abundance, the core must have less than $(1.1 \text{ to } 1.8) \times 10^{24}$ g H. The core H content is therefore < 570 to 960 ppm H (depending on mantle abundance), in excellent agreement with the 600 ppm estimate of McDonough [8], but far less than experimental estimates [9]. On the basis of Earth Cl content, no more than ~4.6% of

Earth could be sourced by volatile-rich chondrites, regardless of later water loss.

References: [1] Marty B. and Dauphas N. (2002) In *The Early Earth: Physical, Chemical and Biological Development*, Vol. 199 213-230. [2] Bell D. R. and Rossman G. R. (1992) *Science* **255**, 1391-1397. [3] Murakami M., Hirose K., Yurimoto H., Nakashima S., and Takafuji N. (2002) *Science* **295**, 1885-1887. [4] Ohtani E. (2005) *Elements* **1**, 25-30. [5] Ringwood A. E. and A. M. (1967) *Earth Planet. Sci. Lett.* **2**, 130-133. [6] Akimoto S. and Akaogi M. (1980) *Phys. Earth Planet. Interiors* **23**, 268-275. [7] Williams Q. and Hemley R. J. (2001) *Annual Rev. Earth Planet. Sci.* **29**, 365-418. [8] McDonough W. F. (2003) In *Treatise on Geochemistry*, Vol. 2, pp. 547-568. [9] Fukai Y. and Suzuki T. (1986) *J. Geophys. Res.* **91**, 9222-9230. [10] Eggenkamp H. G. M. (1994) The Geochemistry of Chlorine. PhD thesis, Universiteit Utrecht. [12] Abe Y., Ohtani E., Okuchi T., Righter K., and Drake M. (2000) In *Origin of the Earth and Moon*, 413-434. [13] Wasson J. T. and Kallemeyn G. W. (1988) *Phil. Trans. Royal Soc. London* **325**, 535-544. [14] Lodders, K. and Fegley, B. (1998) *The Planetary Scientists' Companion*, 371 pp. [15] Asplund M., Grevesse N., and Sauval A. J. (2006) *Nuclear Physics A* **777**, 1-4. [16] Dreibus G. and Wanke H. (1987) *Icarus* **71**, 225-240. [17] Flynn G. J. and others (2006) *Science* **314**, 1731-1735.

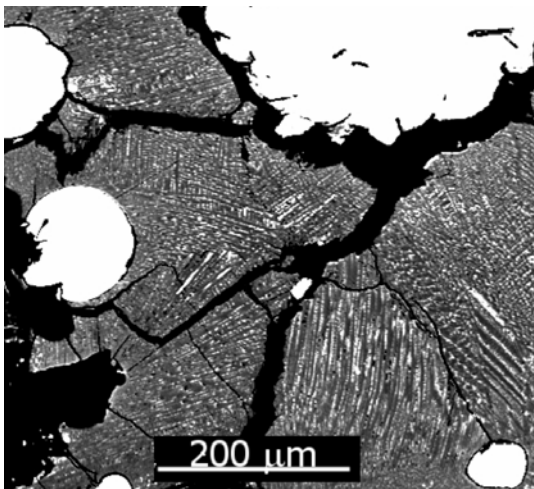


Fig. 2. BSE image showing metallic liquid spheres (white) in quenched basalt with 'spinifex' texture. All Cl is in silicate and below detection in metal.