

**ORIGIN OF MAJOR VOLATILES (H,C,N,S) IN THE BULK EARTH: INSIGHTS FROM MODERATELY VOLATILE ELEMENTS, AND FROM C/S VS. C SYSTEMATICS OF CHONDRITIC AND ACHONDRITIC METEORITES** M.M. Hirschmann<sup>1</sup>, J. Li<sup>2</sup>, E.A. Bergin<sup>3</sup>, F. Ciesla<sup>4</sup>, G.A. Blake<sup>5</sup>, <sup>1</sup>Dept. Earth Sciences, U. Minnesota (*mmh@umn.edu*), <sup>2</sup>Earth&Env. Sci. U. Michigan <sup>3</sup>Dept. Astro. U. Michigan Dept. <sup>4</sup>Dept. Geophys. Sci. U. Chicago <sup>5</sup>Div. Geol. Planet. Sci. Caltech.

Models for accretion and retention of Earth's major volatile elements (H,C,N,S) must be consistent with processes that produced Earth's systematic depletion in moderately volatile elements (MVEs) [1,2], meaning those with "condensation" temperatures ( $T_C$ ) <1400 K [3]. To better understand the acquisition of major volatile elements to the growing Earth, we consider the relationship between Earth's C and S and MVE abundances and compare estimated bulk earth (BE) C and S to available concentrations from chondritic and achondritic meteorites.

The well-known correlation of CI-normalized lithophile element concentrations in the Bulk Silicate Earth (BSE) [4] with  $T_C$  [3] (Fig. 1) reflects a depletion process that likely occurred owing to heating and degassing on precursor planetesimals or embryos. Here,  $T_C$  is taken as a measure of the propensity of an element to volatilize into a H-rich vapor, and does not necessarily imply actual condensation of solids from a gas. Unlike MVE depletions in chondrites, which could derive from an admixture of processed depleted material with a primitive volatile-rich "matrix" [5], the MVE depletion pattern of the BSE does not show a plateau at low  $T_C$ . The favored site of depletion is in small bodies because volatile loss from bodies with significant gravity should correlate with molecular mass, rather than chemical propensity to reside in the gas [1]. The systematic depletion of MVEs with condensation temperature is not easily reconciled with models of Earth accretion chiefly from large embryos formed by pebble accretion or streaming instabilities, which are thought to deliver comparatively primitive (e.g., chondritic) highly volatile (e.g., H<sub>2</sub>O) cargos to the growing planet [6].

Because C and S are both siderophile, much of their BE inventories are likely in the core. The trend in lithophile MVE concentrations and effective condensation temperature can be used to estimate BE C and S, similar to previous efforts based chiefly on Zn [7,8]. This correlation using the BSE concentrations of 11 MVEs (chiefly lithophile, showing a coherent trend on Fig. 1) indicates a BE S concentration of 9400 ppmw, which in turn implies 2.8±0.4 wt.% S in the outer core, consistent with constraints from seismology [9,10]. Similar estimates for C depend on the assumed principle phase controlling C condensation: clathrate ices ( $T_C$ =40 K [3]), refractory organics ( $T_C$ ~400 K [11]), or graphite ( $T_C$ =626 [3]). Resulting BE C concentration estimates range from 670-5300 ppmw C, or a maxi-

imum of 0.18-1.6 wt.% in the outer core, if inner core C is negligible. These BE abundances are based on the assumption that  $T_C$ , the temperature controlling volatilization of elements on planetesimals, correspond to those occurring in an H-rich gas, which could be appropriate for planetesimals differentiating before the dissipation of the solar nebula. Later devolatilization in the presence of a protoplanetary vapor [12] would predict somewhat different BE S and C.

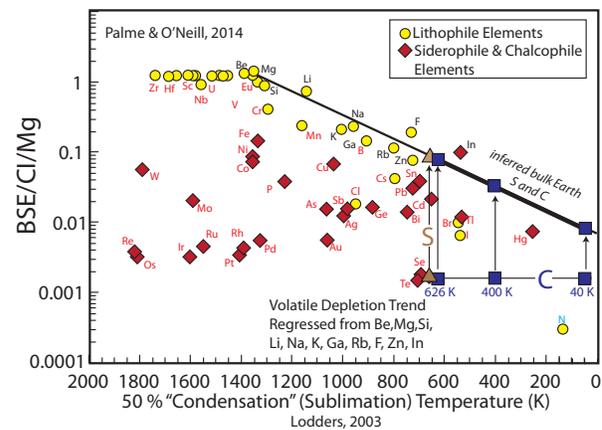


Fig. 1 The BE S and C concentrations estimated from linear regression of the trend of lithophile element depletion in the BSE (normalized to CI and Mg) [4] as a function of condensation temperature [3]. Uncertainties in the phase controlling C volatilization result in large uncertainties in BE C.

Unsurprisingly, the estimated BE S and C concentrations, plotted as  $\log(C/S)$  vs.  $\log(C)$ , are distinct from those of chondrites (Fig. 2), consistent with the observation that MVE depletions in the BE arise from different processes than those responsible for MVE patterns on chondritic parent bodies. Achondritic C/S vs. C concentration patterns provide possible insights into the effects of planetesimal differentiation on major volatile depletions. Caution is warranted because achondrite sample populations likely represent only part of their parent bodies, e.g., achondritic basalts give indication about the concentrations in planetesimal crusts, but not (directly) their interior. Also, sampling biases adds considerable uncertainty to parent body concentration estimates, particularly for irons.

Stony achondrites plot along a linear trend in  $\log C/S$  vs.  $\log C$  space (Fig. 2). The reason for this empirical correlation is not clear, as the trend includes parent

bodies ranging from highly depleted in C (HED) to highly enriched (ureilites) and both differentiated achondrites (HEDs, angrites, etc.) representing planetesimal crusts, and primitive achondrites (acapulcoites, winonaites), representing possible whole parent body compositions. Displacement of this trend relative to the chondritic trend and to the BE composition reflects greater S depletion in stony achondrite parent bodies.

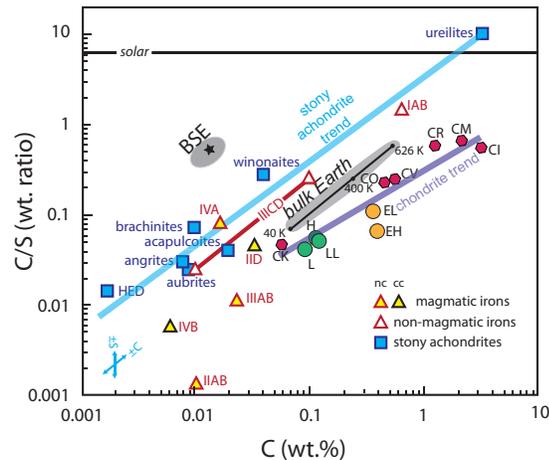


Fig. 2  $C/S$  versus  $C$  systematics for the BSE [15], BE (this work) and chondritic and achondritic meteorites compiled from the literature [many sources]. The range of BE  $C/S$  vs.  $C$  reflects chiefly the uncertainty in the phase controlling  $C$  volatilization (see text).

Inferred iron parent body  $\log C/S$  vs.  $\log C$  systematics are highly variable, owing at least in part to analytical uncertainties, sampling biases, and iron meteorite heterogeneity. However, iron bodies with both non-carbonaceous (NC) and carbonaceous (CC) affinities based on Ru and Mo isotopes [13] are not enriched in S and C relative to chondrites. As cores formed from chondrites should be S- and C- enriched compared to their parent bodies (and therefore would plot to higher C and lower  $C/S$  compared to the chondrite trend shown in Fig. 2), the depleted character of irons strongly indicates devolatilization affected iron parent bodies. It has been suggested that such devolatilization could be owing to accretion in hot portions of the solar nebula [14], but the depletions evident in CC irons suggest this also occurred as part of a parent body process.

Though achondrites may or may not be good analogs of differentiated planetesimals that contributed to terrestrial accretion, their  $C/S$  versus  $C$  systematics illustrated in Fig. 2 render them plausible as representative of compositions that contributed to BE major volatile accretion. The  $C/S$  versus  $C$  trends in Fig. 2 allow for the possibility that the BE major volatiles were contributed by a combination of undifferentiated (chondritic) and differentiated (achondritic) precursor parent bodies or that they originated from differentiat-

ed precursors that experienced less extreme devolatilization than represented by the empirical stony achondritic trend.

**Concluding Remarks** Because depletion of BSE and BE MVEs likely occurred on small precursor planetesimals and embryos, these volatile-loss processes also affected major (H,C,N,S) volatiles. Models attempting to account for the BSE or BE inventory of major volatiles and especially their relative depletions compared to chondrites must not only consider possible primitive (chondritic) sources and planetary differentiation processes, but also the effects of volatile loss on small differentiated precursor bodies.

**References** [1] Albarede F. (2009) *Nature*, 461, 1227-1244. [2] Albarede F. *Icarus*, 222 44-52. [3] Lodders K.A. (2003) *ApJ*, 591,1220-1247. [5] Braukmüller N. et al. *GCA* 239, 17-48. [6] Wu J. et al. (2018) *JGR*, 123, #E005698. [7] Dreibus G. & Palme H. (1996) *GCA*, 60,1125-1130. [8] Mahan B et al. (2017) *GCA*, 196,252-270. [9] Badro J. et al. (2014) *PNAS*, 111,7542-7545. [10] Zhang Y. et al. (2016) *Sci. Reports*, 6,22473. [11] Nakano H. et al. (2013) *ApJ*, 592,1252-1262. [12] Norris C.A. & Wood B.J. (2017) *Nature*, 549, 507-510. [13] Kruijer T.S. et al. (2017) *PNAS*, 114, 6712-6716. [14] Bland P.A. & Ciesla F.J. (2010) *LPSC XLI*, #1817. [15] Hirschmann M.M. (2016) *Am. Mineral.*, 101,540-553.