

**DANA MEDAL PAPER**

**Constraints on the early delivery and fractionation of Earth's major volatiles from C/H, C/N, and C/S ratios**

**MARC M. HIRSCHMANN<sup>1,\*</sup>**

<sup>1</sup>Department of Earth Sciences, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

**ABSTRACT**

Earth's inventory of principle volatiles C, H, N, and S is a legacy of its early stages of accretion and differentiation. Elemental ratios (C/H, C/N, C/S) are powerful tools for understanding early processing of Earth's volatiles, as they monitor relative fractionations through important processes even when absolute concentrations are less well defined. The C/H ratio of the bulk silicate Earth (BSE), defined from surface reservoirs and minimally degassed oceanic basalts is  $1.3 \pm 0.3$ , which is 5–15 times lower than the C/H ratio of carbonaceous and enstatite chondrites and 2–5 times lower than ordinary chondrites. The BSE C/N ratio is superchondritic ( $40 \pm 8$ ; Bergin et al. 2015) while the C/S ratio ( $0.49 \pm 0.14$ ) is nearly chondritic. Successful models of volatile acquisition and processing must account for the effects of accretion, core formation, and atmospheric loss on all three of these ratios.

Simple models of equilibration between a magma ocean, the overlying atmosphere, and alloy destined for the core are used to explore the influence of core formation and atmospheric loss on major volatile concentrations and ratios. Among major volatile elements, C is most siderophile, and consequently core formation leaves behind a non-metallic Earth with low C/H, C/N, and C/S ratios compared to originally accreted materials and compared to the BSE. Compared to the predicted effect of early differentiation, the relatively high C/X ratios of the BSE argue in part that significant volatile replenishment occurred after core formation ceased, possibly in the form of a late veneer. However, a late veneer with chondritic composition is insufficient to explain the pattern of major volatile enrichments and depletions because BSE C/H and C/N ratios are non-chondritic. The C/H ratio is best explained if an appreciable fraction of H in the BSE predates delivery in the late veneer. Although atmospheric blow-off is an attractive explanation for the high C/N ratio, available data for C and N solubility and metal/silicate partitioning suggest that atmospheric blow-off cannot counter core formation to produce subchondritic C/N. Thus, unless virtually all core-forming metal segregated prior to volatile accretion (or relative C and N solubilities are appreciably different from those assumed here), the BSE C/N ratio suggests that accreting materials had elevated ratios compared to carbonaceous chondrites. One possibility is that a fraction of Earth's volatiles accreted from differentiated C-rich planetesimals similar to the ureilite parent body. Reconciling C/H, C/N, and C/S ratios of the BSE simultaneously presents a major challenge that almost certainly involves a combination of parent body processing, core formation, catastrophic atmospheric loss, and partial replenishment by a late veneer. The chondritic C/S ratio of the BSE and relatively low S content of the BSE constrains the BSE C concentration, but a potential complicating factor in interpreting the BSE C/S ratio is the possible effect of segregation of an S-rich matte to the core during the later parts of core-mantle differentiation.

**Keywords:** Volatiles, magma ocean, core formation, accretion