THE ORIGIN OF EARTH'S MAJOR VOLATILES VIA ACCRETION OF A LARGE PLANETARY EMBRYO

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Introduction: Earth's habitable surface environment are the result of well-tuned fluxes of life-essential volatile elements (LEVEs) such as carbon (C), nitrogen (N), sulfur (S), and hydrogen (H) involving the exosphere and the solid silicate Earth. However, the abundance pattern of C-N-H-S in the bulk silicate Earth (BSE: ocean-atmosphere, crust, and the mantle) remains a mystery. Based on their isotopic signatures, terrestrial volatiles are thought to derive from carbonaceous chondrites, while isotopic compositions of major and trace non-volatile elements suggest enstatite chondrite-like material to be the primary building blocks. However, the C/N ratio in the BSE is superchondritic [1,2], which rules out volatile delivery as a chondritic late veneer, and if delivered during the main phase of the Earth's accretion, then owing to greater siderophile (metal loving) nature of C relative to N, core formation should have left behind a subchondritic C/N ratio in BSE [3]. Core formation should have also produced a subchondritic C/S ratio, although the BSE C/S ratio is chondritic [4]. Here we present high pressure-temperature experiments to constrain the fate of mixed C-N-S volatiles during the core-mantle segregation in the magma oceans (MOs) of planetary embryos and show that C becomes much less siderophile in N-bearing and S-rich alloys, while the siderophile character of N remains largely unaffected in the presence of S. Using the new data and inverse Monte Carlo simulations, we show that the impact of a volatile-bearing Mars-sized planet, coinciding with the Moon forming event, can be the source of major volatiles in the BSE [5]. We also show that the volatile budget of the planetary embryo can be generated via only a small contribution from volatile-rich carbonaceous chondrites.

Methods: We performed high P-T experiments using piston cylinder and multi anvil devices with Fe-Ni-N-C±S alloys and mafic silicate mixtures in graphite capsules at 1-7 GPa, 1600-1800 °C, and a limited oxygen fugacity range (fO$_2$) of IW –1.31 to IW –0.83 (IW refers to fO$_2$, defined by the coexistence of Fe and FeO). Relatively low P of our experiments is justified as we explored the effect of alloy-silicate equilibration on C-N-S budgets in the bulk silicate reservoirs of planetary embryos that are much smaller relative to the Earth, while a relatively oxidized fO$_2$ range was explored to simulate the late stage accretion of relatively oxidized planetary embryos to a more reduced proto-Earth.

Concentrations of the major elements, N, and C in the experimental alloy phases, and the major elements and N in the quenched silicate melts were determined using a JEOL JXA8530F Hyperprobe EPMA at Rice University. C and H content of the silicate glasses were determined using ion microprobe. Raman and FTIR spectroscopy was employed to evaluate C-O-N-H speciation in the silicate glasses.

Results: All experiments produced quenched metal blobs in silicate matrix.

N is mildly siderophile ($D_N^{alloy/silicate} \sim 10$-31) across the entire range from the S-free to the S-rich systems with the S-free to the intermediate-S alloy bearing systems having slightly higher values relative to the high-S alloy bearing systems (Fig. 1A). However, in the presence of N, high-S in the alloy leads to a drop in $D_C^{alloy/silicate}$ by an order of magnitude in comparison to values in the intermediate-S or the S-free alloy bearing systems (Fig. 1B). Due to simultaneous expulsion of C from the alloy melt and an increase in its solubility in silicate melt caused by N, $D_C^{alloy/silicate}$ is distinctly lower in comparison to those in the N-free systems [e.g., 6, 7] (Fig. 1B). Because $D_N^{alloy/silicate}$ is largely unaffected by the presence of S in the alloy, while $D_C^{alloy/silicate}$ drops considerably mainly due to increase in the S content of the alloy and also partly because of C-N complexation in the silicate melt, our $D_C^{alloy/silicate}/D_N^{alloy/silicate}$ and $D_C^{alloy/silicate}/D_S^{alloy/silicate}$ values reveal that C is less siderophile than both N and S for MO systems with >25 wt.% S in the alloy, while with ~12-25 wt. % S in the alloy, C is more siderophile than N but less siderophile than S.
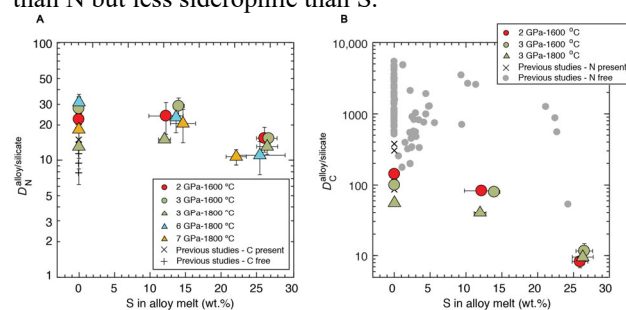

Fig. 1: $D_N^{alloy/silicate}$ (A) and $D_C^{alloy/silicate}$ (B) as a function of sulfur content of the alloy melt.

Discussion: Our results suggest that for a planetary embryo whose core forming alloy is S-rich, the super-chondritic C/N ratio in its silicate reservoir resulting from the core-mantle separation can either be attained via a C-undersaturated core if $D_C^{alloy/silicate} < D_N^{alloy/silicate}$, or via a C-saturated core if $D_C^{alloy/silicate} > D_N^{alloy/silicate}$. In the latter case, graphite or diamond would be expelled from the core and get added to the overlying MO, leading to generation of a superchondritic C/N ratio. The question is whether a planetary body with an S-rich core could be responsible for delivering the volatiles to the Earth.

Inverse Monte-Carlo simulation: To test whether a differentiated planetary body of a reasonable composition can deliver the major volatiles to the proto- Earth and to determine its possible size and architecture, we performed multiple sets of ~10^9 inverse Monte-Carlo simulations exploring the composition and the mass range of the impactor which on merger with a volatile-depleted proto-Earth satisfies the present-day BSE C, N, and S abundances as well as their ratios. The bulk C and S contents in the impactor were varied from 0.05 to 6 wt.% and 0.05 to 8 wt.%, respectively, to test the complete spectrum of chondritic values, while the bulk N was fixed by the average CI chondrite C/N ratio of 21. The alloy/silicate mass ratio of the impactor (alloy/silicate$_{imp}$) was varied from 0.05 to 0.5 (within the range for all rocky bodies in the Inner Solar System except Mercury) while the mass of the impactor to the present-day Earth's mass ($M_{impactor}/M_{Earth}$) was varied from 0.01 to 0.5. In agreement with the recent suggestions based on geochemical [e.g., 8] and dynamical studies [9], we assumed that the core of a large differentiated planetary embryo merges with that of the proto-Earth with no equilibration with the proto Earth's mantle.

Through our simulations we independently constrained the impactor's mass, its bulk C content and the S content of its core ($S_{alloy,imp}$). The bulk S content of the impactor and the alloy/silicate$_{imp}$ were dependent variables set by the $S_{alloy,imp}$. The required bulk C content of the impactor, with maximum number of solutions at ~3000 ppm C, increases with increasing bulk S and the alloy/silicate$_{imp}$. All the model solutions favor a C-saturated core of the impactor because alloy/silicate partitioning alone yields subchondritic C/N and C/S in the impactor's mantle. The mass of the impactor was constrained to be $0.085^{+0.03}_{-0.04}$ M$_{Earth}$, which is close to the mass of Mars. If the impactor's core undergoes small degrees of equilibration with the post-merger MO of the proto-Earth, then some C-N-S budget of the Earth's BSE can also be supplied by the

impactor's core along with its mantle. Most probable bulk C of the impactor increases, while the mass of the impactor decreases with increasing degree of equilibration of impactor's core.
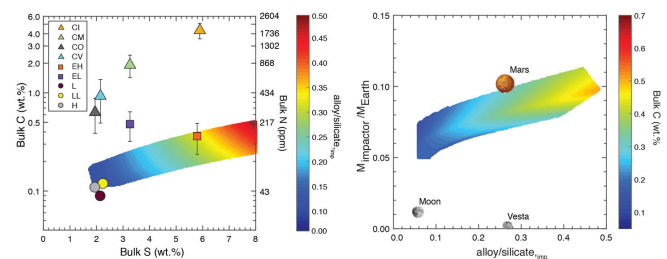

Fig. 2: The results of inverse Monte Carlo simulations to obtain the composition and the mass of the differentiated impactor that could establish the C-N-S abundance pattern of the BSE.

The volatile delivery by a Mars-sized impactor predicted by our simulations may point towards volatile delivery during the Moon-forming event [10]. Because the Earth and the Moon have C, N and H isotopic composition indistinguishable from CI-chondrites [e.g., 11] whereas O, Ca, Ti, and Cr isotopic composition akin to E-type chondrites [12] we suggest that the impactor that brought C-N-S to BSE could be the Moon-forming impactor, if it was made from a small contribution from CI-chondrites. Our study also explains the similarity of the terrestrial isotopic ratios of C, N, and H with the eucrite meteorites [11], which suggests an early accretion of CI chondritic material in the Inner Solar System. This along with the early formation of differentiated planetary embryos may indicate that the timing of the accretion of the volatiles in the impactor, similar to the accretion of the volatiles in Vesta [11], was within ~5-20 Myrs of the Solar System formation (8). However, the delivery of the volatiles to the Earth via the merger of a larger planetary embryo was at a later stage.

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