

# Tracing the ingredients for a habitable earth from interstellar space through planet formation

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**We use the C/N ratio as a monitor of the delivery of key ingredients of life to nascent terrestrial worlds. Total elemental C and N contents, and their ratio, are examined for the interstellar medium, comets, chondritic meteorites, and terrestrial planets; we include an updated estimate for the bulk silicate Earth (C/N = 49.0 ± 9.3). Using a kinetic model of disk chemistry, and the sublimation/condensation temperatures of primitive molecules, we suggest that organic ices and macromolecular (refractory or carbonaceous dust) organic material are the likely initial C and N carriers. Chemical reactions in the disk can produce nebular C/N ratios of ~1–12, comparable to those of comets and the low end estimated for planetesimals. An increase of the C/N ratio is traced between volatile-rich pristine bodies and larger volatile-depleted objects subjected to thermal/accretional metamorphism. The C/N ratios of the dominant materials accreted to terrestrial planets should therefore be higher than those seen in carbonaceous chondrites or comets. During planetary formation, we explore scenarios leading to further volatile loss and associated C/N variations owing to core formation and atmospheric escape. Key processes include relative enrichment of nitrogen in the atmosphere and preferential sequestration of carbon by the core. The high C/N bulk silicate Earth ratio therefore is best satisfied by accretion of thermally processed objects followed by large-scale atmospheric loss. These two effects must be more profound if volatile sequestration in the core is effective. The stochastic nature of these processes hints that the surface/atmospheric abundances of biosphere-essential materials will likely be variable.**

terrestrial worlds | elements | interstellar medium | comets | meteorites

The development of a habitable world and a stable biosphere requires the delivery of biogenic elements of which carbon and nitrogen are crucial. Carbon is the backbone for the chemistry of life and, in the form of CO<sub>2</sub>, combines with water to provide the greenhouse needed for a habitable Earth. Nitrogen is a key component of DNA, RNA, and proteins, while also present as the dominant constituent of our atmosphere. The processes that supply these crucial ingredients remain poorly understood. In interstellar space, C and N are abundant, but inherently volatile and so chiefly remain in the gas. Thus, the terrestrial planets, which accrete primarily from rocks and ices, are fed from C- and N-depleted materials and are carbon and nitrogen poor compared with the nebular disk from which they descend (1, 2). The carbon and nitrogen depletion of rocky bodies is a general phenomenon, observable not just in our solar system, but also in the polluted atmospheres of white dwarf stars, which trace the composition of disrupted planetesimals (3, 4). This volatile poor state of terrestrial planets is partially imparted from the starting materials. However, further differential loss of C and N can occur due to parent body processes such as thermal metamorphism, core segregation, planetary outgassing, and atmospheric loss (5–11).

In this work we document the evolution in the relative concentrations of C and N from the interstellar medium (ISM) through planetary assembly. We show that the C/N ratio contains clues regarding the formation of terrestrial planets and the delivery/fate of

crucial volatile compounds. We first discuss the relative carbon and nitrogen inventories beginning with the ISM as it evolves to the protoplanetary disk, using the perspectives of kinetic chemistry, our growing understanding regarding the composition of planet-forming disks, and volatile loss within thermally processed planetesimals. We then explore the evolution of C/N during geochemical differentiation of a young Earth-like planet, built up by accretion of planetesimals of a range of sizes. Key processes during this last stage of C/N evolution include sequestration into the metallic core and outgassing to the nascent atmosphere. It is, of course, the latter that can provide ingredients for early environments and life, but early atmospheres are also prone to impact-driven escape, providing additional mechanisms for C and N processing and alteration.

## Carbon and Nitrogen Inventories

Fig. 1 displays the carbon-to-nitrogen ratio observed in the Sun, bulk silicate Earth (BSE) (defined in *SI Text*), meteoritic samples, comets, and that inferred in the ISM. To provide an absolute reference frame, Fig. 2 provides bulk C and N abundances normalized to Si. (Further details regarding this compilation, including technique where appropriate, are found in *SI Text* and *Table S1*.) Key considerations include the following:

- i) In the ISM, significantly more carbon than nitrogen is incorporated into carbonaceous dust (e.g., Fig. 2), with a correspondingly lower C/N ratio (less than solar) in the gas. The primary form of condensed carbon is uncertain, but models assume it is an aliphatic/aromatic hydrocarbon mixture (12, 13). Interstellar ices have elevated C/N ratios, with a median value of C/N ~ 12 (14). However, this does not account for N or N<sub>2</sub>, which are infrared inactive. Correcting for the presence of N<sub>2</sub> in ices (*SI Text*) leads to a C/N ratio for ices of ~1.8.

## Significance

With the rapid pace at which exoplanets are being discovered, many efforts have now been dedicated to identifying which planets are expected to have the ingredients necessary for the development of life. In this work we explore the relative disposition of the essential elements carbon and nitrogen in each stage of star and planet formation, using the Earth and our solar system as grounding data. Our results suggest that planets like the Earth are readily supplied with these key elements, but their relative amounts on the surface and in the atmosphere will be highly variable.

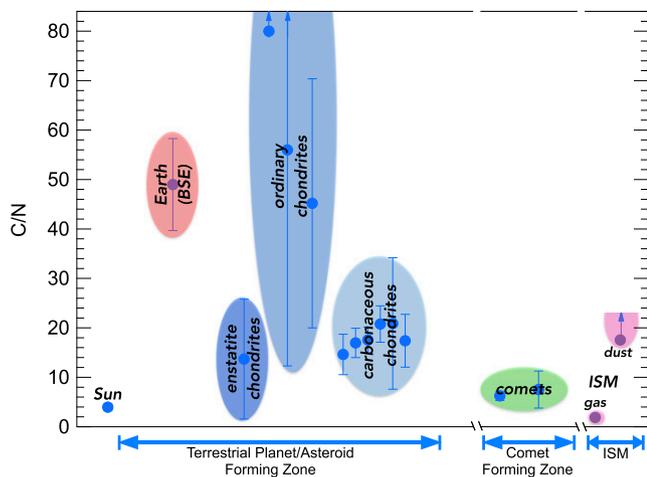
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**Fig. 1.** Atomic ratios of bulk carbon relative to nitrogen in various solar system bodies and the ISM, based on the compilation in Table S1 and references in SI Text. The shaded ovals represent the range/errors in the measured data for each class. Ovals that are not complete indicate that the listed value is an upper/lower limit. For chondrites the errors represent the range of determined values, whereas for other bodies the errors are  $1\sigma$  measurement uncertainties. For additional details, an expanded version of this figure with labels for each point is provided as Fig. S1.

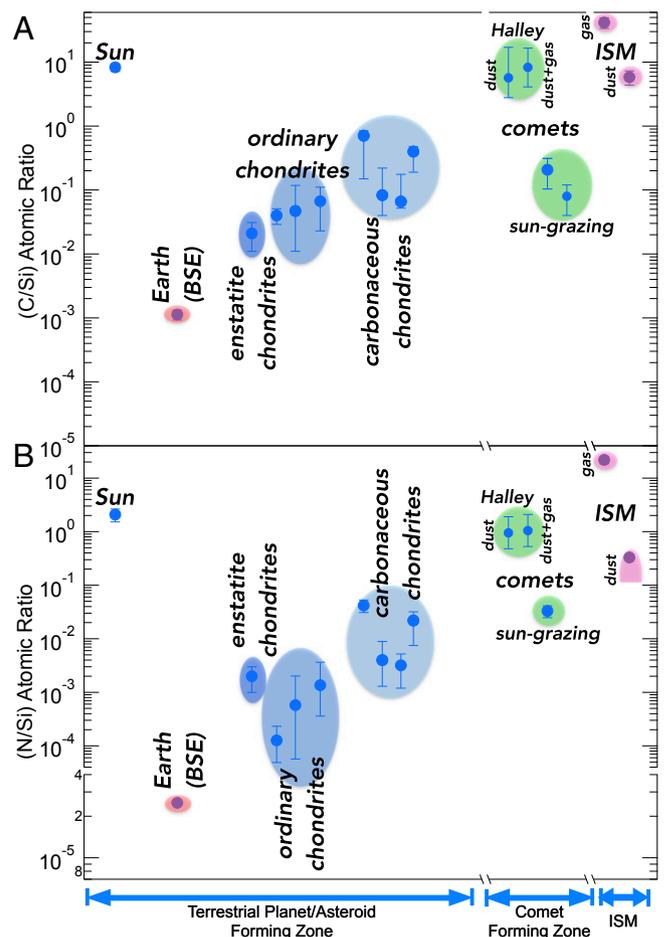
- ii) Owing to low levels of observed nitrogen, particularly in ices (e.g.,  $N_2$ ), comets have elevated C/N ratios compared with the Sun (15). Based on the relative disposition of C and N in the ISM this can be partially achieved as comets accrete ISM carbonaceous dust with low nitrogen content. In this light, Halley is inferred to have more N in solid dust than its gaseous coma (15), which is also higher than estimates for interstellar dust (Fig. 2). There is also a sharp difference in the absolute C and N content of Halley compared with the Sun-grazing comets, which have chondritic abundances. However, their C/N ratios are comparable. Anhydrous interplanetary dust particles (IDPs), which are argued to be of cometary origin (16), are also characterized by a high carbon content,  $(C/Si)_{IDP} \sim 2$  (17).
- iii) Carbonaceous, enstatite, and ordinary chondrites have elevated C/N ratios compared with both the Sun and comets. All meteorites are carbon poor compared with the Sun, ISM dust, and comet Halley, but the key distinction is owing to comparative nitrogen depletion in chondrites. Among meteorites, carbonaceous and enstatite chondrites have similar ratios, but ordinary chondrites have higher and more variable C/N, with mean values closer to those of the bulk silicate Earth.
- iv) For the Earth, both the surface reservoir and bulk silicate Earth have elevated C/N ratios compared with the Sun. The surface reservoir is comparable to chondritic, owing to preferential volcanic degassing of  $N_2$ , leading to the N-rich atmosphere. There are two other estimates of the C/N ratio for the Earth,  $C/N \sim 53 \pm 20$  (1) and  $425 \pm 329$  (7) (see SI Text and Fig. S3); in each case the estimated C/N ratio of the BSE is quite high. (Limited estimates for Mars and Venus are supplied in SI Text.)

These points tell a tale of an increasing C/N ratio from the cold ISM, to cold cometary formation zones, to the inner nebula, to planets. Although there is a broad overall trend, it is also clear that local processes can lead to variations within and between certain classes. Although much of this secular variation must be due to high N volatility, additional processes including preferential dissolution in molten Fe,Ni metal may contribute during assembly of planetesimals and planets. Notably, the BSE has the

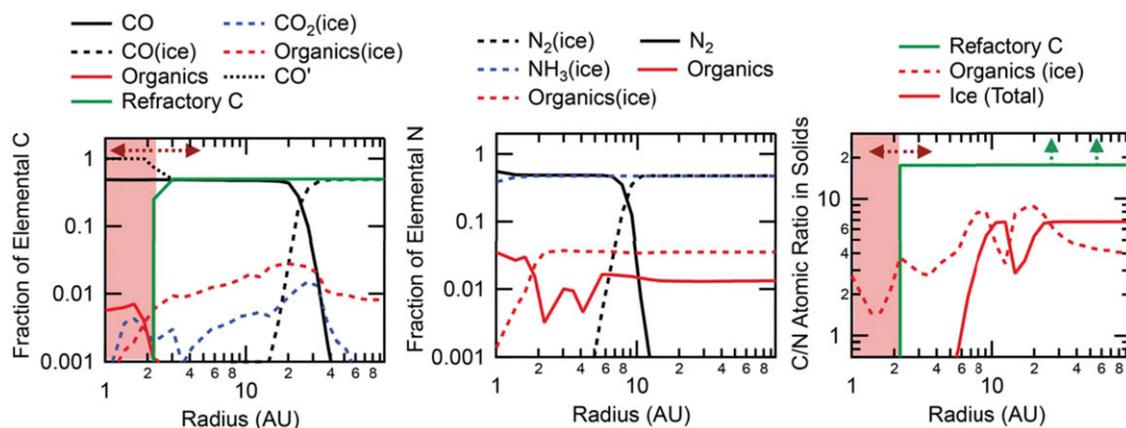
highest C/N ratios compared with most solar system material, except for ordinary chondrites. This high C/N ratio, coupled to overall depletion of the BSE in absolute C and N concentrations, indicates that processing and loss of these key volatiles occurred during planetary assembly. Thus, there are several processes active early in the young solar system that control how planets are seeded with C and N. Below we explore the processes responsible for these trends, which must relate to the supply and fate of two of the key ingredients of our biosphere.

### C/N-ISM to Solar System Rocks and Ices

**Elemental Condensation/Sublimation.** The depletion of carbon and nitrogen within meteorites and Sun-grazing comets is partially related to the high volatility of primary carriers within ices (e.g.,  $CO$ ,  $N_2$ ), as opposed to the carbonaceous dust component. In the case of C, it is further complicated by the fact that interstellar carbon grains provided to the disk need to be destroyed at some level. This must be the case as the C/Si ratio of meteorites (and Sun-grazing comets) is an order of magnitude below that of the ISM dust (e.g., Fig. 2). Carbonaceous dust destruction mechanisms likely include reactions with atomic O and OH (oxidation), photodissociation of small ( $<50$  C,H atom) clusters (18–20), and parent body processing (see *Loss During Parent Body Processing in the Inner Solar System*). Oxidation can destroy carbon grains, but not silicates, provided high gas temperatures exist (above a few hundred kelvins). This process can be active on the surface of the inner disk and/or during the hot, early evolution stages



**Fig. 2.** (A) Bulk carbon-to-silicon and (B) nitrogen-to-silicon ratios. Symbols are identical to those in Fig. 1. For additional details, an expanded version of this figure with labels for each point is provided as Fig. S2.



**Fig. 3.** Fraction of elemental C (*Left*) and N (*Center*) in molecular gases or ices from a kinetic chemical mode (age = 1 Myr). (*Right*) C/N ratio predicted for organic ices, for the total ice mantle (organics and other volatiles shown in *Left* and *Center*), and for refractory carbon (carbonaceous dust). For C the evolution is complicated by the uncertain fate of carbonaceous dust, which carries ~50% of elemental inventory. Based on the composition of meteorites, some destruction of carbon-rich dust is required. The red shaded area represents the (uncertain) radii where carbon grains might be destroyed (19). Within this zone we artificially reduce C incorporated in carbonaceous dust to zero. The principal product of the destruction is CO, which is artificially shown as CO'.

leading to C depletion in solar system rocks (18, 19). At greater distances from the Sun, or at later times, interstellar carbon grains need to be significantly preserved, or perhaps gain additional carbon by extraction from CO (21), to match the carbon content of comet Halley and IDPs. The difference between comet Halley, IDPs, and the Sun-grazing comets may relate to the processes discussed above. [In *SI Text* we discuss the available information regarding the formation location(s) of Halley and the Sun-grazing comets.]

To explore this chemical evolution, we present the main carriers of elemental C and N within a generic protoplanetary disk kinetic chemical model (*SI Text* with adopted physical model shown in Fig. S4) in Fig. 3. The temperature of microscopic solids from 0.5 astronomical unit (1 Earth–Sun distance; hereafter AU) to 3 AU will be uniformly above the CO condensation temperature of ~20 K. Nitrogen, primarily N<sub>2</sub>, is also gaseous here, although NH<sub>3</sub> (condensation temperature of ~80 K) has lower volatility than the main carbon ice carriers (CO, CO<sub>2</sub>) and could provide nitrogen to some solids. In this example, it is only inside 2 AU that NH<sub>3</sub> ice begins to sublimate. Organics are present at these radii and, due to gas-phase chemical processing, some of the C in CO and N in N<sub>2</sub> can be reprocessed in the gas, leading to organic ices (21).

Thus, as seen in Fig. 3, the carbon carriers with the lowest volatility and the primary carriers of C in inner solar system solids will be organic ices and/or carbonaceous dust grains. These are the carriers of elevated C/N ratios into the warmer inner disk. We provide a brief discussion of the relative sublimation temperature of organic materials in *SI Text*. In the comet-forming zones ( $R \gtrsim 5$  AU), carbon is primarily found as carbonaceous dust and as CO ice (> 20 AU) or CO vapor (< 20 AU). At least 50% of the carbon resides in dust with the condensation/sublimation temperature  $\geq 400$  K. For the case of nitrogen, in this model the inner 10 AU are dominated by NH<sub>3</sub> ice and N<sub>2</sub> gas, whereas beyond 10 AU there is even partitioning between N<sub>2</sub> ice and NH<sub>3</sub> ice.

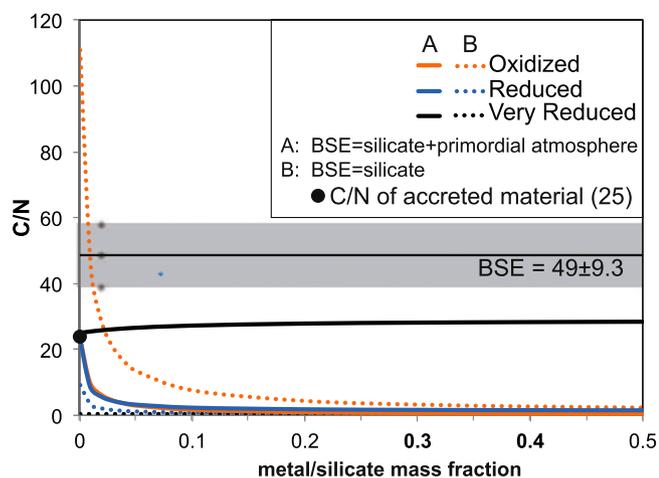
Based on this analysis, the C/N ratio in the starting materials for planets depends on the mixture of carbon in carbonaceous dust and organic ices coating dust grains. Given the low carbon content of chondritic meteorites, the presence of interstellar carbonaceous dust grains might be time/distance variable in the disk. In contrast, organic ices might be created in situ at all radii with C/N of 1–6 (Fig. 3), whereas incorporating some carbonaceous dust would give higher values. Comet Halley provides a

limit for the carbonaceous dust and ice content in the ice giant planet-forming zone, with C/N = 3.7–11.5. Disk chemistry can thus implant C/N ratios ranging from 1 to ~12, values consistent with comets and the low end of the primitive chondrites.

**Loss During Parent Body Processing in the Inner Solar System.** A key issue in interpreting the C/N ratios of meteorites is that they are not pristine records of the dust and ice that accreted to form planetesimals in the solar nebula. Meteorites may provide a good analog to such processes, as their parent bodies have been heated and differentiated, modifying both their C and N concentrations (5, 6). Chondritic meteorites are believed to be direct aggregates of dust grains from the solar nebula, but were exposed to high temperatures (up to 1,300 K) and experienced different degrees of thermal metamorphism, in some cases resulting in elevated C/N. This does not mean that high-C/N meteorites, such as ordinary chondrites (Fig. 1), were direct sources of high-C/N materials delivered to Earth, as chemical and isotopic arguments rule out these samples as primary terrestrial precursors (22). Rather, the processes that they experienced may have been analogous to processes that occurred on parent bodies of objects from which the Earth accreted.

Volatile species, including some organics, would decompose in meteorite parent bodies at high temperatures and the liberated C and N could migrate to the surface as a gas and be lost to space or could be incorporated into metallic Fe,Ni (kamacite and taenite), owing to their siderophilic behavior (23). Thus, the abundances of both C and N are expected to diminish within bodies that were exposed to higher temperatures and more prolonged heating. This is seen in both ordinary (24–26) and carbonaceous chondrites (27); additional evidence is found in the volatility of organic components and their carbon and nitrogen isotopic ratios (28).

The extent of C and N loss during parent body processing is determined by the initial compounds accreted, the chemistry that occurs during heating, and the intensity of heating. For example, the vigor of C and N release from organics during thermal metamorphism depends on the redox conditions, particularly for C, which is incorporated into a gas under oxidizing conditions, but is stabilized in refractory compounds at more reducing conditions (23). This could account for much of the variation in C/N ratio seen in ordinary chondrites. However, enstatite chondrites have most of their N in the form of nitrides whereas carbon is found chiefly as graphite and carbides (29). The reduced character of enstatite chondrites likely stabilizes solid C



**Fig. 4.** Calculated C/N for the BSE resulting from a whole-mantle magma ocean equilibrated with an overlying atmosphere and variable amounts of core-forming metal (43). All calculations assume the proto-Earth begins with C/N = 25 and these elements are initially present in the silicate. *A* shows C/N for a BSE deriving from the sum of the magma ocean and the atmosphere, and *B* shows the BSE C/N derived only from the magma ocean, assuming that the primordial atmosphere is lost to space. Oxidized: C in vapor is assumed to be chiefly CO<sub>2</sub> and N is dissolved as N<sub>2</sub>. Reduced: C in vapor is assumed to be chiefly CO (47). N is dissolved as N<sub>2</sub>. Very reduced: C is highly insoluble and N highly soluble. Quantitative solubilities for the very reduced case are poorly constrained, but for C and N must be very low and high, respectively. See [SI Text](#) for calculation details.

and N compounds to higher temperatures, inhibiting large-scale modification of the original C/N value.

Continued heating on parent bodies would lead to melting, and the formation of iron cores surrounded by silicate mantles and any C and N not lost to space would be distributed according to their low-pressure metal/silicate partition coefficients. Growing planets accrete both silicate and metal portions of such a body, either in individual events or, if fragmentation occurs (30), in aggregate of multiple accretion events. However, it is chiefly the volatile loss that occurs during heating that would determine the final inventory of materials delivered to a growing planet. Thermally processed ordinary chondrites may thus show us the type of processing that occurred on the planetesimals and embryos accreted to the Earth: Thermal evolution of small bodies derived from nebular dust and ice produced differentiated bodies with enhanced C/N ratios.

### C/N-Forming Terrestrial Worlds

Volatiles accreted to the Earth influence climate and biosphere development if they are available to the near-surface environment, either as remnants of the early primordial atmosphere or from material incorporated into the silicate Earth and later outgassed via volcanism. Because the early atmosphere was susceptible to loss via impacts (31, 32), the latter may be most important. However, volatiles contained in silicate could be drawn down into the core during the era of silicate–metal segregation. Consequently, the volatiles presently in the BSE have escaped loss to space or sequestration by the core, leaving them potentially available to the modern surface environment.

Current models of early planetary differentiation postulate that formation of the core and of an early massive atmosphere are associated with a deep magma ocean, with metal–silicate partitioning established at high mean pressures and temperatures (33, 34)—possibly at conditions that became more oxidizing with time (35, 36) and with a significant fraction of the planetary volatile budget released from the molten silicates into the atmosphere (37, 38). Both C and N are moderately to highly

soluble in molten Fe-rich alloy (8, 9, 39) and comparatively insoluble in silicate (40–42). Thus, much of the Earth's initial C and N inventories likely segregated to its metallic core or were released to the atmosphere. The quantitative effects of these processes on BSE C and N content, and on the C/N ratio, depend on partitioning between molten Fe-rich alloy and molten silicate, which in turn depends on the conditions of metal–silicate exchange and on the solubilities of C and N in silicate at the magma ocean–protoatmosphere interface. Also, the effects of core segregation depend on the fraction of metal equilibrated with volatile-bearing silicate (43), as much of the core may have segregated before bulk volatile delivery (44).

Experimental studies establish that C and N partition strongly into molten Fe-rich alloy coexisting with silicate melt. Although values for both elements vary with experimental conditions and compositions, C partitions more strongly into metal than does N. Characteristic mass partition coefficients for C ( $D_C^{\text{met/sil}}$ ) are  $10^2$ – $10^4$  (8, 10, 45–47), compared with those for N ( $D_N^{\text{met/sil}}$ ) of  $\sim 20$  (9). The solubilities of C and N depend strongly on oxygen fugacity, with C more soluble than N in silicate melt under oxidizing conditions and the opposite under highly reducing conditions (41, 46, 47).

Although terrestrial volatile accretion and differentiation were dynamic processes evolving over a range of conditions, insight can be gained from simple models that begin with a molten mantle in equilibrium with some fraction of core-forming metal and with an overlying atmosphere (37, 43). To track the evolution of the C/N ratio during planetary processing, in Fig. 4 we consider two end-member cases, both adopting an initial stage of chemical equilibrium among a fraction of core-forming iron-rich alloy or metal, a molten silicate mantle, and an overlying atmosphere, followed by the segregation and isolation of the core from the mantle. In case A, the atmosphere returns to the silicate mantle to form the BSE, whereas in the other, case B, the atmosphere is blown off to space and lost from the Earth. Motivated by the earlier discussion, we assume an initial C/N ratio of 25.

The most oxidizing condition (orange curves in Fig. 4, oxidized) is a scenario in which carbon in vapor is assumed to be CO<sub>2</sub> and N in vapor as N<sub>2</sub>. We first discuss case A where the magma–silicate Earth is enshrouded by a primordial atmosphere. Here, the initial equilibrium leaves a large portion of N in the atmosphere with most C in the condensed phases and predominantly in the core. Thus, if the primordial atmosphere was retained, the BSE will end up with a C/N ratio slightly reduced from the initial value, provided a small fraction of metal equilibrated with the mantle. The ratio approaches zero if the entire core (metal/silicate  $\sim 0.5$ ) equilibrated with the molten silicate and sequestered most C away. In case B (atmosphere blow-off) the BSE C/N ratio would be elevated with respect to the initial value if core sequestration is limited, but reduced if a large fraction of the core equilibrated with the mantle and strongly depleted the C of the molten silicate.

The second scenario (blue curves in Fig. 4, reduced) represents moderately reducing conditions wherein carbon in vapor is assumed to be CO and nitrogen as N<sub>2</sub>. If the atmosphere is retained, the results are qualitatively similar to the first case, but if the atmosphere is blown off, this results in a BSE C/N ratio that does not exceed the initial value even if no C was sequestered by the core. The lower than initial C/N ratio is derived from the smaller solubility of C in molten silicate.

The final scenario (black curves in Fig. 4, very reduced) represents a highly reducing condition where C is assumed to be highly insoluble, with a speculated solubility of 0.05 ppm/MPa, and N highly soluble, with a speculated value of 50 ppm/MPa. Contrary to the previous two cases, initial equilibrium among metal, silicate, and atmosphere leaves most N in the condensed phase and a significant portion in the silicate, whereas C resides primarily in the atmosphere. For case A, the BSE C/N ratio is

slightly elevated from the initial value because some N was sequestered by the core and C escaped core sequestration by being part of the primordial atmosphere. On the other hand, for atmospheric blow-off (case B), most C would be lost and the C/N ratio of the BSE would be markedly reduced.

All models assume that  $D_C^{\text{met/sil}} \gg D_N^{\text{met/sil}}$  so the consequences for the BSE C/N are affected by (i) the relative solubilities of C and N in silicate melt and (ii) the proportion of metal that equilibrates with the magma ocean. As illustrated by Fig. 4, if C is modestly soluble in silicate and N insoluble, as is true under oxidizing or modestly reducing conditions, then C is chiefly dissolved in condensed phases and predominantly so in metal. The BSE (silicate plus atmosphere) thus has greatly diminished C/N, even for small fractions of available molten alloy. If, however, the amount of metal is small, then following atmospheric loss, the residual silicate mantle may have high C/N. Alternatively, if C is highly insoluble and N very soluble, as may be true under very reduced conditions (41, 47), then the proportion of N dissolved in condensed phases, including core-forming metal, is enhanced. The atmosphere is therefore carbon rich, and so the BSE can have a high C/N ratio.

In sum, under most plausible scenarios, magma ocean-related core formation, combined with atmospheric blow-off, produces much lower C/N ratios than observed. The exception is a speculative circumstance of highly reduced conditions where N is more soluble than C in silicate. More likely, N-rich atmospheric blow-off is necessary to elevate the C/N ratio from carbon-depleted levels (Fig. 4) to the current value.

## Discussion

The C/N ratio provides diagnostic information regarding physical processes active during the earliest stage of planetary birth and assembly. The most likely initial carriers of C and N are low-to-moderate volatility organics and carbonaceous grains. The organics can derive in part from the dense ISM before stellar birth, but also can be created inside the gas-rich disk. Based on models and observations, disk chemistry and transport can imprint variable C/N ratios (1–12) in ices comparable to those of comets and

primitive meteorites. During the stages of planetesimal formation when bodies grow to large sizes (greater than tens of kilometers), impact processing and thermal metamorphism can lead to greater disparity in the C/N content of preplanetary material (Fig. 1). This results in greater C retention relative to N, leading to great variability in the C/N ratio between planetesimals of different sizes and within individual bodies. Such effects are well illustrated by the large dispersion in the C/N ratios measured in ordinary chondrites. Although cosmochemical constraints indicate that ordinary chondrites are not the sole source of Earth's volatiles (22), analogous processes may have elevated C/N ratios on many planetesimals. As a consequence, the mean C/N ratio of materials accreted to the Earth may have been greater than those evident in primitive bodies such as carbonaceous chondrites or comets.

Even assuming that the mean C/N ratio of material accreting to the growing Earth was enhanced, explaining the high C/N of the BSE remains a challenge because core formation should drastically reduce C/N (Fig. 4). Thus, substantial loss of N to space seems to be required. This may be most consistent with scenarios that include (i) late delivery of volatiles, chiefly from comparatively oxidized and metal-poor bodies (48), thereby adding volatile-rich material to the mantle without loss of metal to the core; (ii) multiple magma oceans punctuated by large atmospheric loss events (11); and (iii) atmospheric ablation from many smaller impacts following magma ocean solidification (32). The high C/N ratio of the BSE therefore appears to be a sensitive indicator of the balance of volatile accretion and loss during the final stages of the Earth's assembly. Viewed more broadly, such a scenario will likely result in a highly variable supply and retention of these key ingredients to the surface reservoirs of terrestrial worlds.

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