

# 1    **Loss of Immiscible Nitrogen from Metallic Melt Explains Earth's Missing Nitrogen**

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9    **Nitrogen and carbon are essential elements for life, and their relative abundances in**  
10 **planetary bodies are important for understanding planetary evolution and**  
11 **habitability. The high C/N ratio in the bulk silicate Earth (BSE) relative to chondrites**  
12 **has been difficult to explain through partitioning during core formation and**  
13 **outgassing from molten silicate. Here we propose a new model that may have released**  
14 **nitrogen from the metallic cores of accreting bodies during impacts with the early**  
15 **Earth. Experimental observations of melting in the Fe-N-C system via synchrotron**  
16 **X-ray radiography of samples in a Paris-Edinburgh press reveal that above the**  
17 **liquidus, iron-rich liquid and nitrogen-rich fluid coexist at pressures up to at least 7**  
18 **GPa. The combined effects of N-rich fluid lost to Earth's atmosphere and/or space as**  
19 **well as N-depleted alloy equilibrating with the magma ocean on its way to the core**  
20 **would help increase the BSE C/N ratio to match current estimates.**

## 21 22    **Introduction**

23        The habitability of Earth and other planetary bodies depends on the incorporation,  
24 distribution, and speciation of volatile elements including carbon and nitrogen. In Earth,  
25 the BSE C/N ratio is estimated to be higher than that of planetary building blocks  
26 including enstatite and carbonaceous chondrites and interstellar dust and gas (e.g. Bergin  
27 *et al.*, 2015; Marty, 2012). Recent studies estimate the BSE C/N ratio to be  
28 superchondritic based on measurements of gas bubbles trapped in mid-ocean ridge and  
29 ocean island basalts (Bergin *et al.*, 2015; Halliday, 2013; Marty, 2012), and the estimated

BSE C/N ratio converges to  $46 \pm 9$  recently (Bergin *et al.*, 2015). In contrast, C/N ratios measured in primitive CI chondrites ( $17 \pm 3$ , Alexander *et al.*, 2013) and enstatite chondrites ( $14 \pm 12$ , Grady and Wright, 2003) are significantly lower. Explaining these observations thus requires one or more mechanisms that preferentially deplete N relative to C from the mantle source of basaltic magmas.

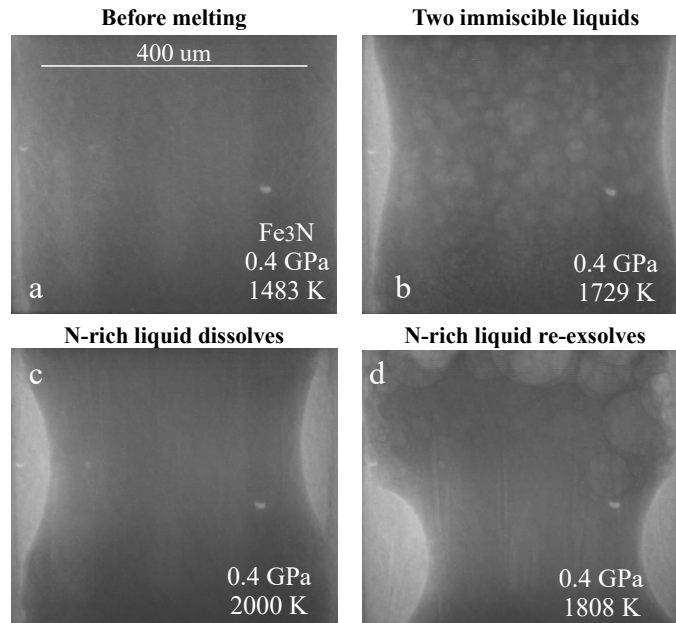
The key processes responsible for C and N redistribution among Earth reservoirs were equilibrium partitioning the magma ocean and the growing metallic core, plus degassing of the magma ocean to the early atmosphere, but these processes have been insufficient to explain the estimated high BSE C/N ratio (Bergin *et al.*, 2015; Dalou *et al.*, 2017; Hirschmann, 2016). Core formation is expected to decrease the BSE C/N ratio because at relevant conditions C is a much stronger siderophile element than N (Dalou *et al.*, 2017). Degassing has been thought to not significantly affect the C/N ratio, as chemical analysis of volatiles in silicate glasses quenched from high pressure-temperature (*P-T*) experiments indicates that the solubilities of C and N in the magma ocean are comparable (Hirschmann, 2016).

The major host phase for both C and N in the solidifying planet is likely to be core-forming alloy, therefore the Fe-N-C system under relevant conditions may hold the key to the paradox of the high BSE C/N ratio. While the Fe-C phase diagram has been well studied over a wide range of pressures (Fei and Brosh, 2014), very limited data are available on the phase relations of the Fe-N system (Guillermot and Du, 1994). However, melting behavior is expected to be different in these two systems with enrichment in the light element, as the C-rich end member, graphite/diamond, has a melting point of 4000-5000 K at relevant pressures (Grumbach and Martin, 1996), while the N-rich end member would be gas/supercritical fluid in the BSE.

### **Immiscible N-rich Fluid**

In order to test whether the mobility of N-rich gas/fluid could provide a possible mechanism to leak N during accretion and core formation, we investigated melting relations in the Fe-N-C system under high pressures by *in-situ* X-ray radiography and X-

ray diffraction (XRD) coupled with Paris-Edinburgh cells and *ex-situ* chemical analysis. The starting materials are either iron nitrides ( $\text{Fe}_3\text{N}$  and  $\text{Fe}_4\text{N}$ ) or a mixture of iron and iron nitride powders with or without graphite powder with starting N and C contents ranging from 0-7.7 wt% and 0-10.0 wt.%, respectively (Table S-1). A standard PE sample assembly configuration is employed (Kono *et al.*, 2014), which uses X-ray transparent MgO as the sample capsule and cylindrical graphite tube outside sample capsule as the heater. Assemblages were first compressed to target pressures and gradually heated to fully melt the samples. Then the molten samples were quenched below 500 K within 5 seconds to preserve compositions for *ex-situ* chemical analysis (Table S-1).

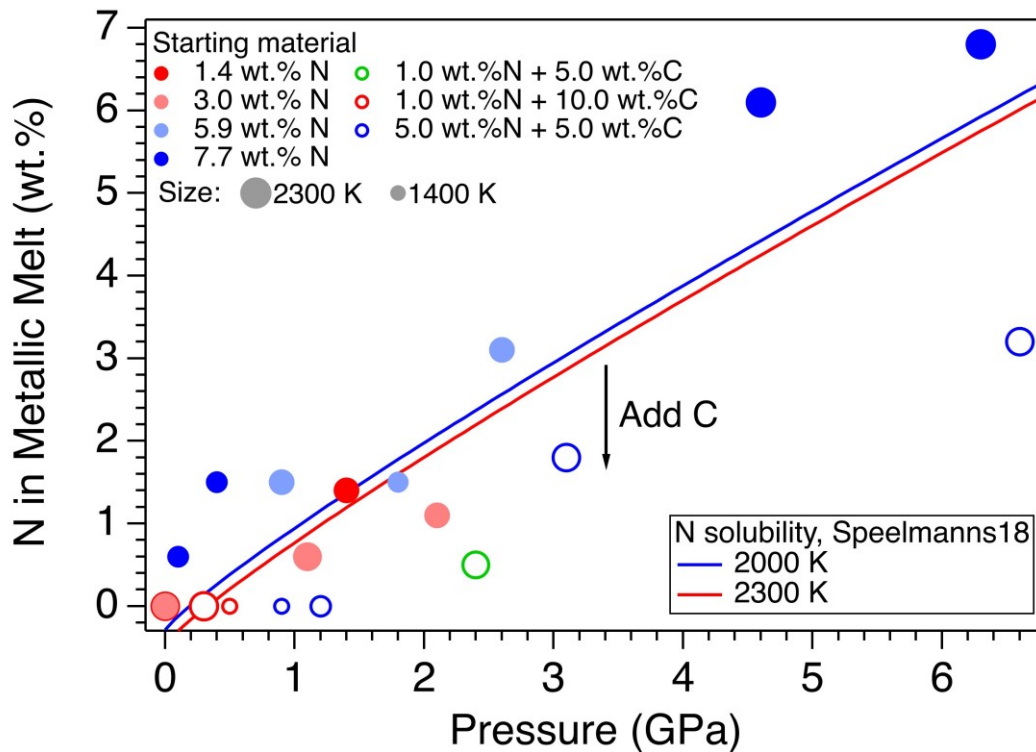


**Figure 1 Representative X-ray radiographic images showing the evolution of miscibility gap in Fe-N-C system under high-pressure and high-temperature conditions (run 4-17).** This *in-situ* X-ray radiography experiment starts at 0.4 GPa with  $\text{Fe}_3\text{N}$  as the starting material. **a**, The sample is below solidus at 0.4 GPa and 1483 K. **b**, Around 1729 K, immiscible N-rich supercritical fluid coexists with metallic liquid. **c**, At higher temperatures, N-rich supercritical fluid partially dissolves into metallic liquid. **d**, Lowering temperatures re-exsolves N-rich supercritical fluid from metallic liquid. The corresponding video is shown in Movie S-1.

Below the solidus, starting materials for all runs were homogenous at  $\sim 3 \mu\text{m}$  spatial resolution of X-ray radiographic images (e.g. Fig. 1a). An upper bound for the onset of partial melting at higher temperature was indicated by the appearance of 10s-micron regions of low X-ray absorption (e.g. Fig. 1b). At higher temperatures, these lighter regions merge to form 10s to 100s-micron droplets which move vigorously (Fig. 1b). XRD patterns during heating also recorded the melting process (Fig. S-1d): at 0.4 GPa and 300 K, the XRD pattern confirmed  $\text{Fe}_3\text{N}$  as the starting material; at  $\sim 1690 \text{ K}$ , most crystalline peaks disappeared with obvious background lifting at  $\sim 34\text{-}80 \text{ keV}$  (Fig. S-1d), which originated from diffuse scattering. The corresponding X-ray radiographic image (Fig. S1-b) showed the ubiquitous occurrence of the low X-ray absorption regions. Therefore, both XRD and X-ray radiographic image indicated a partially molten state of the Fe-N sample. Turbulent flow of two phases occurred above  $\sim 1725 \text{ K}$  (Movie S-1), and XRD patterns exhibited diffuse scattering with no XRD peaks (Fig. S-1d) and thus indicated conditions above the liquidus but below a solvus. At higher temperatures, the immiscible droplets partially dissolved into the metallic liquid but persisted to the highest temperature investigated of run 4-17 ( $\sim 2000 \text{ K}$ , Fig. 1c). Lowering temperature makes more immiscible droplets re-exsolved (Fig. 1d), confirming that the disappearance of the immiscible droplets from Fig. 1b to 1c cannot be explained by loss through the MgO capsule. In comparison, no inhomogeneity appeared at all in Fe melting experiment at 0.8 GPa up to  $2103 \text{ K}$  (Fig. S-2).

The immiscible droplets with lighter colors in X-ray radiographic images are enriched in N because the contrast in X-ray radiographic images reflects density difference (Kono *et al.*, 2015). The N-rich nature of the immiscible fluid is confirmed by *ex-situ* chemical analysis of the quenched samples: for experiments quenched with the presence of immiscible liquids, the regions which are lighter in X-ray radiographic images correspond to voids in recovered samples (e.g. Fig. S-3, S-5 and S-6); N contents in the recovered samples are lower than the starting values when immiscible melting occurs (Table S-1). For example, N content in run 4-16 decreases from 5.9% in the starting materials to 1.5% in the recovered sample (Fig. S-3). With increasing temperature, the increase of N solubility in metallic melt (e.g. Fig. 1 and Movie S-1) can be explained by the concave-down shape of the solvus, which marks the phase boundary between one

miscible liquid and two immiscible liquids (Fig. S-4). Similar phenomenon has been observed in Fe-O system (Kowalski and Spencer, 1995; Tsuno *et al.*, 2007): at 1 bar, O solubility increases from ~0 to ~5 mol.% when temperature increases from ~1811 K to ~2340 K (Kowalski and Spencer, 1995). Such a miscibility gap persists to at least 21 GPa in Fe-O system and O solubility in metallic melt increases with a rate of 0.01-0.03 mol./K between 15-21 GPa and 2050-2350 K (Tsuno *et al.*, 2007). For experiments with C added to the starting materials, immiscible melting still occurs (Fig. S-5 and S-6). C contents in the recovered samples are the same as starting materials within uncertainty (Table S-1). This indicates that C did not dissolve into N-rich fluid during immiscible melting.



**Figure 2 The pressure dependence of N solubility in Fe-N-C melt.** The circles are from our experiments: the solid ones are for Fe-N starting materials; the open ones are for Fe-N-C starting materials. Symbol size is proportional to the temperature (1400-2300 K) at which the experiments were quenched and color indicates initial composition (see legend). The blue and red curves are modeled N solubility in Fe-N-C melt at 2000 K and 2300 K, respectively, from Speelmanns *et al.* (2018).

The combination of *in-situ* and *ex-situ* analysis was employed to constrain the solubility of N in Fe-N-C alloys (Fig. 2). Near 1 bar in all compositions up to 7.7 wt% N

and 10.0 wt.% C, immiscibility of N-rich supercritical fluid and metallic melt observed *in-situ* persists to 2273 K, the highest temperature investigated here. Solubility of N in Fe-N-C alloy increases from almost 0 near 1-bar conditions to ~6.8 wt.% N at 6.3 GPa, as the highest pressure investigated here (Fig. 2). And the pressure required for closing the miscibility gap increases with the starting N and C contents (Fig. 2). For Fe-1.4 wt.%N starting material at about 0-0.1 GPa, immiscible liquids persist to at least 1980 K, but no immiscible liquids appear at ~1.4 GPa up to 2000 K (Fig. S-7). In contrast, for Fe-7.7 wt.% N starting composition the solvus persists to at least 6.3 GPa (Fig. 2). Adding 5-10 wt% C in the starting materials expands the pressure range of the solvus by about 2-5 GPa (Fig. 2). This is because C is more siderophilic than N and it expels N from metallic melt to the immiscible fluid.

A recent study also infers the presence of N-rich fluid from Fe-N-C melt based on the *ex-situ* analysis of quenched samples (Speelmanns *et al.*, 2018). The trend of their N solubility model is consistent with our data as it increases with pressure (Fig. S-8). However, due to C and Pt contaminations from sample capsules (Speelmanns *et al.*, 2018), the effect of C on N solubility is not incorporated in their model. The presence of 5.0 wt.% C lowers N solubility by 1-3 wt.% (Fig. S-8), therefore C and other more siderophilic elements (e.g. sulfur) significantly lower N solubility in metallic liquid at high pressures (e.g. Dalou *et al.*, 2017). The presence of immiscible N-rich fluid in silicate-alloy system has been observed in a previous partitioning study on metallic-silicate melts up to 10 GPa (Roskosz *et al.*, 2013), supporting that this immiscible phenomenon could occur in a realistic magma ocean phase assemblage.

### **Missing N in the Mantle**

The conundrum of missing N in the mantle can be solved by accounting for immiscibility of N in the Fe-N-C system in modeling Earth's N budget. Our model calculates the BSE C/N ratio in three steps (Fig. S-9 and SI): First, we assume Earth-forming impactors have alloy core and silicate mantle in equilibrium with average alloy/silicate mass ratio of 0.46, same as the Earth's core/mantle mass ratio. The amount of N stored in metallic core is controlled by oxygen fugacity (Dalou *et al.*, 2017): 90.2% N would stay in the core at oxidized bodies ( $\Delta IW$ -0.5 to -1.0); this number decreases to

69.7% and 12.1% at modestly reduced ( $\Delta IW$ -1.8 to -2.2) and more reduced bodies ( $\Delta IW$ -3.4 to -3.6), respectively (Fig. S-10). In contrast, previous models assume all C and N were initially stored in silicate (Bergin *et al.*, 2015; Dalou *et al.*, 2017; Hirschmann, 2016). This assumption sets the initial BSE C/N ratio at 25 without loss of the primordial atmosphere, which is about 20-24 higher than our initial BSE C/N ratios (Fig. 3).

Secondly, we assume that extensive melting of alloy during high-energy impacts induces immiscible melting, resulting in loss of all N stored in impactor cores to space. In general, the fraction of N released from an impactor depends on the core/mantle mass ratios in the accreting bodies; the degree of melting during accretion/melting; the extent of immiscibility between N-rich supercritical fluid and metallic melt, and the fraction of atmospheric N loss to space. As our model assumes impactor cores melt completely and release N at the magma ocean surface, it yields an upper limit for N loss at this stage. The loss of N results in extremely large C/N ratio in the metallic phase. Once such N-depleted metallic droplets sink below the depth where solubility of N in alloy increases (Fig. S-9), N could partition from the magma ocean into N-depleted alloy droplets and therefore elevate the BSE C/N ratio as the alloy joins Earth's growing core.

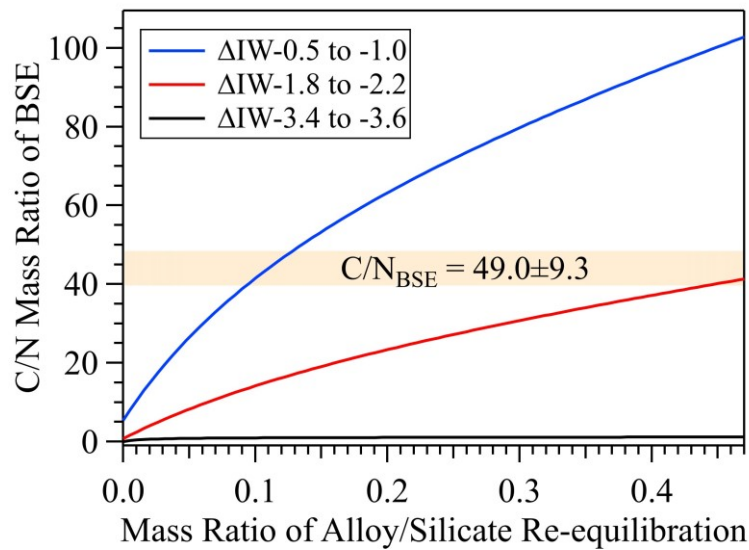
Overall, the loss of N from impactor cores could significantly lower Earth's bulk N budget and therefore raise the BSE C/N ratio (Fig. 3). Because N partitions more strongly into alloy under more oxidized conditions, more N is subject to loss from oxidized accreting bodies (Fig. S-10). Similarly, the subsequent core formation would also result in higher C/N ratio of the BSE under oxidized conditions. Over time during core formation,  $f_{O_2}$  is estimated to evolve from lower values of  $\Delta IW$ -3.9 to  $\Delta IW$ -1.9 to higher values of  $\Delta IW$ -1.9 to  $\Delta IW$ -1.0 (Rubie *et al.*, 2011, Badro *et al.*, 2015). Therefore, the BSE C/N ratio is expected to evolve from 0.03-0.5 at very reduced conditions to 0.7-41.4 at reduced conditions and finally to 5-130.0 at slightly reduced conditions (Fig. 3).

Compared with previous models (Bergin *et al.*, 2015), our model matches the estimated BSE C/N ratio for an extensive range of redox conditions, the degree of alloy-silicate re-equilibration and extent of loss of nascent atmosphere during accretion and core formation. Notably, both C and N form accessory minerals, such as diamonds, iron carbides, iron/titanium/chromium nitrides (e.g. Fegley, 1983; Javoy, 1997; Kaminsky and Wirth, 2017), which has not been considered in the estimated BSE C/N ratio yet. In



addition, the presence of deep-mantle carbonates (e.g. Brenker *et al.*, 2007) and high solubilities (10s to 1000s  $\mu\text{g/g}$ ) of N in transition zone and lower mantle minerals (Yoshioka *et al.*, 2018), both of which are sensitive to redox and pH conditions (e.g. Mikhail *et al.*, 2017; Rohrbach and Schmidt, 2011), would also influence the estimation of the BSE C/N ratio.

Vaporization during accretion has recently been evoked to explain Mg, Si and Fe isotopic compositions in the BSE (Hin *et al.*, 2017) and the pattern of volatile element depletion (Norris and Wood, 2017), indicating its critical role in the early stage of Earth evolution. Considering the high C/N ratios ( $>10$ ) of most planetary bodies (Bergin *et al.*, 2015), the C/N ratios of the impactors' cores would be even higher and therefore promote immiscible melting during impact. In addition, the loss of N through immiscible fluid could be even more significant for Earth-like planets at a synestia stage (Lock and Stewart, 2017): in this stage, the magma ocean is surrounded by massive vaporized materials, which are at pressures between 0.1 bar and 1.0 GPa.



**Figure 3 The evolution of the BSE C/N ratio with the degree of re-equilibration between alloy and silicate during core formation.** The blue curve is calculated at reduced conditions ( $\Delta\text{IW}-0.5$  to  $\Delta\text{IW}-1.0$ ); the red curve is for reduced conditions



( $\Delta IW$ -1.8 to  $\Delta IW$ -2.2) and the black curve is for very reduced conditions ( $\Delta IW$ -3.4 to  $\Delta W$ -3.6). The horizontal yellow bar marks the range of the **estimated** present BSE C/N ratio (Bergin *et al.*, 2015).

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