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Nitrogen and carbon fractionation during core-mantle differentiation at shallow depth

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ABSTRACT

One of the most remarkable observations regarding volatile elements in the solar system is the depletion of N in the bulk silicate Earth (BSE) relative to chondrites, leading to a particularly high and non-chondritic C:N ratio. The N depletion may reflect large-scale differentiation events such as sequestration in Earth's core or massive blow off of Earth's early atmosphere, or alternatively the characteristics of a late-added volatile-rich veneer. As the behavior of N during early planetary differentiation processes is poorly constrained, we determined together the partitioning of N and C between Fe–N–C metal alloy and two different silicate melts (a terrestrial and a martian basalt). Conditions spanned a range of f_{02} from $\Delta IW-0.4$ to $\Delta IW-3.5$ at 1.2 to 3 GPa, and 1400 °C or 1600 °C, where ΔIW is the logarithmic difference between experimental f_{02} and that imposed by the coexistence of crystalline Fe and wüstite. N partitioning ($D_N^{\text{metal/silicate}}$) depends chiefly on f_{02} , decreasing from 24±3 to 0.3±0.1 with decreasing

N partitioning $(D_N^{\text{Interl/suicate}})$ depends chiefly on f_{O_2} , decreasing from 24 ± 3 to 0.3 ± 0.1 with decreasing f_{O_2} . $D_N^{\text{metal/suicate}}$ also decreases with increasing temperature and pressure at similar f_{O_2} , though the effect is subordinate. In contrast, C partition coefficients $(D_C^{\text{metal/silicate}})$ show no evidence of a pressure dependence but diminish with temperature. At 1400 °C, $D_C^{\text{metal/silicate}}$ partition coefficients increase linearly with decreasing f_{O_2} from 300 ± 30 to 670 ± 50 . At 1600 °C, however, they increase from Δ IW-0.7 to Δ IW-2 (87 ± 3 to 240 ± 50) and decrease from Δ IW-2 to Δ IW-3.3 (99 ± 6). Enhanced C in melts at high temperatures under reduced conditions may reflect stabilization of C–H species (most likely CH₄). No significant compositional dependence for either N or C partitioning is evident, perhaps owing to the comparatively similar basalts investigated.

At modestly reduced conditions ($\Delta IW-0.4$ to -2.2), N is more compatible in core-forming metal than in molten silicate ($1 \le D_N^{metal/silicate} \le 24$), while at more reduced conditions ($\Delta IW-2.2$ to $\Delta IW-3.5$), N becomes more compatible in the magma ocean than in the metal phase. In contrast, C is highly siderophile at all conditions investigated ($100 \le D_C^{metal/silicate} \le 700$). Therefore, sequestration of volatiles in the core affects C more than N, and lowers the C:N ratio of the BSE. Consequently, the N depletion and the high C:N ratio of the BSE cannot be explained by core formation. Mass balance modeling suggests that core formation combined with atmosphere blow-off also cannot produce a non-metallic Earth with a C:N ratio similar to the BSE, but that the accretion of a C-rich late veneer can account for the observed high BSE C:N ratio.

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1. Introduction

The global reservoirs and fluxes of nitrogen and carbon are key considerations for the maintenance of the terrestrial atmosphere, habitability, and biosphere (e.g. Sleep and Zahnle, 2001). In the last decade, the deep carbon cycle and inventories have received considerable attention (cf., Dasgupta, 2013), and in recent years there

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http://dx.doi.org/10.1016/j.epsl.2016.10.026 0012-821X/© 2016 Elsevier B.V. All rights reserved. has been growing focus on nitrogen (e.g., Johnson and Goldblatt, 2015 and the references therein). When examining the origin of global inventories and deep cycling, it is natural to compare nitrogen and carbon together because both are volatile during mantle degassing, incompatible during mantle melting and siderophile during core formation (e.g., Miyazaki et al., 2004; Dasgupta, 2013; Roskosz et al., 2013; Li et al., 2016).

A remarkable feature of BSE N inventory is the apparent depletion relative to C as well as other major volatiles and rare gases, though the magnitude of this depletion is debated (e.g. C. Dalou et al. / Earth and Planetary Science Letters ••• (••••) •••-•••

Marty, 2012; Johnson and Goldblatt, 2015; Hirschmann, 2016). Evidence for the depletion of volatile ratios such as C/N derives from mass balance calculations inventorying the mantle, crust and atmosphere (Marty, 2012; Bergin et al., 2015). Possible explanations for the apparent N depletion include atmospheric escape (Tucker and Mukhopadhyay, 2014; Hirschmann, 2016) or a deep N reservoir not sampled by oceanic basalt generation (Johnson and Goldblatt, 2015). Alternatively, the N depletion of the BSE could have been caused by the segregation of core-forming metal segregated from the magma ocean (Marty, 2012; Roskosz et al., 2013). Iron nitrides are stable at high pressure and temperature (Adler and Williams, 2005) and N solubility in molten alloys is 3–4 orders of magnitude larger than in silicates at low pressure (e.g. Miyazaki et al., 2004), consistent with the hypothesis that the core may be an appreciable N reservoir.

Determining the fraction of terrestrial N that was removed from the BSE by core formation requires constraints on N partitioning between molten Fe-rich alloy and silicate melt $(D_{\rm N}^{\rm metal/silicate})$. Preliminary estimates based on comparison between low-pressure solubilities of N2 in alloy and silicate melt suggested extremely strong siderophile behavior, with $D_{\rm N}^{\rm metal/silicate}$ similar to 10,000 (Miyazaki et al., 2004). If applicable to core formation, such extreme values imply N masses in the core hundreds of times greater than that in the atmosphere (Miyazaki et al., 2004). However, such estimates are likely misleading, as they are predicated on the limited solubility of molecular N2 in silicate melts, whereas melts in equilibrium with molten Fe would likely dissolve N more readily in a reduced species such as N³⁻ or N-H complexes (Miyazaki et al., 2004; Mysen and Fogel, 2010; Kadik et al., 2015). N partitioning between metal and silicate measured at high pressure is more modest. Coexisting Fe-Ni-N molten alloy and silicate liquid similar in composition to chondritic meteorites (Roskosz et al., 2013) yielded $D_{\rm N}^{\rm metal/silicate}$ values that range from ~3 to 20, with values increasing modestly with pressure from 1.8 to 17.7 GPa (at 2227 to 2577 °C) over a narrow range of oxygen fugacity, f_{0_2} (ΔIW -2.2 to -1.0, where ΔIW is the logarithmic difference between experimental f_{0_2} and that of the iron-wüstite buffer, and all published values of ΔIW have been adjusted according to the calculator of Wade and Wood (2005), as described in greater detail below). The effect of variable f_{0_2} (ΔIW -0.7 to -3.7) on N partitioning was explored by Kadik et al. (2011, 2015) for Fe-rich alloys and silicic (62-75 wt.% SiO₂) FeO-Na₂O-Al₂O₃-SiO₂ melts at 1.5 GPa and 1400 °C, and comparatively small (0.5–2.9) $D_{\rm N}^{\rm metal/silicate}$ values were found which show a crude trend to greater $D_{\rm N}^{\rm metal/silicate}$ at greater $f_{\rm O_2}$. In comparison, at less reduced conditions (ΔIW –0.8 to 0.5), Li et al. (2016) measured larger $D_{\rm N}^{\rm metal/silicate}(8-149)$ between 1.5 and 7 GPa and 1600-1700°C, and suggested a linear increase in $\log D_{\rm N}^{\rm metal/silicate}$ with $\log f_{\rm O_2}$.

It is well established that C is highly siderophile over a large range of pressures, temperatures, and f_{O_2} (Dasgupta et al., 2013 at 1 to 5 GPa, 1600 and 2000 °C and Δ IW-0.5 to -1.8; Chi et al., 2014 at 1 to 3 GPa, 1500 and 1800 °C and Δ IW-0.4 to -1.5; Stanley et al., 2014 at 1 to 3 GPa, 1350 and 1620 °C and Δ IW-0.3 to -0.6; Li et al., 2015 at 3 GPa, 1600 °C and Δ IW-0.6 to -4.7; Armstrong et al., 2015 at 1.2 GPa, 1400 °C and Δ IW-0.1 to -3.0). Accordingly, the core is thought to be a significant sink for terrestrial C (e.g. Wood, 1993; Dasgupta et al., 2009; Wood et al. 2013), and C is considered to be among the light elements likely to contribute to the physical properties of the core, together with S, O, Si and H (e.g. Righter, 2003). However, constraining the influence of core formation on the C:N ratio of the BSE requires data on both N and C partitioning between metal alloy and silicate melts, and to date no study has determined these simultaneously.

In the present work, N and C partition coefficients between metal alloy and silicate melts were measured from the same experiments at conditions relevant to core–mantle differentiation at shallow depth. We present 29 new alloy/glass pairs to compare the effects of f_{O_2} , *P*, *T*, and melt composition on both N and C partition coefficients. The experiments were conducted at 1.2 to 3 and 1400 °C or 1600 °C, over a large range of f_{O_2} (Δ IW–0.4 to -3.5), employing either a terrestrial or martian basalt.

2. Methods

2.1. Experimental and analytical techniques

Two starting materials were used. The first is a martian basalt based on the Adirondack-class Humphrey basalts from Gusev Crater, Mars, close in composition to those used by Stanley et al. (2014) and Armstrong et al. (2015). The second is modeled after primary normal MORB (N-MORB) close in composition to that used by Armstrong et al. (2015). Both were prepared initially iron-free by mixing pre-dried spectroscopically pure oxides and carbonates in ethanol in an agate mortar for 1 h. The mixes were decarbonated by slow heating (200°C/h) up to 900°C and then held for 2 h and ground again in ethanol in an agate mortar for 1 h. After decarbonation, Fe oxide was added as FeO, as iron in the melt should be nearly entirely ferrous under the reducing conditions anticipated.

Nitrogen was introduced as Fe₄N and/or Si₃N₄ (Table 1). Up to 16 wt.% of Fe₄N was added to yield charges with 1 wt.% N in the starting material. Because of its strong reducing effect (Eq. (1)), Si₃N₄ was used chiefly to control the f_{O_2} of experiments based on the reaction:

$$6 \operatorname{FeO}_{\text{silicate melt}} + \operatorname{Si}_{3} \operatorname{N}_{4} = 6 \operatorname{Fe}_{\text{alloy}} + 3 \operatorname{SiO}_{2} + 2 \operatorname{N}_{2}$$
(1)

Samples were loaded into graphite capsules to avoid Fe and N loss to metal containers, ensure reducing conditions, and to provide a source of C. Up to six different compositions were loaded into individual holes drilled in to a single graphite capsule in order to achieve variable f_{O_2} conditions at fixed *P* and *T* in the same experiment (Table 1).

Experiments were carried out in a half-inch piston cylinder at 1.2, 2, 2.2, or 3 GPa and 1400 or 1600 °C (Table 1). Assemblies comprise, from inside to outside: MgO cell parts (dried at 1000 °C for 4 h and stored in a drying oven at 110 °C) surrounded by a graphite furnace and either CaF₂ sleeves (experiments at 1400 °C) or BaCO3 sleeves (experiments at 1600 °C). The graphite capsule was placed in an MgO sleeve and isolated from the thermocouple by a 1 mm MgO disc, leading to a 12°C difference between the top of the sample and the tip of the thermocouple based on previous calibrations (Xirouchakis et al., 2001). The temperature was measured to within $\pm 2^{\circ}$ C of the set point using a type B (Pt₇₀Rh₃₀/Pt₉₄Rh₆) thermocouple. From pressure-calibration using the reaction grossular + kyanite + quartz = anorthite (Xirouchakis et al., 2001), a pressure correction of 0.2 GPa was applied to the experiments using BaCO₃ cells. No friction correction was applied to experiments in the CaF2 cells. Experimental durations were 6 h for 1400 °C experiments following previous work (Stanley et al., 2014; Armstrong et al., 2015), and 4 h for 1600 °C experiments. Experiments were quenched at rates of $\sim 125 \,^\circ\text{C/s}$ for BaCO₃ and 175 °C/s for CaF₂ cells, respectively (Zhang et al., 2016), by cutting power to the furnace. Recovered capsules were mounted in ethyl-2-cyanoacrylate ("superglue") and polished for electron microprobe analysis (EPMA). Subsequently the samples were removed from the superglue with acetone and prepared for secondary ion mass spectrometry (SIMS) analysis as described below.

Major element and N concentrations of silicate glasses and alloys were analyzed on a JEOL JXA-8900R EPMA at the University Download English Version:

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