Nitrogen Solubility in Core Materials
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Abstract During accretion, nitrogen was distributed between metal melt, silicate melt, and the atmosphere and today’s N deficit of bulk silicate Earth with respect to chondrites may be due to segregation into the core and/or atmospheric losses. To examine the former, we experimentally determined N solubilities in Fe-dominated metal melts at 1200–1800 °C, 0.4–9.0 GPa. Results show that pressure has a strong positive influence on N solubility, increasing from 1.0 to 7.4 wt% at 1–9 GPa (1400 °C) while temperature has the inverse effect, N solubility decreasing from 1.3 to 0.6 wt% at 1200–1800 °C (1 GPa). The solubility data are parameterized as function of pressure and temperature. Our results suggest that core-forming metal melts can dissolve large quantities of N, and the potential N contribution to the Earth’s core density deficit could hence be much larger than previously assumed. Most importantly, N in the deep reduced mantle should be stored in the small metal fractions and not in silicates.

Plain Language Summary On the early Earth nitrogen was redistributed between three prevailing reservoirs: the core forming metal, the silicate magma ocean, and the atmosphere. To shed light on the behavior of N during core segregation, we have experimentally determined N solubilities in Fe-dominated metal melts at high temperatures and pressures (1200–1800 °C, 0.4–9.0 GPa) using high-pressure devices. Based on our experimental results a model has been developed to describe N solubility into metal melts as a function of pressure and temperature. The model suggests that core-forming metal melts can dissolve N quantities that are as high as the Earth’s core density deficit. However, the N concentrations in the core-forming metal are dependent on the accretionary scenario and its partitioning with silicate magma ocean; our solubilities provide an upper limit for possible N concentrations within the Earth’s core. Nevertheless, this study shows that N in the modern mantle will largely dissolve in its small metal fraction and not in the dominating silicates.

1. Introduction

The abundance of N and its partitioning between different terrestrial reservoirs over geological history still remains poorly constrained (e.g., Marty, 2012). While the present-day distribution and concentration of N among surface reservoirs, namely, atmosphere, sediments and crust is well understood (e.g., Cartigny & Marty, 2013; Galloway, 2003; Sadofsky & Bebout, 2004; Thomazo & Papineau, 2013); the mantle concentration, on the other hand, remains highly debated. Proposed N contents of the mantle vary over two orders of magnitude from 0.3 to 40 ppm (e.g., Halama et al., 2012; Javoy, 1997; Marty & Dauphas, 2003). However, knowledge of the silicate and bulk Earth compositions is essential to understand the long-term evolution of the internal and external reservoirs of the Earth.

A number of experimental studies focused on the behavior of nitrogen in silicate melts (Kadik et al., 2011; Libourel et al., 2003; Miyazaki et al., 2004; Mysen & Fogel, 2010; Roskosz et al., 2013). These data suggest that the solubility of nitrogen in silicate melts may reach 1.5 wt% N and strongly depends on pressure, temperature, melt composition, and oxygen fugacity. Nitrogen solubility in metallic liquids, where N dissolves as monoatomic species, was found to be up to 4 orders of magnitude larger than in silicate melts at ambient pressures (e.g., Kowanda & Speidel, 2003; Miyazaki et al., 2004). The high metal affinity of N compared to silicates suggests that the depletion of N in the bulk silicate Earth, when compared to other volatile elements, could be due to its segregation into the core-forming material (e.g., Marty, 2012; Roskosz et al., 2013), and thus, N could be one of the potential light elements in the Earth’s core (e.g., Litasov et al., 2017). Similarly, at greater 200 km depth, the modern mantle becomes reduced and metal saturated with 0.1–1 wt% present at 200–700 km depth (Frost et al., 2004; Rohrbach & Schmidt, 2011). This reduced phase contains almost all of the C and S of the deep mantle and was shown to be at least partially molten at adiabatic conditions (Rohrbach et al., 2014); it could hence host the N of the deep mantle.
The affinity of N to the metal phase and its potential to contribute to the Earth’s core composition and density deficit demands for an understanding of its behavior in metallic liquids. Here we investigate the effect of both pressure and temperature on N solubility in Fe-dominated metallic liquids. For this purpose, we have established a new bulk analytical routine to quantify N in high-pressure experimental melts and to finally provide a solubility model as a function of pressure and temperature.

2. Experimental and Analytical Techniques

The metal melt was prepared by mixing iron, graphite, and iron nitride in eutectic Fe–C proportions, but with variable N contents ranging from 0.5 to 7 wt% (Table S3). Several batches of the iron nitride (Alfa Aesar, nominally Fe$_2$N) were bulk analyzed yielding 7.0 ± 0.1 wt% N. As solubility is expected to increase with pressure, a layer of magnesium nitride (Mg$_3$N$_2$) powder was placed at the bottom of the capsule in ≥5 GPa experiments, providing an additional source for N through the decomposition reaction Mg$_3$N$_2$ ➔ 3Mg + N$_2$. Carbon was added to the metal in most experiments to avoid dissolution of the graphite capsule in the Fe melt. The effect of carbon on the solubility of N in the metallic liquid was tested with experiments of two additional starting mixtures run in Al$_2$O$_3$ capsules. One was prepared with 1.9 wt% C and one was C-free consisting only of pure iron nitride.

At 1–3.5 GPa (1400–1800 °C), experiments were performed in an end-loaded piston cylinder. The utilized 14-mm-diameter assembly consists of talc and Pyrex sleeves, a straight graphite heater, and inner crushable MgO spacers. A thin crushable MgO sleeve was placed around the sample capsule to avoid direct contact with the heater. It was found that N loss through the capsule wall is a serious problem; depending on run conditions, only between 40 and 63% of the initial N was recovered after the experiment. Unwelded capsules led to an almost complete loss of N (5% recovery rate). To minimize this loss, the sample material was placed inside double capsules made of an inner graphite or crushable alumina capsule (4.5 mm outer diameter, 6 mm in length) or in a dense Al$_2$O$_3$ capsule (99.7% density, 2.6 mm outer diameter, 4 mm length) each surrounded by a welded outer Pt capsule (of 5 or 3 mm outer diameter).

Experiments at 6–9 GPa were conducted in a 2000-t multianvil press, with 25/17 (octahedral edge length/tungsten-carbide anvil truncation given in mm) pressure cells. The prefabricated octahedral pressure medium consists of MgO doped with Cr$_2$O$_3$. Assemblies were composed of ZrO$_2$ sleeves, stepped graphite or LaCrO$_3$ heaters, internal MgO spacers, and a molybdenum end disk and ring. The relatively large assembly allowed comparably large capsule sizes (5 mm in length and 3 mm in diameter) providing the required amount of sample material necessary for bulk analyses (see below). Again, a graphite-Pt double-capsule setup was chosen to minimize loss of N from the system. The inner graphite capsules (2.6 mm outer diameter) were first filled with a layer of magnesium nitride (making up to 80% of the available space for the highest initial N contents) followed by a layer of metal on top. Multianvil experiments above 6 GPa were run in crushable Al$_2$O$_3$ capsules and a C-free metal melt to avoid diamond formation. In both experimental setups, temperature was controlled using type B or type C thermocouples to 1500 and 1600–1800 °C, respectively.

Quenched run products were mounted in epoxy and polished for analysis. Nitrogen was measured either using a LECO ONH 836 elemental analyzer or a JEOL JXA 8200 electron probe microanalyzer (EPMA). EPMA analysis, carried out for some samples prior to the LECO combustion method, was also used to measure Fe and C contents of the metal and monitor possible Pt contaminations that may result from interaction of the Fe-dominated alloy with the capsule. Analyses were carried out in wavelength dispersive mode at a beam current of 150 nA and acceleration voltages of 10 kV for N and 15 kV for Fe, C, and Pt. A 10–20 μm defocused beam was used to average over the typical dendritic quench textures consisting of Fe metal, carbides, and nitrides (Figure 1). Nitrogen was measured on a LDE1H crystal. High-purity Fe and Pt metals and synthetic cementite (Fe$_3$C, synthesized from a stoichiometric mix at 1150 °C, 15 kbar for 71 hr) were used for calibration. Sample chips of previous experiments analyzed by precision bulk analysis (see below) were used as standards for the analysis of N on the EPMA. The detection limit for N was 0.05 wt %. Counting time for both N and C were 40 s on the peak and 20 s on the background, whereas Fe and Pt were measured for 20 and 10 s, respectively. The carbon blank value of our instrument was ~0.3 wt%. This blank, determined prior to each session by repeated measurements on pure Fe, was subtracted from the measured sample concentrations.
After microprobe analysis, a 300 μm diamond wire saw was used to remove the sample from the polished epoxy block by cutting the four visible sides of the metal melt. The capsule material on the remaining side was then removed by polishing with Al2O3 grinding paper. The resulting clean piece of metal was then gently crushed into smaller pieces for repeated bulk N analysis on the LECO ONH 836 elemental analyzer. The samples are, via an evacuated sample chamber, placed in predegassed graphite crucibles and combusted at ~2200 °C. Such high temperatures are necessary to release all N from the sample. An inert carrier gas (He) flushes the liberated sample gas into a thermal conductivity cell, which measures the thermal difference between the carrier and analyte gases. Steel standards were used for calibration and their mass adjusted such that they cover the range of absolute amounts of N (4 × 10⁻⁷ to 9 × 10⁻⁴ g) in the experimental samples. To monitor instrumental sensitivity and potential drift, standards were measured every 10 analyses. The N blank was determined by measuring 5–10 empty graphite crucibles prior to each session. If possible, at least three chips (5–20 mg) of each sample were measured. Further details on the calibration of the bulk analyzer and a comparison of N measurements between this method and EPMA data are shown in the supporting information.

3. Results

In total, 21 piston cylinder and 6 multianvil experiments define the solubility of N in Fe-based alloys. Metal melt compositions and run conditions are reported in Tables S2 and S3 in the supporting information.
3.1. Run Products

All run products are texturally similar and dendritic with needles consisting of Fe-metal, Fe-carbide, and Fe-nitride (Figures 1a and 1b), an indication that all samples were completely molten during the experimental run. All experiments at \( \leq 6 \) GPa were graphite saturated and graphite flakes (<300 \( \mu \)m) can be found in the melt close to the rims of the graphite capsule. In experiments run with dense Al\(_2\)O\(_3\) capsules, bubbles could be observed in the melt (Figure 1c) testifying for gas saturation. Most but not all experiments in graphite capsules were bubble free, probably a result of N gas accumulating in the porosity of the graphite capsule (22% porosity compared to 0.3% in dense alumina). In experiments where large bubbles (typically 5–15 \( \mu \)m) were observed, they appeared in similar size and evenly distributed within the sample, suggesting that they formed in equilibrium with the melt. In contrast, small bubbles of various but generally <1 \( \mu \)m size are interstitial between quench phases, suggesting that these form upon quench. Most experiments show higher C concentrations than the initial starting material, a consequence of graphite capsule dissolution at temperatures above the eutectic.

Magnesium nitride in the multianvil experiments decomposed to Mg and MgO that formed with the oxygen contained in the 40% porosity of the crushable alumina capsule. The Fe-metal did not dissolve any measurable Mg, the detection limit being \( \sim 0.05 \) wt%. These experimental charges show a more brittle structure (Figure 1d) than from the piston cylinder experiments, probably due to higher gas contents in the pore spaces. Again, heterogeneous quench textures could be observed (Figure 1e). Nevertheless, samples were never impregnated with epoxy, thus preventing contamination by N-bearing organic compounds.

3.2. The Effect of Pressure and Temperature

To determine whether maximum solubility was reached in our experiments, we have applied two criteria. First, the existence of an equilibrium vapor phase, indicated by large homogeneously distributed vesicles (as described above; Figure 1c), is evidence that the metal solubility limit is reached. Exsolution of nitrogen gas during quench is expected to result in much finer interstitial vesicle textures, which, however, was not observed at low pressures. Second, maximum solubility is determined from the formation of a concentration plateau in the recovered samples that is independent of the added bulk N content in the capsule. The second criterion considers that the double capsules with crushable alumina or graphite provide open pore space in which a vapor phase can exist without causing bubble formation in the metal liquid. The formation of a plateau as seen in Figure 2a therefore indicates saturation of the vapor phase. It has to be further considered that there is serious N loss (36–60% relative) during the experiments in welded capsules such that a large volume of gas phase is apparently not stable but rapidly lost through diffusion of N through the Pt capsule walls.

Increasing pressure has a strong positive effect on N solubility. Figure 2a summarizes the results of the different sets of experiments at 1400 °C and 1 to 9 GPa and various amounts of N in the starting material. At 1 GPa, measured N concentrations of the samples increase until a plateau is reached at 1.03 ± 0.01 wt % N, indicating that these melts saturated in N. At 2, 3, and 6.8 GPa, these plateaus were reached at 2.3, 3.6, and 6.0 wt% N, respectively. The highest N solubility of 7.4 wt% N was measured at 9 GPa.

Two series at 1 and 3 GPa were conducted over temperatures ranging from 1200 to 1800 °C. The results show that increasing temperature decreases N concentrations in the metal melt, from 1.27 to 0.57 wt% at 1200 to 1800 °C, at 1 GPa. A similar amplitude of solubility decrease is observed at 3 GPa (see Figure 2b). These negative trends are consistent with a general decrease of gas solubilities in liquids with increasing temperature (e.g., Blank & Brooker, 1994; Goranson, 1936; Yamashita, 1999).

4. Discussion

4.1. Nitrogen Solubility at High Pressures and the Influence of Alloying Elements

At low pressures, the solubility of N into metal melts may be described by Sievert’s law (e.g., Kowanda & Speidel, 2003). Following the reaction

\[
\frac{1}{2} N_2(gas) \leftrightarrow N_{metal}
\]

the equilibrium constant \( K \) for this reaction is
using the terms of the steel industry where $a_N$ is the activity of nitrogen; $f_N$ is the activity coefficient in the liquid alloy; $[\% N]$ is the amount of dissolved nitrogen in the alloy, given in wt%; and $p_{N_2}$ is the partial pressure of $N$ in the gas phase (in bar). In the framework of Sievert’s law, the standard state is the hypothetical solution of 1 wt% $N$ into pure iron and the related reference state is the dissolution of nitrogen at infinite dilution. N dissolution was successfully described by Sievert’s law for Fe–C alloys with up to 5.2 wt% carbon (Jang et al., 2014) and various binary Ni dominated alloys with Fe, Co, Cr, Mo, W, and Mn investigated up to 60 bar (Kowanda & Speidel, 2003). If Sievert’s law is followed, the dissolved amount of nitrogen in the melt is directly proportional to the square root of pressure:

$$K = \frac{a_N}{\sqrt{p_{N_2}}} = f_N \times \frac{[\% N]}{\sqrt{p_{N_2}}}$$

(2)

where $Ks$ is the Sievert constant, which represents the nitrogen concentration at a partial $N$ pressure of 1 atm. Sievert’s law is a formulation of ideal solution of a monoatomic species in the metal where $[N]_{metal}$ only depends on the partial pressure of $N_2$ in an ideal gas. There is no term of interaction whatsoever, and hence at higher concentrations and higher pressures deviations are to be expected. In solid Fe, $N$ occupies
octahedral interstices in the lattice. There is an intermediate compound Fe₁₆N₂ (3.0 wt% N) dubbed α” (Jack, 1951) where N is fully ordered such that no Fe has two N neighbors. This concentration may hence be taken as a rough value above which nonideality should occur, typically leading to lower solubilities. It is thus not a surprise that Sievert’s law cannot describe N solubility in metal melt at high concentrations, in this case equivalent to high pressures (Figure 2c).

Roskosz et al. (2013) investigated N solubility in metal melt using a laser-heated diamond cell from 1.8 to 17.7 GPa and approximately 2200–2600 °C. They find systematically higher N solubilities, in the overlapping pressure range of 2–9 GPa by ~2 wt% N (Figure 2c). Apart from the experimental technique used, the fundamental differences between the two studies are 20–27 wt% Ni in the metal, no C in the system, and temperatures of ~2400 ± 200 °C in Roskosz et al. (2013), contrasting no Ni, 3–4 wt% C, and temperatures of 1200–1800 °C in this study.

At low pressures, the effect of Ni is a drastic lowering of N solubility (Kowanda & Speidel, 2003; Stein & Hucklenbroich, 2004); the Sievert constant Kᵢ (equivalent to the solubility at a N₂ pressure of 1 atm) for pure Fe is 0.046 while that for pure Ni amounts to only 0.009, exactly the opposite sense than required to explain the observed differences in N solubility. Higher temperatures lead to lower gas solubilities in metals (see Figure 2b and discussion below), also the opposite sense of the observed solubilities. As carbon occupies the same interstices in the metal (melt) structure, one can expect that carbon and nitrogen compete for these interstices and hence carbon should lower N solubilities. Also, carbon provides excess electrons (compared to Fe, Ni, and N) and thus decreases N solubility (Stein & Hucklenbroich, 2004). This could explain at least part of the difference between the two studies; however, we have performed two C-free experiments and find only ~0.75 wt% higher N concentrations at 1400 °C. This does neither explain the observed difference of 2 wt% nor does it counterbalance the effects of temperature (depending on pressure 1 to 2 wt% N at 1400 compared to 2400 °C), nor those of Ni.

The higher N concentrations observed by Roskosz et al. (2013) could in principle result from the interplay between the silicate and metal melt in that study. The partitioning of N between a silicate and a metal melt depends on oxygen fugacity (Libourel et al., 2003), which is between IW and IW-2.8 in Roskosz et al. (2013) and not well defined but rather more reducing in our study, at least in those experiments where Mg-metal is present. As N solubility increases with decreasing oxygen fugacity (Libourel et al., 2003), this would again have an effect opposite to the observed one. Both studies investigate N solubility under excess N₂ gas and reduced species (i.e., compounds with H) should be relatively minor in both setups with wt% of N and nominally no H. Further differences could result from the more complex system in Roskosz et al. (2013); however, this is little plausible as Roskosz et al. (2013) do not report further elements in the metal and still, both studies investigate the gas-metal equilibrium which does not depend on the presence or absence of another phase.

Other alloying elements, especially the light elements (Si, S, or O) that are thought to have participated in core formation, most likely influence N solubility in metal melts. Bouchard and Bale (1995) investigated N solubility in the framework of steelmaking and found that there is no effect of S on N solubility in the range of 0–4 wt% S. However, increasing Si concentrations from 0 to 8 wt% results in a decrease of N solubilities from 0.043 to 0.017 wt%, similar to the negative correlations observed for C. Silica as well as C have an excess of two ions in their outer electron shell (compared to Fe), which cause negative interactions (Stein & Hucklenbroich, 2004). Keeping in mind that these data are from the steel literature at atmospheric pressures, these effects would need to be tested at higher pressures.

Nevertheless, we have modified the functional form of Sievert’s law such that it results in a good fit that describes N solubility at high pressures, following

\[ N(P) = a \times P^b \]  

with \( a \) and \( b \) being the solubility coefficients for Fe-dominated metal melts and P pressure in GPa. Fitting our data (for C-bearing metal melts) results in a solubility coefficient \( a \) of 1.20 ± 0.17 and \( b \) of 0.84 ± 0.07 for Fe melts, fitting Roskosz’ data results in solubility coefficients of 3.68 ± 0.58 and 0.43 ± 0.06 for \( a \) and \( b \), respectively. This functional form is based on the dissolution of monoatomic N (in octahedral defects) from a N₂ gas; the good description of the experimental results by this simple functional form suggests that both speciations are likely to be dominant also at high pressures.
4.2. Effect of Temperature on Nitrogen Solubility

While pressure shows a strong positive effect on N solubility, our experimental data reveal the opposite for temperature. The observed negative dependence of N solubility with increasing temperature can be fit best with an exponential relationship following

\[ N(T) = e^{ct} + d \]  

with T in °C and c and d being the solubility coefficients for an Fe-dominated metal melt.

This approach is only valid for temperatures >1150 °C as there is no Fe-dominated metal melt at lower temperatures (Kumar, 2008). For our set of experiments run at 1 GPa and 1200–1800 °C we derive solubility coefficients of 1160 ± 133 for c and −1.35 ± 0.27 for d. At 3 GPa, the N solubility shows a similar negative behavior, yet higher N concentrations due to a higher pressure.

4.3. Nitrogen Solubility Model as a Function of Pressure and Temperature

To model N solubility in Fe-dominated metal melts, we have combined equations (4) and (5) into

\[ N(P, T) = a \times P^b + e^{ct} + d \]  

where a and b are the solubility coefficients for the pressure effect and c and d describe the temperature dependence. We have then fitted (6) to our complete experimental data set and derive the following parameters to model N solubility as a function of both pressure (>0.1 GPa) and temperature:

\[ N(P, T) = 1.23 \pm 0.54 \times P^{0.88 \pm 0.19} + e^{(1120/T)} - 2.2 \pm 0.6 \]  

The result of our parameterization is graphically shown in Figure 1d as a contour plot of N solubility as function of pressure and temperature. Note, that with increasing pressure, the dominant parameter controlling solubility becomes pressure, for example, only to 1 GPa pressure and temperature have comparable effects on solubility, above 1 GPa the decrease in solubility with increasing temperature at constant pressure is small compared to the positive effect of pressure.

4.4. Nitrogen Solubility During Earth’s Core Formation

The growth of Earth was characterized by a continuous to stepwise accretion process. Impacting planetesimals and larger bodies supplied sufficient energy to cause large-scale melting and the formation of one or several successive deep magma oceans possibly 500–1000 km deep (15–35 GPa; e.g., Wood et al., 2006). This early stage has played a key role for the modern N distribution. First, the silicate magma ocean has partially degassed, the outgassing being largely dependent on the atmospheric pressure, which may have reached ~100 bar (e.g., Abe, 1997; Matsui & Abe, 1986) with a correspondingly high N partial pressure. On the other hand, large impacts potentially blew off such an atmosphere, which then may or may not have re-accreted into the consolidating body.

Second, N was sequestered from the silicate magma ocean by metal segregation. The partitioning of N in core-forming metal liquids is controlled by the equilibration depth, commonly assumed to lie near the base of the magma ocean, relatively small metal droplets equilibrating until they collect gravitationally at the magma ocean basis. The pressure–temperature relation at the magma ocean basis is necessarily close to the peridotite liquidus (Figure 2d) on which maximum solubilities reach several wt% at as little as 2 GPa. Experimental studies (Dalou et al., 2017; Kadik et al., 2011; Li et al., 2016; Roskosz et al., 2013) investigating the partitioning of N between metal and silicate melt found N to be a moderately siderophile element \(D_N^{\text{metal/silicate}} \approx 0.5–150\). The chondritic building blocks of Earth contain 425–1500 ppm bulk N (enstatite chondrites to C1 chondrites; e.g., Kerridge, 1985; Javoy, 1998). With a characteristic partition coefficient \(D_N^{\text{metal/silicate}} \approx 10\), full conservation of N in a C1 chondritic planetesimal would lead to as much as ~4000 ppm N in the metal, a quantity easily soluble if the planetesimals have sizes of a few hundred kilometers. Nevertheless, iron meteorites, thought to represent relics of core material from small differentiated bodies formed in the early solar system, contain up to 1 wt% N (Sugiura, 1998), demonstrating that the maximum nitrogen solubility as determined here may constitute an important upper limit for the amount of N stored in the metal.
The density deficit of the Earth’s core with respect to pure Fe–Ni alloy is caused by ~5 to 10 wt% of light elements (e.g., Birch, 1952, 1964). According to our results, N solubilities in Fe metal melt at magma ocean basis conditions would allow for sufficient N, but it appears unlikely that enough N would be available. Estimates of core N concentrations range in fact from 75 ppm (McDonough, 2003, 2014), mainly based on a modern N content of the silicate Earth of a few ppm and a partition coefficient of the order detailed above, to as much as 0.5–3.3 wt% based on the high stability of iron nitrides and their potential to replace carbides at core conditions (e.g., Fe7N3, Fe4N; Adler & Williams, 2005; Litasov et al., 2016, 2017). It appears hence likely that in the inner solar system, the solubility limit determined here may play a role for small planetesimals while Mars- to Earth-sized objects would have higher N solubilities than N availabilities. Instead, the 3100 and 5200 km diameter Galilean moons Europa and Ganymede do have a metal core formed in the much more N-rich environment of the outer solar system (e.g., Kuchner, 2003; Pollack et al., 1996). It is well possible that these cores are N (and probably C) saturated. Whatever, our solubility limits provide fundamental data and need to be combined with other controls of, for example, alloying element(s), pressure, temperature, and oxygen fugacity.

4.5. Nitrogen in the Reduced Mantle

It is now well established that the deep mantle (>200 km) is metal saturated (e.g., Frost et al., 2004; Rohrbach et al., 2007; Rohrbach & Schmidt, 2011). The affinity of majorite and perovskite for FeIII causes FeII to disproportionate to FeIII and a metal phase. This metal phase amounts to 0.1 to 1.5 wt% at 200–700 km depth and scavenges all C and S from the mantle. Because of the low Fe-S and Fe-C eutectic temperatures, this metal phase is either partially or fully molten at adiabatic temperatures (Rohrbach et al., 2014). Mantle mineral-metal melt partition coefficients have not been measured but the N solubility in mantle minerals is exceedingly low (~10–100 ppm; Li et al., 2013). Partition coefficients between metal and silicate melt at an oxygen fugacity one log-unit below the iron-wustite buffer (ΔIW-1; as appropriate for the deeper mantle) are 10–30, and it is likely that partition coefficients of metal melt and clinopyroxene (the silicate mineral with the highest N concentration) partition coefficients (e.g., Waterphul et al., 2010) are much higher, leading to a bulk metal melt/mantle mineral partition coefficient of at least 100. The high affinity of N for metal hence leads to the expectation that the small Fe-rich metal fraction in the deep mantle hosts all of the N of the deep mantle. An upper bound of 40 ppm N in the mantle (e.g., Javoy, 1997) combined with the lower abundance of the metal phase at 200 km depth yields 4 wt% of N in this metal melt, a value that is about 50% of the N solubility at the appropriate conditions (7 GPa, 1480 °C for the adiabat; see Figure 2d).

5. Conclusions

This study provides fundamental data on N solubility in Fe-dominated metal melts as a function of both pressure and temperature, which may be applied to core formation on rocky moons and planets and to the metal fraction of the deep silicate Earth. The experimental results show that at high pressures, large amounts of N can potentially be stored in core-forming metal. Our N solubility model offers a high upper solubility of N in the Earth’s core, for example, ~13.3–25 wt% at the magma ocean’s base of 500–1000 km (2000–2500 °C; e.g., Abe, 1997) or of several wt% for smaller planetesimals. Volatile loss of N from any silicate magma ocean is hence a two-way street, one to an early atmosphere and one to the core-forming material. The pronounced negative effect of C on N solubility in Fe-dominated metal melt is a key observation and needs to be further explored in its significance for N redistribution between metal and silicate melts. From our results, it appears likely that small C-rich planetesimals may have cores, which N content is solubility limited.

References


