Magnesiowüstite as a major nitrogen reservoir in Earth’s lowermost mantle

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Abstract

Ferropericlase (Mg,Fe)O is after bridgmanite the most abundant phase in the lower mantle. The ultralow velocity zones above the core-mantle boundary may contain very Fe-rich magnesiowüstite (Fe,Mg)O, possibly as result of the fractional crystallisation of a basal magma ocean. We have experimentally studied the solubility of nitrogen in the ferropericlase-magnesiowüstite solid solution series as function of iron content. Multi-anvil experiments were performed at 20–33 GPa and 1600–1800 °C in equilibrium with Fe metal. Nitrogen solubility increases from a few tens ppm (μg/g) for Mg-rich ferropericlase to more than 10 wt. % for nearly pure wüstite. Such high solubilities appear to be due to solid solution with NiAs-type FeN. Our data suggest that during fractional crystallisation of a magma ocean, the core-mantle boundary would have become extremely enriched with nitrogen, such that the deep mantle today could be the largest nitrogen reservoir on Earth. The often discussed “subchondritic N/C” ratio of the bulk silicate Earth may be an artefact of insufficient sampling of this deep reservoir.

Introduction

Nitrogen is the main constituent of Earth’s atmosphere. Nitrogen concentrations in the oceans, biomass and sediments and other near surface reservoirs are well constrained (Johnson and Goldblatt, 2015). The nitrogen abundance in the convecting upper mantle is also quite well known from measurements of N/40Ar ratios of MORB samples (Marty, 1995), which appear to be nearly unfractionated during partial melting and degassing (Kepler et al., 2022). If one considers the upper mantle to be representative of the entire bulk silicate Earth, these data would suggest that nitrogen on Earth is selectively depleted relative to carbon (Marty, 2012). This “subchondritic N/C ratio” has been extensively discussed and has often been used to constrain details of models for the early evolution of Earth (e.g., Hirschmann, 2016; Li et al., 2023).

There are, however, reasons to believe that the transition zone and lower mantle may be enriched in nitrogen, which would obviously call into question the concept of the “subchondritic N/C ratio” of the bulk Earth. Some samples from ocean island basalts have much higher N/40Ar ratios than MORB (Johnson and Goldblatt, 2015), which could hint at a deep seated N-rich reservoir. Moreover, experimental studies (Yoshioka et al., 2018) suggest that in particular, the main minerals of the mantle transition zone, wadsleyite and ringwoodite, may store much more nitrogen than the minerals of the shallow mantle. Nitrogen solubility in minerals of the lower mantle, however, is poorly constrained. There are very few data on bridgmanite, the most abundant phase (Yoshioka et al., 2018) and no data at all on ferropericlase, the second most abundant phase. In the present study we systematically investigated N solubility in the ferropericlase (Mg,Fe)-magnesiowüstite (Fe,Mg)O solid solution series.

Methods

Ferropericlase or magnesiowüstite were synthesised together with other minerals (mostly bridgmanite) at 20–33 GPa and 1600–1800 °C in the presence of a N-rich fluid phase. Starting materials were oxide (SiO2-MgO) hydroxide (Mg(OH)2-Al(OH)3) mixtures with bridgmanite (MgSiO3) stoichiometry, sometimes containing up to 10 wt. % Al2O3. Metallic Fe was added to all charges either as powder or as 1mm thick disks to buffer oxygen fugacity near the Fe-FeO (iron wüstite) equilibrium, which is realistic for the lower mantle (Frost and McCammon, 2008). A N-rich fluid phase was generated by adding isotopically labelled ammonium nitrate (15NH415NO3) to the charge, which was sealed into Pt capsules. The weight ratio of metallic Fe to 15NH415NO3 and to the oxide-hydroxide mixture loaded in each capsule was about 5:1:2. Experiments up to 24 GPa were carried out in a conventional, Kawai-type multi-anvil apparatus. For experiments at higher pressures, a multi-anvil press of new design was used (Ishii et al., 2016).

The samples recovered from high pressure experiments were embedded into epoxy resin, sectioned and polished. Nitrogen contents were measured both by electron microprobe
Nitrogen Solubility in Ferropericlase-Magnesiowüstite

A summary of all our high pressure experiments and analytical results is given in Tables S-1 and S-2. Figure 1 shows a typical run product. At pressures above 24 GPa, magnesiowüstite (or ferropericlase, depending on composition) coexists with bridgmanite and a metallic phase containing iron, as expected for the lower mantle. Other phases, in particular stishovite, are occasionally observed. In the majority of the experiments, most of the magnesiowüstite formed by the oxidation of a portion of the Fe metal that was initially added, which explains the rather Fe-rich compositions in most experiments. Measured nitrogen contents in the (Fe,Mg)O phase are shown in Figure 2 as function of FeO content. Nitrogen solubility in ferropericlase-magnesiowüstite increases from a few 10 μg/g for Mg-rich compositions to 18 wt. % (!) for the Fe end member. In general, the data from SIMS measurements define a consistent trend with only few outliers. The microprobe measurements (see also Table S-1) overlap with the SIMS data but most of them are displaced to lower values. This is likely due to degassing during the microprobe measurements, as the sample is heated in vacuum by the electron beam. Indeed, in a scan of the X-ray spectrum of the most N-rich samples, the nitrogen Kα line was clearly visible before the measurements, while it was invisible afterwards. Despite these analytical problems, we show the microprobe data here, as they provide an independent confirmation of the very high nitrogen contents obtained by SIMS. We cannot exclude that local heating may also occur during SIMS measurements, therefore our SIMS and microprobe measurements were never carried out at exactly the same locations. Some of the scatter seen in Figure 2 may also be related to variations in oxygen fugacity. The Fe metal in the runs is to a variable extent alloyed with Pt (see Table S-1) and this effect will shift the oxygen fugacity to values above the Fe-FeO buffer, which is expected to reduce nitrogen solubility in minerals (e.g., Li et al., 2013). The FeO contents in Figure 2 and Table S-1 were obtained by the usual standard procedures used for oxide and silicate analyses, i.e. all Fe was assumed to be Fe2+ and expressed as FeO. However, in reality (see the discussion below), some Fe is present as nitride in solid solution. For the most Fe-rich samples, this procedure produces totals (FeO + MgO + N) that may exceed 100 %. No attempt was made to correct for this.

Nitrogen Substitution Mechanism in Ferropericlase-Magnesiowüstite

Wüstite is a non-stoichiometric phase, often written as Fe1-xO. This is because some of the iron is present as Fe3+ (even at low oxygen fugacities), which is then charge compensated by Fe2+ vacancies. An alternative possibility of charge compensation for Fe3+ would be the substitution of Fe2+ by a univalent cation, such as Na+. Indeed, samples of ferropericlase from the mantle can have elevated sodium contents (Brey et al., 2004). Instead of Na+, perhaps also the ammonium ion NH4+ could be incorporated into magnesiowüstite, which would be a possible mechanism for accommodating the exceptionally high nitrogen solubilities reported here. NH4+ would be easily detectable by Raman spectroscopy due to the N-H stretching vibrations near 3100 cm⁻¹. We therefore measured Raman spectra of some
The molar fraction of Fe in ferropericlase in a pyritic lower mantle is likely between 0.1 and 0.3 depending on depth (e.g., Irifune et al., 2010; Muir and Brodholt, 2016). This translates into a composition of 16–43 wt. % FeO. As one may see from Figure 2, this corresponds to a nitrogen solubility in the range of a few tens μg/g. These numbers are comparable to the nitrogen solubility in bridgmanite (near 20 μg/g for Al-free bridgmanite; Yoshioka et al., 2018). The estimates of Yoshioka et al. (2018) of the total nitrogen storage capacity of the lower mantle of 25 PAN (present atmospheric masses of nitrogen) would therefore require a significant upward revision. Even more interesting than the situation in the bulk lower mantle are the consequences of the data presented here for nitrogen sequestration just above the core-mantle boundary.

Numerous seismic studies have detected zones of ultralow seismic velocities (ULVZs) at various locations just above the core-mantle boundary (e.g., Williams et al., 1998; Cottaar and Romanowicz, 2012; Thorne et al., 2013). Various hypotheses have been proposed to explain these features. Initially, it was widely believed that the presence of partial melt (e.g., Williams et al., 1998) might be responsible for the observed drop in seismic velocities. However, over the last decade, alternative models have received more support, which attribute these zones to chemical anomalies with very Fe-rich compositions containing near end member magnesiowüstite (Wicks et al., 2010; Sun et al., 2013; Brown et al., 2015). Various models have been proposed for the origin of these Fe-enriched zones. They may perhaps be “sediments” of material exsolved from the liquid core (Buffett et al., 2000) or consist of subducted banded iron formation (Dobson and Brodholt, 2005). An alternative idea is that these Fe-rich zones are remnants of the fractional crystallisation of a deep magma ocean, which caused increasingly Fe-rich minerals to be deposited at the core-mantle boundary during the Hadean (Llabrosse et al., 2007). If this latter model is correct, it would imply that these ULVZs may have concentrated most of the nitrogen that was originally dissolved in a magma ocean. This is so because the nitrogen solubility in magnesiowüstite measured here is one to two orders of magnitude higher than the nitrogen solubility in a silicate melt measured under comparable conditions of pressure, temperature, and oxygen fugacity (Roskosz et al., 2013). While nitrogen is more or less incompatible in all other phases that may crystallise from a magma ocean (Li et al., 2018), the data presented here suggest that it would be highly enriched in Fe-rich magnesiowüstite that would precipitate just above the core-mantle boundary.

A rough calculation may demonstrate that the ULVZs above the core-mantle boundary may very well be a major nitrogen reservoir in the solid Earth. For the following discussion, we ignore any nitrogen partitioning into the core, since for the very reducing conditions of Earth’s early accretion predicted by current models, N behaves as a lithophile element (e.g., Speelman et al., 2019). Enstatite chondrites, which may resemble most of the material that accreted to form the Earth, contain about 605 μg/g N, whereas the concentration of N in carbonaceous chondrites is on average more than twice as high (Johnson and Goldblatt, 2015). If the bulk N content of the accreting Earth was near that of enstatite chondrites, this would translate in a N2 partial pressure of about 700 bar in a primordial atmosphere above a magma ocean (Yoshioka et al., 2018). According to Libourel et al. (2003), N2 solubility in a
basaltic melt is about 0.06 (μg/g)/bar at conditions near the iron wüstite buffer; it may become even larger at more reducing conditions and at high H2O fugacities (Li et al., 2015; Bernadou et al., 2021). If one accepts the rather conservative solubility of 0.06 (μg/g)/bar, this would imply that the magma ocean in equilibrium with the primordial atmosphere may have contained 42 μg/g N, equivalent to 1.70 · 10²⁰ kg. If only 20% of the mass of this magma ocean had been trapped somewhere deep in the mantle during progressive crystallisation, as suggested by Labrosse et al. (2007), it would contain a N reservoir of 3.4 · 10¹⁹ kg, more than 8 PAN (present atmospheric masses of nitrogen). Upon crystallisation of this deep magma reservoir, both nitrogen and Fe would become enriched in the residual melt, ultimately leading to the precipitation of very Fe-rich magnesiowüstite that is presently contained in the ULVZs. If one assumes that these ULVZs are about 15 km thick (e.g., Cottaar and Romanovicz, 2012) and cover approximately 10% of the core-mantle boundary, they would contain 13 wt. % N, if all the N in the deep melt reservoir were sequestered in there. This number is quite consistent with the measured solubilities of N in magnesiowüstite.

Is the “Subchondritic N/C Ratio of the Earth” Real?

Maybe not. The data presented here show that a very small and probably very poorly sampled reservoir near the core-mantle boundary could contain enough nitrogen to make the roughly one order of magnitude (Marty, 2012) apparent depletion of N relative to C in the bulk Earth disappear. This further emphasises a conclusion reached already by Yoshioka et al. (2018) that the solubilities of N in ordinary minerals of the transition zone or the lower mantle are large enough that the deep mantle could have sequestered a large fraction of Earth’s nitrogen during magma ocean crystallisation. On the other hand, while the N content of the depleted MORB-source mantle (e.g., Marty, 1995) is very well constrained, data on the deep mantle are sparse. While many ocean island basalts do indeed have N/40Ar ratios similar to MORB, there are also some samples with much higher values (Johnson and Goldblatt, 2015) that may hint at a deep hidden reservoir. Based on our current state of knowledge, the bulk N/C ratio of the Earth appears to be rather uncertain and this ratio should not be used as a parameter for constraining...
planetesimal accretion models (e.g., Hirschmann, 2016; Li et al., 2023).

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Additional Information

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