

THE ROLE OF THE HYDROGEN AND OXYGEN FUGACITY ON THE INCORPORATION OF NITROGEN IN REDUCED MAGMAS OF THE EARLY EARTH'S MANTLE. A.A.Kadik¹ and Yu.A. Litvin², ¹V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Kosygin St. 19, Moscow 119991, Russia kadik@geokhi.ru, ²Institute of Experimental Mineralogy, RAS, Chernogolovka, Moscow distr. 142432, Russia litvin@iem.ac.ru

Problem: Among volatile elements, nitrogen is a major forming element of the Earth's. Knowledge of its behavior is therefore of importance to understand processes which might have controlled the exchange of nitrogen between the mantle and the atmosphere through time. In this respect, extraction of volatiles from a hypothetical magma ocean or from the solid Earth through partial melting and degassing of mantle-derived magmas played a central role. Experimental researches show that the nitrogen solubility is very sensitive to the oxygen fugacity (fO_2), and its incorporation in silicate melt follows two different mechanisms [1-6]. In oxidizing conditions, fO_2 above $fO_2(IW)$ (iron - wüstite oxygen buffer), the incorporation of nitrogen corresponds to dissolution of N_2 molecule, with no covalent or ionic bounding between N atoms and the silicate network, while in reducing conditions, fO_2 below fO_2 of IW , dissolved nitrogen is chemically bounded with atoms constituting the silicate melt network and the nitrogen solubility increases drastically by several orders of magnitude. However the nature of last mechanism of nitrogen dissolution in many respects remains insufficiently studied.

In theories of the formation of the Earth, the composition of gases extracted by primary planetary magmas is accounted for by the large-scale melting of the early mantle in the presence of the metallic Fe phase at fO_2 below $fO_2(IW)$ [7]. The melting should have been accompanied by the formation of volatile compounds, whose composition was controlled by the interaction of H, C and N with silicate and metallic melts, a process that remains largely unknown as of yet.

In a series of experiments in the system Fe-bearing melt + molten Fe metallic phase + N+ H conducted at 4 GPa and 1550°C and $\log fO_2$ from 2 to 4 below $\log fO_2(IW)$, we have characterised the nature and quantified the abundance's of N- and H-compound dissolved in an model silicate melt (NaAlSi₃O₈ 80% wt + FeO 20% wt).

Experiments: Experiments were carried out in an anvil-with-hole apparatus [8, 9]. The sample is placed in a sealed Pt capsule 10 mm in diameter and 5 mm in height. The charges were isolated from the Pt capsule walls by tungsten foil (0.05 mm thick), which reduces the interaction between the Fe-bearing melt and platinum. The runs lasted 30-60 min.

The technique of fO_2 buffering employed here relies upon the diffusion of H_2 through Pt to achieve equal chemical potentials of H_2 in the inner Pt capsule and outer solid fO_2 buffer assembly in the presence of H_2O

[5,6]. The fH_2 was buffered by the furnace assembly functions at the iron (Fe) –wüstite (FeO) buffer. The fO_2 imposed on the charge is controlled by the equilibrium between H_2 buffered externally, and the the Fe-bearing melt. The reduction of FeO in melt with the formation of Fe alloy leads to liberation of oxygen that reacts with H_2 diffusing into the capsule from the buffer assemblage forming nitrogen and hydrogen species in silicate liquid. To create a low fO_2 in the experiments, 2, 3, 5 and 7 wt % of finely dispersed Si₃N₄ was added to the glass powder (NaAlSi₃O₈ 80% + FeO 20% wt). The initial Si₃N₄ was unstable under experimental conditions and was completely consumed according to the reactions: $Si_3N_4(\text{initial}) + 3O_2 \rightarrow 3SiO_2(\text{melt}) + 4N(\text{melt})$ with the subsequent participation of nitrogen in reactions with hydrogen and components of silicate melts. The fO_2 was calculated based on the Fe and FeO contents of the metal and silicate liquids, respectively. The fO_2 for the melt–iron equilibrium yields an fO_2 of 2.2-3.9 log units below $fO_2(IW)$.

Results: The products are greenish and colorless glasses and iron-rich globules 10-20 μm in size. No bubbles were visible. The depletion in FeO from 20 wt % in the starting glasses to 10 - 2 wt % after runs is a result of FeO reduction with the formation of a liquid Fe phase.

The solubility of Si in metal increases with decreasing fO_2 from 0.1 wt % at $\Delta\log fO_2(IW) = -2.2$ to 1.6 wt % at $\Delta\log fO_2(IW) = -3.9$. Nitrogen content in iron-rich globules to be fixed 1.5 wt % at $\Delta\log fO_2(IW) = -3.9$. The amount of H and N dissolved in the glasses was measured by ion microprobe, microprobe and CHN analysis. Hydrogen content increases with decreasing fO_2 from 0.3 wt % at $\Delta\log fO_2(IW) = -2.2$ to 0.4 wt % at $\Delta\log fO_2(IW) = -3.9$. Nitrogen content increases with decreasing fO_2 from 0.5 wt% at $\Delta\log fO_2(IW) = -2.2$ to 1.9 wt % at $\Delta\log fO_2(IW) = -3.9$ (Fig 1). Concentration of nitrogen in the glasses in each of run approximately correspond to its contents in initial mixes. Absence in products of experiment hydrogen- and nitrogen-bearing vapor phase allows to assume, that fluid–melt equilibrium were not achieved during experiment. Thus, solubility of nitrogen in investigated T–P– fO_2 field can be higher, than is established in our experiment. Nevertheless, the experimental data unequivocally testify to considerably higher solubility of nitrogen in silicate melts at $fO_2 < fO_2(IW)$ in comparison with that solubility which is characteristic for $fO_2 > fO_2(IW)$.

The infrared and Raman spectroscopy of glasses (Fig. 2) indicates a remarkable feature of N-H interaction with a reduced silicate: an appreciable change in the mechanism of their dissolution with a decrease in fO_2 . The nitrogen behavior observed in this study is consistent with the qualitative observation of [1-6] that there exists at least two fundamentally different mechanisms of nitrogen trapping in silicate melts. Some nitrogen is present in a melt in the molecular form. The most part of nitrogen reacts with hydrogen with formation of N-H complexes. The most likely nitrogen-bearing species is represented by NH_3 and NH_4^+ group. Except for N-H complexes hydrogen is expressed under the oxidized form OH and H_2O . Some hydrogen is present in a melt in the molecular form.

Discussion: The present results strongly suggest that under reducing conditions nitrogen interacts with hydrogen and the silicate network. The most likely nitrogen-bearing species that can account for Raman and infrared results N-H groups (NH_3 , NH_4^+). Part of incorporation nitrogen corresponds to dissolution of N_2 molecule. Significant amounts of nitrogen, comparable to those estimated for the present-day mantle, could have been incorporated in the early Earth by dissolution in a magma ocean, under fO_2 conditions relevant to those prevailing during metal segregation. It is suggested that the proportions of oxidized and reduced N, H and C species in the early atmosphere were closely connected to the character of global chemical differentiation during the formation of the metallic core, which could be a multistage process [10]. Nitrogen species in primary melt are likely to be dominated by NH_3 , while N_2 only plays a minor role. These H and N compounds are associated with the formation of OH^- and H_2O in reduced melt be expected in the primary melt.

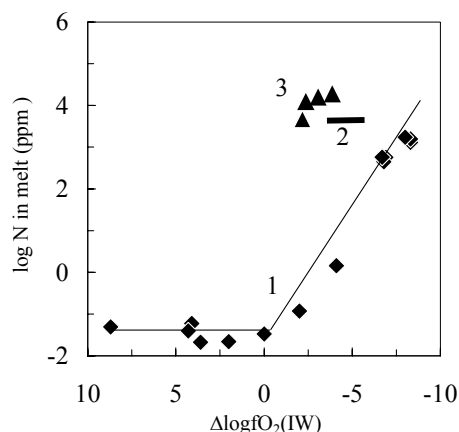


Fig.1. Nitrogen solubility in of oxygen fugacity. 1- MORB-like melt at 1 atm, 1425°C [3]; 2- aubrite and E-chondrite melts at 1 atm, 1550 °C [2]; 3- (NaAlSi₃O₈ + FeO) melt at 4 GPa, 1550°C – the present data.

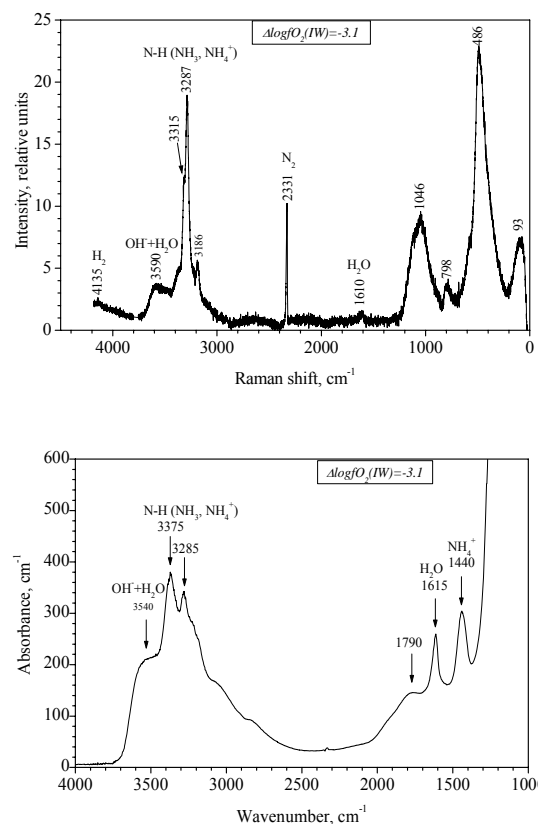


Fig 2. Raman (A) and IR (B) spectra of H and N-bearing glasses after experiment at 4.0 GPa, 1550°C, and $\Delta \log fO_2(IW) = -3.1$

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