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 binding 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 $logfO_2$ from 2 to 4 below $logfO_2(IW)$, we have characterised the nature and quantified the abundance’s of N- and H-compound dissolved in an model silicate melt (NaAlSi$_3$O$_8$ 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$_2$O [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 Si$_3$N$_4$ was added to the glass powder (NaAlSi$_3$O$_8$ 80% wt + FeO 20% wt). The initial Si$_3$N$_4$ was unstable under experimental conditions and was completely consumed according to the reactions: Si$_3$N$_4$(initial) + 3O$_2$ → 3SiO$_2$(melt) + 4N(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 $ΔlogfO_2(IW)$ = -2.2 to 1.6 wt % at $ΔlogfO_2(IW)$ = -3.9. Nitrogen content in iron-rich globules to be fixed 1.5 wt % at $ΔlogfO_2(IW)$=-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 $ΔlogfO_2(IW)$ = -2.2 to 0.4 wt % at $ΔlogfO_2(IW)$ = -3.9. Nitrogen content increases with decreasing $fO_2$ from 0.5 wt% at $ΔlogfO_2(IW)$= -2.2 to 1.9 wt % at $ΔlogfO_2(IW)$= -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$_2$O. 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$_2$O in reduced melt be expected in the primary melt.

**Support:** Prog. No. 18 RAS, RFBR grant, ESD RAS project 7-1.2.

**References:**

---

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- (NaAlSi$_3$O$_8$ + 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.