MAGMATIC TRANSPORT OF CARBON, HYDROGEN AND NITROGEN CONSTITUENTS FROM REDUCED PLANETARY INTERIORS. A.A.Kadik and Yu.A. Litvin, 'V.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

Introduction: In theories of the Earth’s formation, the composition of gases extracted by primary planetary magmas is accounted for the large-scale melting of the early mantle in the presence of the metallic Fe phase [1]. The molten metallic Fe phase and the melted silicate material have experienced gravitational migration that exerted influence upon the formation of the metallic core of the planet. The melting should have been accompanied by the formation of volatile compounds, which composition was controlled by the interaction of H and C with silicate and metallic melts, a process that remains largely unknown as yet. However, the available experimental results on the interaction of CH₄, H₂, elemental C, N₂ and NH₃ with silicate melts revealed an important feature of redox reactions in silicate melts [2-8]. Dual speciation of nitrogen in melt (N₂, N³⁻) under high pressure and fO₂ may have significant implication concerning of N-species’s formation in reduced planetary magmas [8].

In a series of experiments in the system Fe-bearing melt + molten Fe rich metallic phase (0.1-12 % Si) + C (graphite) + H₂ carrried out at 4 GPa and 1520-1600°C and log fO₂ (oxygen fugacity) = 2 -5 below IW (iron -wüstite) oxygen buffer, we have characterised the nature (oxidised versus reduced) and quantified the abundance of C, H and N-compound dissolved in the glasses. Dual speciation of nitrogen in melt (N₂, N³⁻) under high pressure and fO₂ may have significant implication concerning of N-species’s formation in reduced planetary magmas [8].

Experiments: Experiments were carried out in an anvil-with-hole apparatus[5] The researched substance was isolated from the walls of Pt capsule with the tungsten foil. A graphite disc 0.2 mm in thickness was placed above the sample. The experiment runs 30-60 min. This technique relies on the diffusion of H₂ through Pt to achieve equal chemical potentials of H₂ in the inner Pt capsule and outer furnace assembly[5,6]. The reduction of FeO in melt with the formation of Fe alloy leads to liberation of oxygen that reacts with H₂ diffusing into the capsule from the buffer assemblage and with graphite inside of capsule forming carbon and hydrogen species in silicate liquid.

To create a low fO₂ in the experiments, 2, 3, 5 and 7 wt % of finely dispersed SiC was added to the glass powder. The initial SiC was unstable under experimental conditions and was completely consumed according to the reactions: SiC (initial) + O₂ → SiO₂ (melt) + C (graphite). Si₃N₄ was used as a source of nitrogen (2, 3, 5, 7 wt % of initial mix). Si₃N₄ was completely oxidized during experiments with formation of SiO₂ and N species in melt.

The fO₂ was calculated based on the Fe and FeO contents of the metal and silicate liquids, respectively.

Results: The products are yellowish and colorless glasses and iron-rich globules 30-100 μm in size. No bubbles were visible. The depletion in FeO from 18 wt % in the starting glasses to 12-3 wt % after runs is a result of of FeO reduction with the formation of a liquid Fe phase. The solubility of Si in liquid metal increases with decreasing fO₂ from 0.1-0.55 wt % at Δlog fO₂(IV)=-2-3 to 10-12 wt % at Δlog fO₂(IV)=-4-5. Carbon content in iron-rich globules to be fixed between 3 and 6 wt %. The amount of H (as H₂O, OH, H₃, CH₄) and C (as CO₂ , CO₂⁻, CH₄, SiC, C) dissolved in the glasses was measured by ion microprobe and by CNH analysis. Hydrogen content decreases with decreasing fO₂ from 0.3-0.4 wt % at Δlog fO₂(IV)=-2-3 to 0.1-0.2 wt % at Δlog fO₂(IV)=-4-5 as a result decreasing of H₂O in melt (Fig.1). Carbon content increases with decreasing fO₂ from 0.2-0.5 wt % at Δlog fO₂(IV)=-2-3 to 1-2 wt % at Δlog fO₂(IV)=-4-5 as a result of increasing of CH₄ and Si-C-bonds in melt.

Fig.1 Experimentally determined H (as H₂O, OH, H₂, CH₄) the dissolution in reduced melts as function of fO₂ in area of the Fe-Si alloy stability at 4 GPa and 1550-1600 °C.

The infrared and Raman spectroscopy of glasses indicates a remarkable feature of C-H interaction with a reduced silicate: an appreciable change in the mechanism of their dissolution with a decrease in fO₂. At Δlog fO₂(IV)=-2-3 hydrogen is expressed mainly under the oxidized form OH and H₂O. Some hydrogen is present in a melt in the molecular form. Carbon is mainly dissolved in the melt as atomic C and Si-C bond. At Δlog fO₂(IV)=-4-6 hydrogen and carbon are expressed mainly under the reduced form CH₄, Si-
C and C=C bonds. The part of hydrogen is present in the oxidized form OH.

IR spectroscopy indicates that nitrogen is not only physically dissolved as N2 within the melt structure like noble gases, but it interacts strongly with the silicate network. The most likely nitrogen-bearing species is represented by N3- and nytrosyl group.

**Fig 2.** IR spectra of C- and H-bearing glasses. Experiments were at 4.0 GPa, 1550-1600°C and ΔlogfO2(IW) = -3.67 (A); ΔlogfO2(IW) = -5.71 (B).

**Discussion:** In the light of experimental data we argue that magma in reduced environment at in area of the Fe-Si alloy stability could form melts containing dissolved both oxidized, and reduced components of hydrogen and carbon species. The proportions of reduced and oxidized species of carbon in the primary melts substantially depend on the fO2 of the reduced mantle. At ΔlogfO2(IW) ~ -2, that corresponds to the equilibrium of Fe with olivine in the upper mantle, oxidized H species are prevalent in the melt equilibrated with metallic Fe. It appears that a large scale melting of growth Earth at ΔlogfO2(IW) = -2 could be associated with melts containing an oxidised form of hydrogen, although the early Earth was likely a reduced environment. The transport of primary magmas from the planetary interiors to the surface provides the primary supply of H2O of volcanic gases. If the chemical fractionation of the early mantle occurred at lower fO2 values ΔlogfO2(IW) = -3-5, that are expected for the enstatite-chondrite model of the mantle formation [9], then the compounds with C-H bonds (CH4 and other molecules) should be expected in the primary melt, together with oxidized H species (OH- group).

Volatiles in primary melt are likely to be dominated appeared by CH4, H2, while H2O only plays a minor role. These volatile H and C compounds are associated with the formation of a liquid Fe phase enriched in Si.

**Fig 3.** IR spectra of C, H and N-bearing glasses (4.0 GPa, 1550-1600°C, ΔlogfO2(IW) = -3.8)

Under very reduced condition nitrides were probably the main speciation of nitrogen in primary magmas and ammonium was component of volcanic gases.

It is suggested that the proportions of oxidized and reduced 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]. We assume that the first stage of core growth took place under reduced conditions imposed by the pristine terrestrial materials and was accompanied by the emission of CH4, H2, NH3 and minor H2O into the atmosphere.

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