

Solution behavior of reduced N–C–H–O volatiles in reduced silicate melts equilibrated with molten Fe alloy at high pressure and temperature

Arnold Kadik (1), Yuri Litvin (2), Vasily Koltashev (3), Elena Kryukova (1), Victor Plotnichenko (3), Tatiana Tsekhonya (1) (1) V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Russia, kadik@geokhi.ru /7-495-9382054, (2) Institute of Experimental Mineralogy, RAS, Russia, (3) Fiber Optics Research Center, RAS, Russia

Problem

Physical models of planetary accretion suggest that the energy released by giant impacts is sufficient to create a magma ocean. This conclusion is one of the bases for the theory of core formation in the presence of magma ocean, in which molten core materials segregate through a largely molten silicate mantle. The large-scale melting of the early Earth should have been accompanied by a formation of volatile species, which composition was controlled by interaction of the main gas-forming C–N–H–O elements with silicate and metallic melts at low fO_2 values prevailing during metal segregation. Many aspects of this chemical differentiation remain largely unknown. Solubility of volatiles in magmatic melts depends on pressure, temperature, composition, and oxygen fugacity, fO_2 . The redox regime (fO_2) is relevant to N–C–O–H volatiles because nitrogen and carbon can exist in several oxidation states. We will focus on solubility of reduced N–C–H–O volatiles in iron-bearing silicate melts at 4 GPa, 1550 °C as a function of variable redox conditions, and on how nitrogen and hydrogen fractionation between coexisting silicate and metallic melts may vary with fO_2 . The fO_2 range of the mantle has changed over the Earth's history. At the time of metal segregation the Earth's mantle was strongly reduced by 2–5 orders of magnitude below that of the iron–wüstite (IW) equilibrium and became more oxidized as it accreted. It has been argued that changes in the Earth's redox state were caused by fractionation processes, involving Fe, O, and Si [e.g. 1, 2, 3].

Experiment

In a series of experiments conducted at 1.5 GPa, 1400°C and 4 GPa, 1550 °C, and fO_2 from 2 to 5 log units below IW buffer we have characterized the

nature and quantified the abundance of N, C and H species dissolved in a model silicate melt ($FeO-Na_2O-Al_2O_3-SiO_2$) in a manner similar to that reported by [3, 4]. To elucidate the mechanisms of nitrogen and hydrogen dissolution in magmas, we studied the glasses produced by quenching the melts using Infrared and Raman spectroscopy. Experiments indicate that under the reduced conditions corresponding to the fO_2 path during metal segregation and self-oxidized of magma ocean the silicate melt would contain species with N–H bonds (NH_3 , NH_4^+ , NH_2^-) as well as N_2 , C–H bonds (CH_4), H_2 and oxidized H species (OH^- and H_2O) (Fig. 1, 2) In region of fO_2 from IW-2 to IW-5 N, C and H solubility ranges from 0.4 to 1.9 wt. %, 0.4 and 0.3 wt. %, 0.2 and 0.3 wt. %, accordingly.

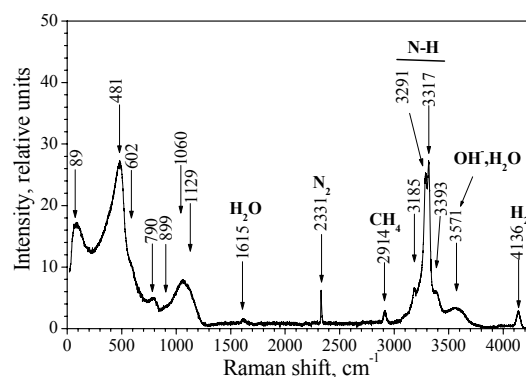


Figure 1: Raman spectra of C–N–H-bearing glasses after experiment at 4GPa, 1550°C and fO_2 =IW-3.2.

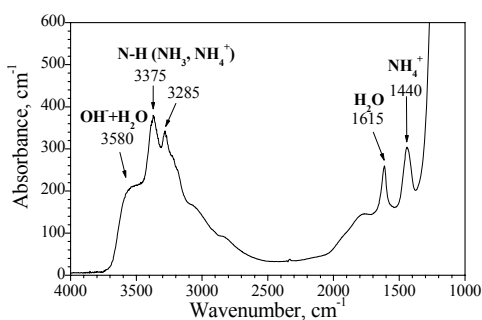


Figure 2: IR spectra of N–H-bearing glasses after experiment at 4GPa, 1550°C and $fO_2=IW-2.9$.

Discussion

We assume that the magmatic transport and chemical evolution of nitrogen, carbon and hydrogen during the reduced episode of early mantle evolution could be very much influenced by low fO_2 values in presence of the metallic Fe phase. The primary melting is a way of providing the formation of the reduced forms of nitrogen, carbon and hydrogen (H_2 , CH_4 , NH_3 together with H_2O , OH) in magmas of the early Earth.

The formation of N–H bonds in the reduced melts equilibrated with molten Fe alloys results in a significant increase in nitrogen solubility that should exceed 1–2 wt. %. Thus, the previous authors' assumption of probably higher nitrogen content in the reduced magma ocean in comparison with the Earth's magmas of later geological epoch [e.g., 6] was verified by our experimental results.

Experimental data testify to a strong influence of pressure, fO_2 , and hydrogen on distribution of nitrogen between metallic and silicate melts, ($D_N^{met/sil}$). It is found that at 1.5 GPa, 1400°C, $\log fO_2=IW-3.7$ and 4 GPa, 1550°C, $fO_2=IW-3.3$ the values of $D_N^{met/sil}$ are equal to 0.5 and 0.4 accordingly. It is expected that high solubility of nitrogen in the molten Fe alloy equilibrated with the N–H-bearing silicate melt can play the important role in extraction of nitrogen during metal segregation in the shallow magma ocean. According to Marty [7], the abundance pattern of major volatile elements and noble gases of the Earth are in chondritic relative proportions, but nitrogen is depleted by one order of magnitude relative to the other volatiles. As is supposed by the author, this is consistent with either nitrogen retention in a mantle phase during magma generation, or nitrogen trapping in the core. The experimental data indicating high nitrogen solubility in the molten Fe alloy at a high pressure should be considered as a confirmation of this assumption.

The experimental studies at a pressure corresponding to a depth of 100–150 km have shown that the self-oxidation of magma ocean with fO_2 increasing from IW-5 to IW-2 [2, 3] is characterized by a decrease in the amount of species with N–H and C–H bonds and an increase in the content of oxidized hydrogen species, such as OH[−] and H_2O . These dissolution features make fO_2 a critical factor in the formation of C–N–O–H volatile species during the large-scale melting of the early Earth. It seems plausible that the volatiles accompanying degassing of an extensively molten outer layer formed during the main accretion phase of the Earth would have been a significant component with respect to the reduced terrestrial atmosphere. Our experiments allow assuming that N_2 , NH_3 , CH_4 , H_2 and H_2O could have been extracted from the reduced magma ocean and come to the surface.

Acknowledgements. This work was made possible through support of Prog. No 28 RAS, RFBR grant No 11-05-00926a, ESD RAS project No9.

References

- [1] Galimov: EPSL, V. 233, pp 263-276, 2005.
- [2] Wood, B.J., Walter, M.J., Wade, J.: Nature, V. 441, pp. 825-833, 2006.
- [3] Javoy, M., Kaminski, E., Guyot, F., Andraut, D., Sanloup, C., Moreiraa, M., Labrosse, S., Jambon, A., Agrinier, P., Davaille, A., Jaupart C.: Earth Planet. Sci. Lett., V293, pp 259–268, 2010.
- [4] Kadik, A.A., Pineau, F., Litvin, Yu.A., Jendrzewski, N., Martinez, I., Javoy, M.: J. Petrol., V.45 (7), pp.1297–1310, 2004.
- [5] Kadik A.A., Kurovskaya N.A., Ignat'ev Yu.A., Kononkova N.N., V.V. Koltashev V.V., Plotnichenko, V. G. : Geochem. Inter., V. 49 (5), pp 429–438, 2011.
- [6] Tolstikhin, I.N., Marty, B.: Chem. Geol., V.147, pp. 27–52, 1998.
- [7] Marty B.: Earth Planet. Sci. Lett. V. 313–314, pp. 56–66, 2012.