

THE HYDROGEN AND CARBON SOLUBILITY

IN THE (NaAlSi₃O₈(80)+FeO(20))–H–C SYSTEM AT 1.5 GPa AND 1400° C

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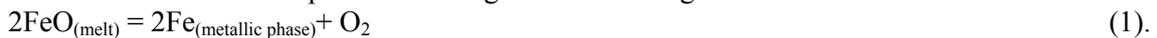
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Processes of volatile interactions with silicate and metallic melts of the early mantle and redox state of the mantle as a volatile source are essential factors determining formation of Earth atmosphere on the early stage its evolution. Experimental data obtained for the «iron-bearing silicate melt (ferrobalt) - iron metallic phase - H₂ - C» system at 4 GPa and 1520 - 1600°C at low oxygen fugacity [1, 2] show that hydrogen and carbon dissolve in silicate melts forming oxidized (OH⁻, H₂O, CO₃²⁻) and reduced (H₂, CH₄, Si-C, C) species. Their relationships are found in essential dependence on fO_2 values.

The present work is a continuation of those researches. The authors performed an experimental investigation of equilibrium in a system: model melt (NaAlSi₃O₈(80) + FeO(20)) - H - C at 1.5 GPa, 1400°C and $\Delta \lg fO_2(IW)$ values between - 2.3 and - 5.7. The aim of this research was to reveal particularities of joint hydrogen and carbon dissolution in the system at low fO_2 values which are characteristic for T-P- fO_2 stability conditions of a metallic Fe phase in equilibrium with silicate substance of the early mantle of the Earth.

Experiments were performed in a piston-cylinder apparatus [3] using sealed platinum capsules at controlled conditions of the hydrogen (oxygen) fugacity. Temperature was controlled by a Pt-Pt₁₀Rh thermocouple with accuracy $\pm 10^\circ\text{C}$. The pressure uncertainty is ± 0.1 GPa. Starting material was a powdered mixture of the synthetic albitic glass NaAlSi₃O₈ (80 wt. %) and iron oxide FeO (20 wt. %) to which powdered SiC in amounts of 2.5 and 7 mas. % was added provided a low fO_2 values in experiments. About 200 mg of powdered glass was put in a Pt capsule 5 mm in diameter and 15 mm in height. The sample was isolated from Pt capsule walls with a tungstic foil to prevent the interaction between the Fe-bearing melt and Pt [4]. Typical run duration was 120 minutes.

fH_2 buffering technique used in experiments is described in detail [4, 1]. In our experiments fH_2 was buffered by the assemblage of the heater at the fO_2 values that correspond to fO_2 values of the Fe-FeO (IW) buffering equilibrium. fH_2 values in the solid assemblage of apparatus are determined by reactions of the H₂O traces with the assemblage elements. The fH_2O/fH_2 ratio in the O-H system at a given temperature, pressure and fO_2 outside the capsule assumes a constant value. fO_2 values inside the platinum capsule are controlled by the equilibrium between graphite, H₂ buffered from the outside and components of the Fe - bearing silicate melt. This melt is reduced with the release of the oxygen and formation of the metallic Fe phase according to the following reaction:



Initial SiC is unstable under experimental conditions and it is completely decomposed according to the reaction:



Equilibria (1) and (2) determine fO_2 values in the studied system during the experiment. The experimental fO_2 values were presented as follows:

$$\lg fO_2^{\text{exp}} = \lg fO_2(IW) - \Delta \lg fO_2(IW), \quad (3)$$

$$\text{where } \Delta \lg fO_2(IW) = \lg fO_2(IW) - \lg fO_2^{\text{exp}} = 2 \lg(a\text{FeO}/a\text{Fe}),$$

$a\text{FeO}$ and $a\text{Fe}$ - activities of FeO and Fe in the Fe-bearing silicate melt at experimental conditions. Activity coefficients of FeO in the melt were calculated from the data reported in [5]. Estimated $\Delta \lg fO_2(IW)$ values are presented in the table.

Experiments were conducted in systems Ab₈₀FeO₂₀-2%SiC-C (run 10S), Ab₈₀FeO₂₀-5%SiC-C (run 11S) and Ab₈₀FeO₂₀-7%SiC-C (run 12S) at 1.5 GPa, 1400°C and $\Delta \lg fO_2(IW)$ values equal to - 2.3, - 3.9 and - 5.7 correspondingly. Run products were preliminary investigated under a microscope in the transmitted and reflected lights. They are translucent yellowish or greenish glasses containing metallic Fe-rich globules and hexagonal and triangular tablets of graphite crystals visible in transmitted light. The texture and a chemical composition of glasses, metallic Fe- phase and Pt, the content of carbon in glasses were investigated by the electron microprobe analysis. Raman spectroscopy was employed to study dissolved C-O-H-species in silicate melts and their possible joint dissolution mechanism as a function of fO_2 values. Analytical results for glasses and metallic Fe phase obtained by the electron microprobe analysis are presented in the table.

Table

Experimental conditions and chemical composition of run products at 1.5 GPa and 1400°C									
Run #	SiC _{initial} , mass %	$\Delta \lg f_{O_2}(IW)$	Glasses						
			SiO ₂	Al ₂ O ₃	FeO	Na ₂ O	C	Total	
10S	2	-2,3	64,23±0,13	17,00±0,09	12,83±0,08	6,10±0,27	0,43±0,11	100,65	
11S	5	-3,9	73,52±0,26	17,70±0,06	2,76±0,06	6,52±0,15	3,37±0,23	103,98	
12S	7	-5,7	76,18±0,25	18,19±0,28	0,26±0,07	7,33±0,42	4,05±0,71	100,36	
Run #	SiC _{initial} , mass %	$\Delta \lg f_{O_2}(IW)$	Metallic Fe phase						
			Fe	Pt	W	C	Al	Si	Total
10S	2	-2,3	95,78±0,1	0,04±0,07	0,07±0,1	2,76±0,23	0,03±0,01	0,07±0,02	98,75
11S	5	-3,9	96,16±0,28	0,01±0,01	0,10±0,09	4,02±0,71	0,02±0,01	0,05±0,01	100,35
12S	7	-5,7	96,34±0,35	0,01±0,01	0,18±0,03	3,63±0,39	0,02±0,01	0,41±0,01	100,58

The main peculiarity of the chemical composition of glasses is a decrease of FeO concentrations from 18 mass %, that corresponds to the FeO content in the starting material, to 0.3 mass % at the lower $\Delta \lg f_{O_2}(IW)$ values equal to -5.7. This is an evidence of FeO reducing in the melt with forming the fluid Fe phase. Fe-rich globules contain 3-4 mass % of carbon that corresponds to compositions of known carbon containing Fe alloys. Carbon contents in glasses determined by the electron microprobe analysis are presented in tab. and fig. 1.

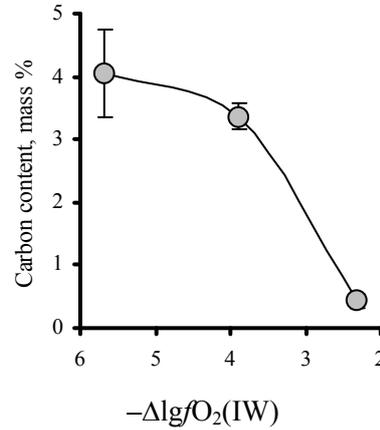


Fig.1. Carbon solubility in the system NaAlSi₃O₈(80) - FeO(20) -H-C as a function of the oxygen fugacity (P=1.5 GPa, T=1400°C)

Very high carbon solubility in reduced albitic melts and its increase by 1 order of magnitude with decreasing of the oxygen fugacity by 3.4 order of magnitude were found.

The characteristic Raman spectra of glasses in the 2500-4500 cm⁻¹ range are shown in fig. 2.

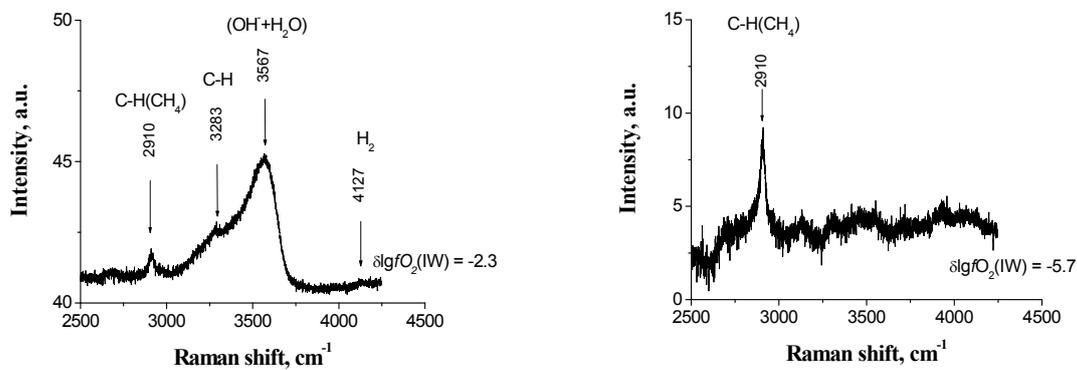


Fig.2. Raman spectra of C-O-H- bearing glasses

The Raman spectra of glasses reveal a series of peaks which may be ascribed to the C-H, O-H and H-H bonds in glasses.

C-H bonds: peaks at 2910 cm^{-1} are observed at all $\Delta\lg f\text{O}_2(\text{IW})$ values (-2.3, -3.9 and -5.7) and may belong to the CH_4 molecule dissolved in glasses.

O-H bonds: wide and asymmetric bands at $3567 - 3593\text{ cm}^{-1}$ correspond to the vibrations of O-H bonds in the molecule H_2O or OH^- groups in the structure of silicate melt. They are observed for glasses with $\Delta\lg f\text{O}_2(\text{IW}) = -2.3$ and -3.9 and are missing from the glasses spectra with $\Delta\lg f\text{O}_2(\text{IW}) = -5.7$.

H-H bonds: it is assumed that weak peaks at about $4122 - 4127\text{ cm}^{-1}$ may belong to the molecular hydrogen H_2 dissolved in glass.

Thus, the obtained experimental results indicate that reduced (H_2 , CH_4) and oxidized (OH , H_2O) species are formed at the interaction of carbon and hydrogen with reduced silicate melt. Characteristic peculiarity of the interaction of carbon and hydrogen with reduced silicate melt is a change of their dissolution mechanism with the $f\text{O}_2$ decreasing: OH^- groups are dominating hydrogen species in the melt at $\Delta\lg f\text{O}_2(\text{IW}) = -2.3$ and -3.9 while hydrogen forms compounds with C-H bonds in the melt at $\Delta\lg f\text{O}_2(\text{IW}) = -5.7$.

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