

## Studying the forms of dissolution of hydrogen, carbon, nitrogen and oxygen volatiles in magmatic melts of the early Earth's mantle by the methods of IR and Raman spectroscopy

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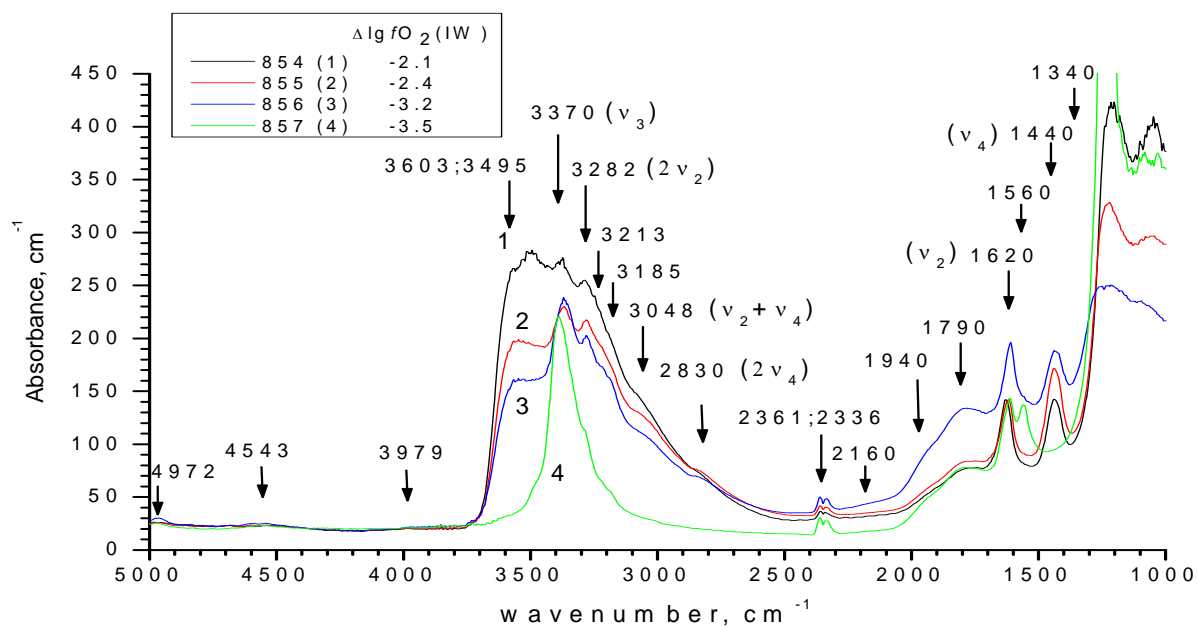
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Experimental studies of the features of dissolution of H, C, N, O volatiles in the melting products of the early Earth's mantle are continued. As a model system we have chosen the **aluminosilicate melt** (albite NaAlSi<sub>3</sub>O<sub>8</sub> 80 wt. %) + **metallic Fe phase** (FeO 20 wt. %) + **H+C+N** with nitrogen addition (Si<sub>3</sub>N<sub>4</sub> 1, 3, 5, 7 wt. %) which at quenching the products of experiments provides H-C-N-O-containing silicate glasses. The quenching was carried out at a high pressure 4 GPa, high temperature 1550°C, and low values of the chemical oxygen potential (fugacity  $fO_2$ ) from -2 to -4 below the iron-wustite buffer equilibrium  $\Delta\lg fO_2$  (IW). The investigation techniques were IR (infrared) micro spectroscopy and micro Raman. The IR absorption spectra (Fig. 1) were measured on a vacuum Fourier-transform FTIR spectrometer "Bruker IFS-113v" with an optical microscope "IR Microscope A590", focusing the radiation passing through the investigated samples into a spot from 15 to 400  $\mu\text{m}$  in diameter. The Raman spectra measurements (Fig. 2) were provided on a Triple Raman spectrograph T-64000 (Jobin Yvon) in which the exciting radiation from Ar<sup>+</sup>-laser was focused on a sample surface into a 2  $\mu\text{m}$  spot. The application of these techniques has allowed to establish the influence oxygen fugacity ( $fO_2$ ) on the ratio between the "oxidized" (H<sub>2</sub>O, OH<sup>-</sup>, CO<sub>2</sub>, C=O, CO<sub>3</sub><sup>2-</sup>) and "reduced" (H<sub>2</sub>, CH<sub>4</sub>, SiC, C-C) H- and C-species in the melts, as well as O<sub>2</sub>, N<sub>2</sub>, N-O, C-N and others N-H complexes (NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, NH<sub>2</sub><sup>-</sup> ( $\equiv\text{Si-NH}_2$ ), NH<sub>2</sub><sup>+</sup> ( $\equiv\text{Si-O-NH}_2$ )) in a rather wide region of the redox state conditions (Fig. 1, Table 1).

The nature of chemical solubility of nitrogen in the silicate melts still remains in many respects insufficiently studied. This is also the case, when the interaction of nitrogen with the silicate melt components occurs in the presence of hydrogen and carbon, i.e. two of the main gas-forming elements of the Earth. Meanwhile, the study of metallurgical systems shows the evidence for a significant influence of H and C on solubility of nitrogen in slags [Mulfinger, 1966; Martinez and Sano, 1990] which is related to a formation of CN<sup>-</sup> and N-H nitrogen species in silicate melts of a basic composition.

The IR spectroscopy of silicate compounds, having N-H bonds [Busigny *et al.*, 2004] in their structure, reveals the absorption bands in the 1400-3400  $\text{cm}^{-1}$  frequency region. These bands belong to normal vibrational modes of a free ammonium NH<sub>4</sub><sup>+</sup> ion of  $T_d$  symmetry, where  $\nu_2$  are symmetric bending vibrations,  $\nu_3$  are antisymmetric stretching vibrations, and  $\nu_4$  are antisymmetric bending vibrations [France *et al.*, 1984; Harlov *et al.*, 2001; Watenphul *et al.*, 2009].

In our experiments the peaks we observe at 3370 ( $\nu_3$ ), 3282 ( $2\nu_2$ ), 3048 ( $\nu_2 + \nu_4$ ), 2830 ( $2\nu_4$ ), 1620 ( $\nu_2$ ) and 1440 ( $\nu_4$ )  $\text{cm}^{-1}$  fit these vibrations very well. It is supposed that in N-H containing glasses, the products of our experiments, the IR absorption bands are connected with the vibration motions of both NH<sub>4</sub><sup>+</sup> ion and other N-H species (NH<sub>3</sub>, NH<sub>2</sub><sup>-</sup> ( $\equiv\text{Si-NH}_2$ ), NH<sub>2</sub><sup>+</sup> ( $\equiv\text{Si-O-NH}_2$ )). Lowering  $fO_2$  in the region of  $\Delta\lg fO_2$  (IW) values from -2 to -4 is characterized by a growth in the content of nitrogen species with N-H (NH<sub>2</sub><sup>-</sup> NH<sub>2</sub><sup>+</sup>) bonds and a reduction of the content of the oxidized forms of hydrogen OH<sup>-</sup> and H<sub>2</sub>O.



**Fig. 1.** IR spectra of H-C-N-O-bearing aluminosilicate glasses with the thickness of 120-180  $\mu\text{m}$ .

**Table 1.** Peak frequencies of the IR absorption bands,  $\text{cm}^{-1}$ .

Sample №	854	855	856	857
C-C (D-bond)	1340	1340	1340	1402
(Na, Mg, Ca) $\text{CO}_3^2$ ; $\text{NH}_4^+$ ( $\nu_4$ )*	1421;1440	1421;1440	1421;1440	1421;1440
C-C (G-bond)	следы	следы	следы	1560
$\text{H}_2\text{O}$ , N-H ( $\text{NH}_2^+$ , $\text{NH}_2^-$ ( $\nu_2$ )*)	1629	1619	1610	1612
C=O	1775	1780	1790	1790
Al-O(Si), N-O ?	1940	1940	1940	1940
Si-O-Si <sup>stretching</sup>	2160	2160	2160	2160
$\text{CO}_2$ (dissolved)	2361; 2341; 2332	2361; 2341; 2332	2361; 2341; 2332	2361;2341; 2332
$\text{NH}_3$ , $\text{NH}_4^+$ ( $2\nu_4$ )*	2830	2830	2830	2830
$\text{CH}_4$	-	3009; 2917	3009; 2917	3009; 2917
$\text{NH}_3$ , $\text{NH}_4^+$ ( $\nu_2+\nu_4$ )*	3048	3048	3048	-
?	3185	3185	3185	3185

C-N	3213	3213	3213	3213
$\text{NH}_2^-$ , $\text{NH}_3$ , $\text{NH}_4^+$ ( $2\nu_2$ )*	3282	3282	3282	3282
$\text{NH}_2^-$ , $\text{NH}_3$ , $\text{NH}_4^+$ ( $\nu_3$ )*	3370	3368	3368	3390
<b>OH+ H<sub>2</sub>O <i>fundamental stretch</i>:</b> <b>OH<sup>stretch</sup> in Si-OH complex (2.8<math>\mu\text{m}</math>)</b>	3603	3603	3603	3603
<b>OH<sup>stretch</sup> in H<sub>2</sub>O complex</b>	3495	3495	3495	3495
<b>Si-OH</b>	3374	3374	3374	3374
<b>OH-phonon<sup>comb</sup> (2.53<math>\mu\text{m}</math>)</b>	3979	3979	3979	3979
<b>Si-OH<sup>comb(stretch+bend)</sup> (2.22<math>\mu\text{m}</math>)</b>	4543	4543	4543	4543
<b>H<sub>2</sub>O<sup>comb(stretch+bend)</sup> (1.91<math>\mu\text{m}</math>)</b>	4972	4972	4972	4972

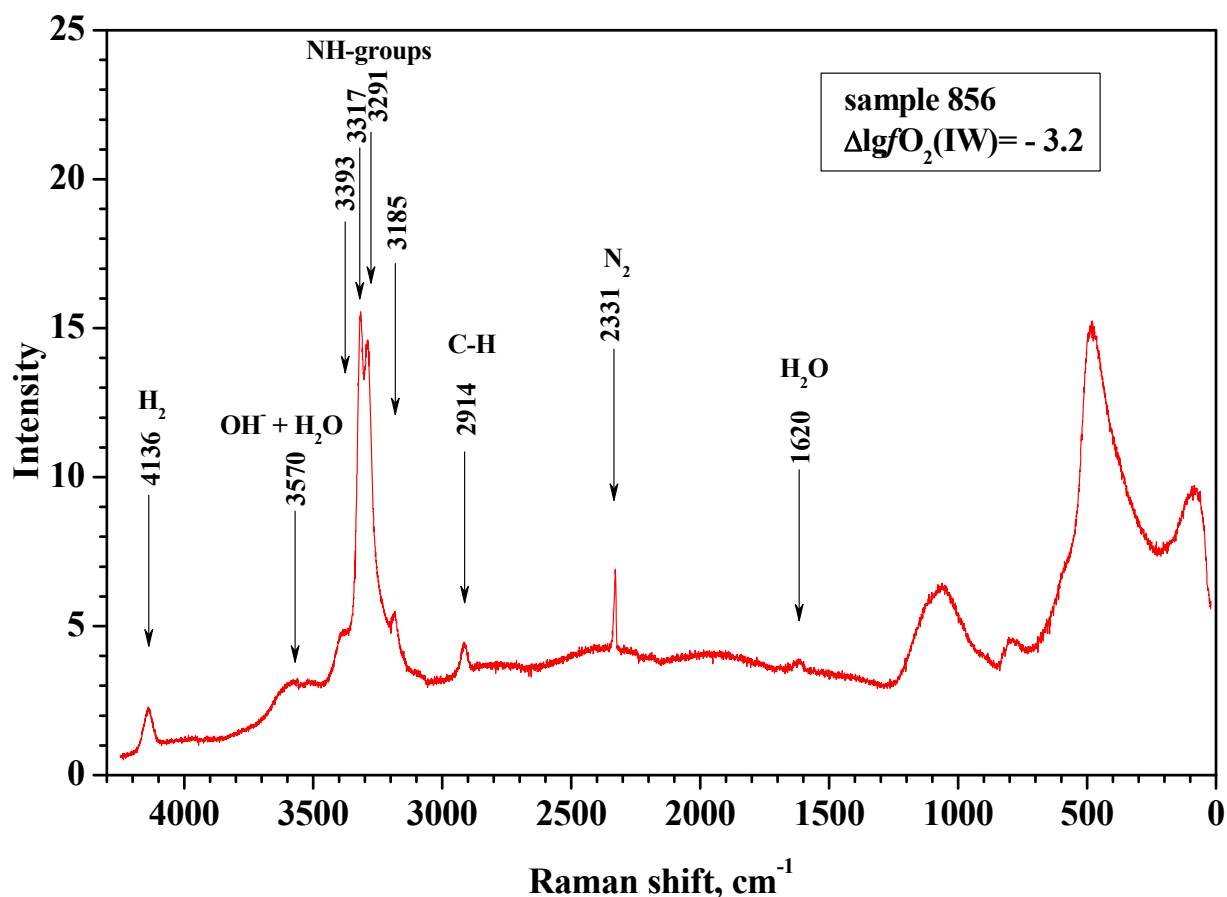


Fig. 2. Raman spectra of the sample 856,  $\Delta \lg f\text{O}_2(\text{IW}) = -3.2$ .

In the Raman spectra of the investigated samples in the 20-4000  $\text{cm}^{-1}$  region a number of peaks characterizing the vibrations of N-H, N-N, N-Si, C-H, H-H and O-H bonds is observed. The position and shape of a wide band at 3200-3700  $\text{cm}^{-1}$  corresponds to the vibrations of O-H bonds in H<sub>2</sub>O

molecules or hydroxyl groups OH<sup>-</sup> in the structure of silicate melts [Mercier *et al.*, 2010]. The dependence on  $fO_2$  of the intensity of this band in the Raman spectra and of the absorption coefficient in the IR spectra unequivocally testify to a reduction of H<sub>2</sub>O+OH<sup>-</sup> content with the oxygen fugacity  $fO_2$  decreasing (Table 2). The weak peak at ~1620 cm<sup>-1</sup> corresponds to the deformational vibration of the H<sub>2</sub>O molecules dissolved in glass. Strip KP on 4136 cm<sup>-1</sup> belongs to the molecular hydrogen H<sub>2</sub> dissolved in glass (Fig. 2). The bands at 3185 and 3291 cm<sup>-1</sup> characterize the centers NH<sub>2</sub><sup>+</sup> (≡Si-O-NH<sub>2</sub>) which intensity is practically independent on  $fO_2$ , and the bands at 3317 and 3393 cm<sup>-1</sup> are the centers NH<sub>2</sub><sup>-</sup> (≡Si-NH<sub>2</sub>) which intensity grows up with  $\Delta \lg fO_2(IW)$  decreasing. A sharp and narrow Raman peak at 2331 cm<sup>-1</sup> belongs to the fundamental vibration of the molecule of nitrogen N<sub>2</sub> in glass [Roskosz *et al.*, 2006]. It is supposed that a small peak observed both in the Raman spectra at 2914 cm<sup>-1</sup> and in the IR spectra at 2917 cm<sup>-1</sup> corresponds to the CH<sub>4</sub> molecule dissolved in the glass matrix.

**Table 2.** Absorption coefficient  $\alpha$  of aluminosilicate samples in OH<sup>-</sup> and H<sub>2</sub>O bands, cm<sup>-1</sup>.

№ образца	OH <sup>-</sup>		H <sub>2</sub> O	
	$\alpha$ , cm <sup>-1</sup>	$\nu$ , cm <sup>-1</sup>	$\alpha$ , cm <sup>-1</sup>	$\nu$ , cm <sup>-1</sup>
<b>854 (1% Si<sub>3</sub>N<sub>4</sub>)</b>	258.4	3495	63.8	1629
<b>855 (3% Si<sub>3</sub>N<sub>4</sub>)</b>	171.5	3495	53.9	1619
<b>856 (5% Si<sub>3</sub>N<sub>4</sub>)</b>	135.7	3495	61.4	1611
<b>857 (7% Si<sub>3</sub>N<sub>4</sub>)</b>	32.8	3495	62.3	1612

Thus, the results of our researches have led to a conclusion about a formation of the early magmatic melts on the Earth with a high concentration of CH<sub>4</sub>, H<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, an influence of the early volcanic activity on the formation of the primary reduced Earth's atmosphere and as a result a creation of conditions for the biosphere formation.

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