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The system $\text{NaAlSi}_3\text{O}_8 - \text{H}_2\text{O} - \text{H}_2$ (1200° C, 2 kbar): the solubility and interaction mechanism of fluid species with melt

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Abstract. The H_2O and H_2 solubilities in an albite melt at 1200° C and 2 kbar over the entire range of gas phase composition, from pure hydrogen to pure water were studied in gas-media pressure vessels. The water solubility initially increases with increasing hydrogen content until a maximum of 9.19 wt% H_2O at $X_{\text{H}_2}^g = 0.1$ is reached, with $X_{\text{H}_2}^g > 0.1$ the water solubility decreases. The hydrogen solubility curve has a maximum at $X_{\text{H}_2}^g = 0.42$ where the concentration reaches 0.206 wt% H_2 . Over the entire compositional range ¹H NMR (nuclear magnetic resonance) spectra show distinct absorption lines due to protons bound to OH groups and to isolated firmly bound water molecules. In NMR and Raman spectra there were no bands attributable to the H-H vibrations of molecular hydrogen. The X-ray photo-electronic spectra of hydrogen-bearing glasses show the Si2p (99 eV) band which corresponds to the zero-valency silicon. The formation of OH groups and molecular water during interaction between hydrogen-bearing fluids and melts under reducing conditions has a qualitative effect: the same as for water dissolution. Another point of interest is that hydrogen-bearing melts undergo more depolymerization than do hydrous melts.

Introduction

The interactions of volatiles with silicate melts has been the subject of active experimental research for many years. The research has concentrated mainly on water and carbon dioxide as the major components of the endogenic fluid. Their solubilities were determined at different T and P in melts of varying composition, and the effect of fluid pressure and composition on the melting temperatures of many minerals and rocks was estimated (Kadik et al. 1971; Burnham 1979; Epelbaum 1980; Bohlen et al. 1982; McMillan and Holloway 1987). Some attention was also given to the solubility

of HF, B_2O_3 and some other species (Sorapure and Hamilton 1984; Mysen and Virgo 1986; Pichavant 1987).

In recent years, experimental data were obtained on the interaction of silicate liquids with hydrogen-bearing and water-hydrogen fluids. This can be attributed to the fact that such reduced gases as CH₄ and H₂ are widely spread in nature. They become particularly important during melting of the mantle (Marakushev and Perchuck 1972; Welhan and Craig 1979; Green 1990; Kadik 1990). These works indicate that the solubility of these gases in silicate melts is rather high (Holloway and Jakobsson 1986; Zharikov et al. 1988). Melting temperatures of silicate minerals, such as albite, diopside and quartz decrease likewise (Luth and Boettcher 1986; Persikov et al. 1986). The solubility of CH₄ results in the expansion of the forsterite field with respect to enstatite (Taylor and Green 1987), which indicates chemical interaction between melt components and the fluid. These papers suggest several variants of interaction of the reduced gases; these variants presuppose redox reactions during which hydrogen should oxidize up to OH- or H₂O and some melt components should become reduced (Taylor and Green 1987).

This paper features solubility in the albite melt at 1200° C and 2 kbar of hydrogen and water, covering the whole compositional range of water-hydrogen fluid ($X_{\text{H}_2\text{O}}^g$ from 0 to 1). It shows also the interaction mechanism between this fluid and the melt.

Experimental technique

Natural albite from rare-metal pegmatites of the Kalbinsky Ridge, Kazakhstan (Zarajskii 1989), were used as starting materials. Albite powder was fused in the furnace assembly at 1250–1300° C for 2 h to obtain homogeneous glass. The analysis of the glass was (wt%): SiO₂–69.02; Al₂O₃–18.29; MgO–0.27; CaO–0.95; Na₂O–11.13; K₂O–0.34. The starting material differed insignificantly from the stoichiometric one, which can be probably attributed to the loss of Na during melting. The works of Silver and Stolper (1989) have demonstrated that the non-stoichiometric effect contributes inconsiderably to both solubility and to the relationship of different types of water solubility in the albite melt.

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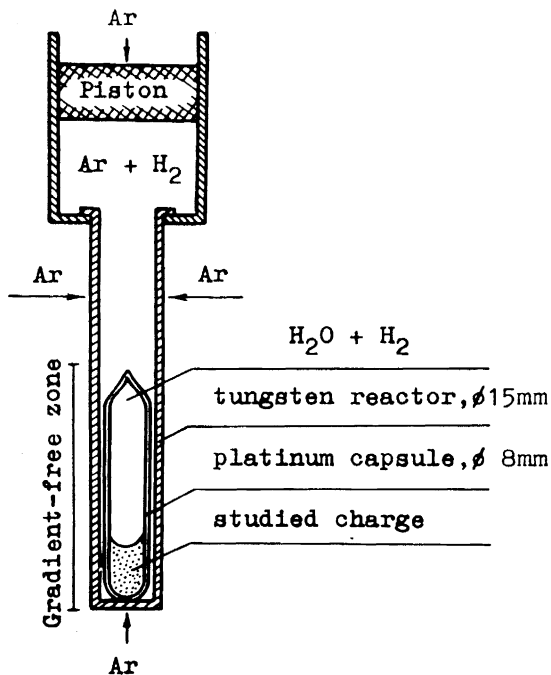


Fig. 1. Reactor set-up for conducting experiments under controlled hydrogen fugacity in a gas-media pressure vessel

The glass was loaded into a 7 mm diameter platinum capsule which was filled with water (250 mg) and sealed. The total weight of the charge was about 80 mg, to suit run durations (2 days) and allow the melt to become completely saturated with water and hydrogen by diffusion. The feature of this experimental technique was that the water and hydrogen contents of the fluid were controlled directly, without the use of solid media buffers, which were employed in other studies (Luth and Boettcher 1986; Holloway and Jakobsson 1986; Taylor and Green 1987).

All experiments were run in gas-media pressure vessels. The loaded capsule was positioned in the tungsten reactor (Fig. 1) which was filled under 130 bar P with the argon-hydrogen mixture previously obtained in a separate container at room temperature. The hydrogen content of the mixture was varied from 0 to 1 mole fraction ($X_{H_2}^v$). For runs under pure hydrogen pressure, the platinum capsule was not pressurized. The inside of the reactor was separated from the pressure-transmitting media (argon gas) by means of the Persikov equilizer (Persikov and Epelbaum 1978). The position of the reactor inside the heater was chosen so as to ensure the occurrence of the capsule in the temperature gradient-free zone. The thermocouple was calibrated against the melting temperature of pure gold; the temperature measurements were accurate to $\pm 7^\circ$ C. The species contents of the water-hydrogen fluids were controlled by allowing hydrogen to diffuse into the platinum capsule from the external argon-hydrogen mixture which was under the specified pressure in the reactor. Because no hydrogen leakage occurred at high temperatures through the 3 mm thick tungsten reactor walls (Bezmen 1989), the proposed technique ensures constant hydrogen activity in the fluid over the entire run duration.

After runs, the glass specimen saturated with water and hydrogen was cut lengthwise into several chips which were analysed for water and hydrogen. The quantitative determination of H_2O and H_2 in the glasses was carried out on a CHN-analyser in two stages. One series of the charges (10–30 mg) was analysed for water accurate to 3 wt% (Koshemchuck and Tikhomirova 1984), the other for hydrogen. To extract fluid species, the platinum containers with the charge (10–30 mg) were slipped into the reactor pyrolysis zone at 1200° C and held there for 10–15 min. In the pyrolysis products, H_2 and H_2O , were blown with the stream of the carrier gas (he-

Table 1. Pyrolysis/gas chromatography analytical results

Run no	$X_{H_2}^v$	H_2 , wt% (average)	H_2 , wt%	H_2O , wt%	H_2O , wt% (average)
Ab-20	0	N.A. ^b	–	6.47 6.55 6.63	6.55
Ab-22	0.05	N.A.	–	7.45 7.87 8.15	7.82
Ab-21	0.1	N.A.	–	9.45 9.39 8.90	9.25
Ab-25	0.1	N.A.	–	9.00 9.22 9.14	9.12
Ab-23	0.15	N.A.	–	6.93 7.42 7.22	7.19
Ab-1 ^a	0.2	0.123 0.137 0.162 1.178	0.150	N.A.	–
Ab-11	0.2	0.109 0.121	0.115	7.25 7.53	7.39
Ab-15	0.2	N.A.	–	6.35 6.42 6.94	6.57
Ab-19	0.2	0.159 0.173	0.166	6.48 6.78	6.63
Ab-2 ^a	0.4	0.184 0.190	0.187	4.10 3.92	4.01
Ab-12	0.4	0.218 0.240	0.229	4.38 4.96	4.67
Ab-16	0.4	0.208 0.228	0.218	4.47 4.61	4.54
Ab-3 ^a	0.6	N.A.	–	1.097 1.101 1.115 1.127	1.110
Ab-17	0.6	0.167 0.201	0.184	1.101 1.153	1.127
Ab-18	0.8	0.112 0.140	0.126	0.312 0.428	0.370
Ab-10	1.0	0.066 0.054 0.046 0.074	0.060	N.A.	–

^a Glass powder charges with starting porosity of 30 vol%

^b N.A., not analysed

lium). Water was sorbed on MSÅ molecular sieves positioned in the rear end of the reactor, whereas hydrogen was carried into the oxidizing zone where it passed through copper oxide at 850° C, converted to H_2O and was analysed. The completeness of sorption was checked with a standard sample CA-1 with 4.1 wt% H_2O , the extent of conversion was checked on the sample ZrH_2 (1–10 mg) and gaseous hydrogen which was fed into the analyses using the chromatographic meter. Stoichiometric ZrH_2 with 2.163 wt% hydrogen was used as the hydrogen standard. The hydrogen sensitivity was 10^{-6} g, the accuracy at the lowest concentrations was

10%. Relative standard deviations in the series of experiments with constant water and hydrogen contents were found to be within 5% for water and 15% for hydrogen.

The solubility mechanism of the H_2O-H_2 fluid in melts was studied by nuclear magnetic resonance (NMR). Raman spectroscopy and X-ray photo-electronic spectroscopy. NMR spectra for 1H (200 MHz frequency), ^{23}Na (52.9 MHz) and ^{27}Al (52.1 MHz) were obtained on a CXP-200 Bruker pulse Fourier-spectrometer; Raman spectra were obtained on the Coderg-PHO spectrometer with a refined registration system; X-ray photo-electronic spectroscopy spectra were taken on a ES-2404: instrument with MgK_{α} radiation (the analyser energy was 20.0 eV; vacuum in the working chamber was 10^{-9} bar, calibration was against carbon $C1s=28.5$ eV). Spectra were obtained in the scanning regime, using 200 spots, they were accumulated 20 times with the accumulation time in each spot-1 sec. This provided for the precision of measurements of the bond energy for narrow lines of ± 0.1 eV.

One of the major problems in solubility studies of fluid species is the formation of gas inclusions in the experimental melt. Such inclusions can be formed both in preparation and during the runs, or at the quench stage at high water content. To evaluate the possible effect of the original porosity on the fluid-species content of the melt, experiments were run on the glasses prepared in different ways. In a few experiments (Table 1) glass powder was pressed into the capsule (diameter 7 mm); the starting porosity of the charge was 25–30 vol.%. In this situation water could have been trapped in the inclusion during the experimental run; one could expect about 3 wt.% (with regard to the melt). This water homogenizes over a certain time period. This duration was determined with experiments of 3, 17 and 48 h. The appearance of liquid water inclusions was monitored by examining the samples under the microscope and in NMR spectra, which will be discussed in detail later. The runs showed that the trapped water can dissolve completely in the melt within 48 h. The second series of experimental runs used a glass pillar with low porosity (to 5 vol.%), which was saturated with water and hydrogen over a period of 48 h by means of diffusion. This glass pillar was prepared in a high-pressure gas vessel by the remelting of the glass powder under dry conditions within a sealed platinum capsule under an argon pressure of 5 kbar at 1250° C for a duration of 5 h. The glass composition remained constant. Glasses synthesized by diffusional saturation with water and hydrogen of pillars with low porosity, also lacked the absorption bands of liquid water or gaseous hydrogen after 48 h runs. To avoid possible interference with the results from inclusions of uncertain nature, most experiments used albite glasses with low porosity (Table 1).

The solubility of water-hydrogen fluid in albite melt

As a result of the present investigation, the solubility of water and hydrogen at 1200° C and 2 kbar total pressure was determined over the entire compositional range of the water-hydrogen fluid, from pure hydrogen to pure water (Table 1; Fig. 2). Figure 2 also presents the water (Kadik et al. 1971; McMillan and Holloway 1987) and hydrogen (Zharikov et al. 1988; Bezmen et al. 1990) solubility data in the albite melt under the pressure of pure volatiles (dashed lines) which is equal to their partial pressure in mixtures. The solubilities are averages over 3–4 analyses of the dissolved gases for each run. Insofar as the total weight of the charge was constrained by the experimental conditions, more precise results were obtained by analysing the products from separate runs only for their hydrogen or water content. This particularly concerned the region of anomalous solubility behaviour. In Table 2, the solubility is calculated as mole

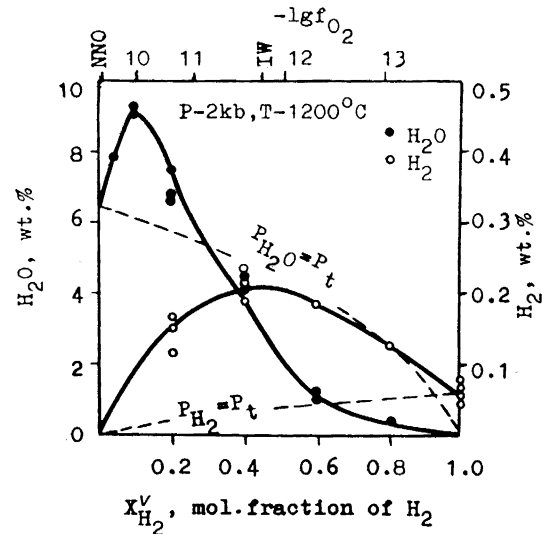


Fig. 2. Solubility of water and hydrogen in the albite melt at 1200° C and 2 kbar as a function of the fluid composition

Table 2. Calculated mole fraction of components in the albite melt at 1200° C and 2 kbar

$X_{H_2}^V$ in the fluid	f_{H_2O}	f_{H_2}	$X_{H_2}^m$	$X_{H_2O}^m$	X_{Ab}^m
0	2040	~0	~0	0.5030	0.4970
0.1	1836	246	0.0502	0.5649	0.3849
0.2	1632	492	0.0916	0.4822	0.4262
0.3	1428	738	0.1232	0.4047	0.4721
0.4	1224	984	0.1465	0.3278	0.5257
0.5	1020	1229	0.1636	0.2311	0.6053
0.6	816	1475	0.1733	0.1199	0.7068
0.7	612	1721	0.1609	0.0720	0.7671
0.8	408	1967	0.1381	0.0362	0.8257
0.9	204	2213	0.1067	0.0128	0.8805
1.0	~0	2460	0.0713	~0	0.9287

fractions, the mole of the albite melt being expressed as the gram-molecule of albite $NaAlSi_3O_8$ with molecular weight 262.24 g (Burnham 1979). Also given in Table 2 are the reference data (Melnik 1978) for pure water and pure hydrogen fugacities under the experimental conditions.

It is evident from Fig. 2 that the solubility of water and hydrogen in the albite melt under the mixed water-hydrogen fluid pressure is not regarded as an additive function. The differences are the following:

1. The addition of hydrogen to the system- H_2O results in an abrupt increase in water solubility, to 9.2 wt% at $X_{H_2O}^V=0.9$; $X_{H_2}^V=0.1$, as compared with about 6.1 wt% in the albite melt under the 1.8 kbar pressure of pure water and the same temperature of 1200° C (McMillan and Holloway 1987).
2. Further addition of hydrogen to the gaseous mixture depresses solubility, and at $X_{H_2}^V > 0.3$, the solubility in the water-hydrogen gaseous mixture becomes much lower than it is in the pure system $NaAlSi_3O_8-H_2O$ (under relevant pressures).

The interaction mechanisms of the albite melt with the water-hydrogen fluid, NMR data

System $\text{NaAlSi}_3\text{O}_8 - \text{H}_2\text{O}$

One of the promising and currently widely used methods for a direct study of the H, Na, Si and Al bonds in the structure of aluminosilicate glasses is nuclear magnetic resonance which can also be used to estimate the quantitative relations between differently bound ions (Bartholomew and Schreurs 1980; Farnan et al. 1987; Eckert et al. 1988). Figure 3 presents typical ^1H NMR spectra obtained at different temperatures for the hydrous glass in which liquid water inclusions were observed under the microscope. At room temperature, the spectrum contains three components: two singlets of varying width and a doublet. The width of the absorption band in the ^1H NMR spectra of solids depends on the nuclei of other elements. Depending on the density of liquid water, its peak ranges in width from tenths to several hundred Hz. In the present sample, because water confined mainly to pores 2–5 μ in size, the width of the peak is 200 Hz. It should be noted that the band from the H_2 -gas contained in inclusions is of the same width but the signal for water disappears as the temperature decreases below 273 K (Fig. 3), whereas the hydrogen peak does not change. The NMR spectra from separate non-equilibrium runs of short durations (less than 24 h) and large charges (>250 mg) contain a line of hydrogen gas.

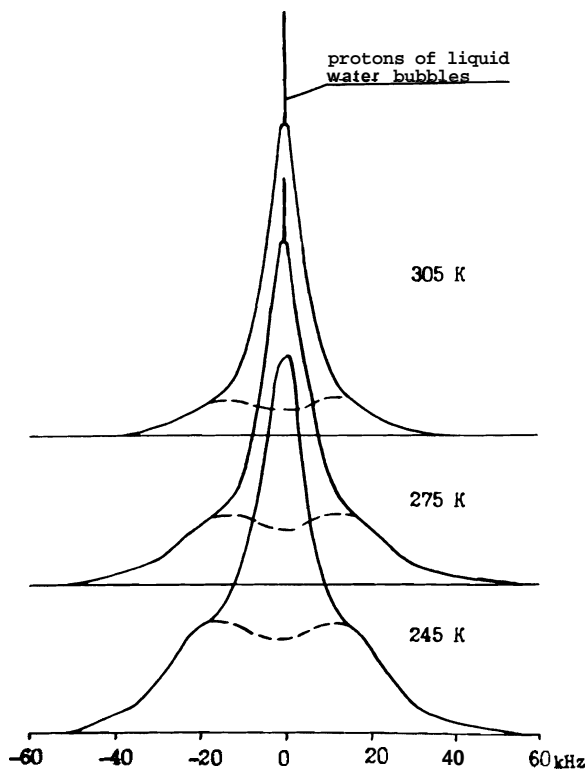


Fig. 3. Disappearance of the signal from the ^1H NMR spectra as a result of freezing of liquid water inclusions

^1H NMR spectra have undergone a considerable temperature evolution (Fig. 4). First of all, we would like to interpret spectra which were obtained at low temperatures, because the decrease in temperature results in the fading of the molecular movements, therefore the shape of the spectra reflect more precisely the nature of the proton bonds within the amorphous albite matrix. Figure 5 presents the 150 K spectra for glasses with different water content. The conditions, which determine the acquisition of the albite glasses and their composition are given in Table 3. The spectra consist of two components. One is a distinct doublet, which is a spectrum of crystalline hydrate-type water with the splitting 43 kHz of spectral lines. This value practically corresponds to a rigidly bound water molecule in a solid (45 kHz) with the interprotonic distance of 1.58 \AA (Abraham 1961). The second component is a singlet of the near-gaussian shape with a full width at half-maximum peak height of 10–13 kHz, depending on water concentration in the glasses. Based on IR (infra-red) spectroscopy data, this signal is attributed to the protons of the OH groups (Bartholomew and Schreurs 1980). The width of the central peak is insensitive to the temperature in samples with $X_{\text{H}_2\text{O}}^m = 0.34$ –0.503, and it is only at $X_{\text{H}_2\text{O}}^m = 0.581$ at about 300 K, that the central peak narrows sharply (Fig. 6b). The energy barrier of the process responsible for this narrowing is 2.95 kilocal/mol which is characteristic of the hydrogen bond break (The hydrogen bond 1976). One may assume therefore that with increasing water content of

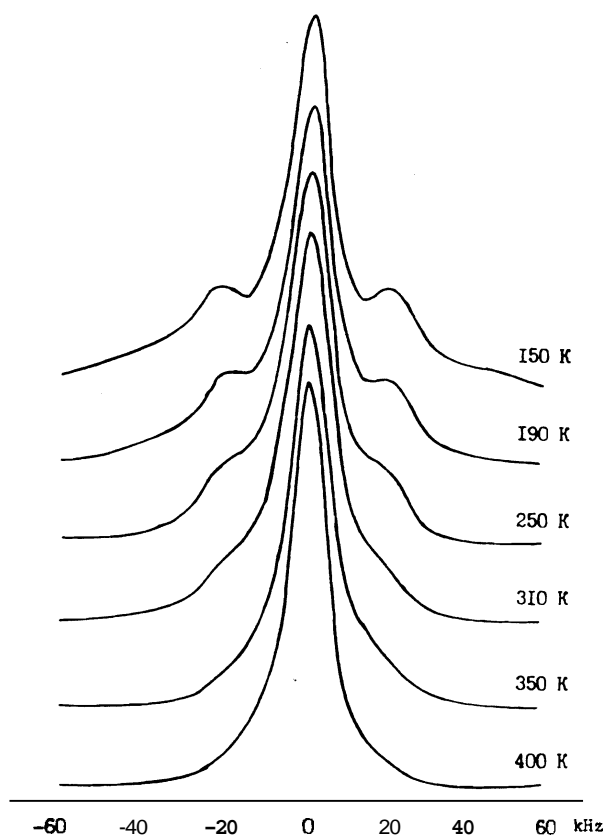


Fig. 4. The temperature evolution of the ^1H NMR spectrum of the hydrous albite glass ($X_{\text{H}_2\text{O}}^m = 0.503$)

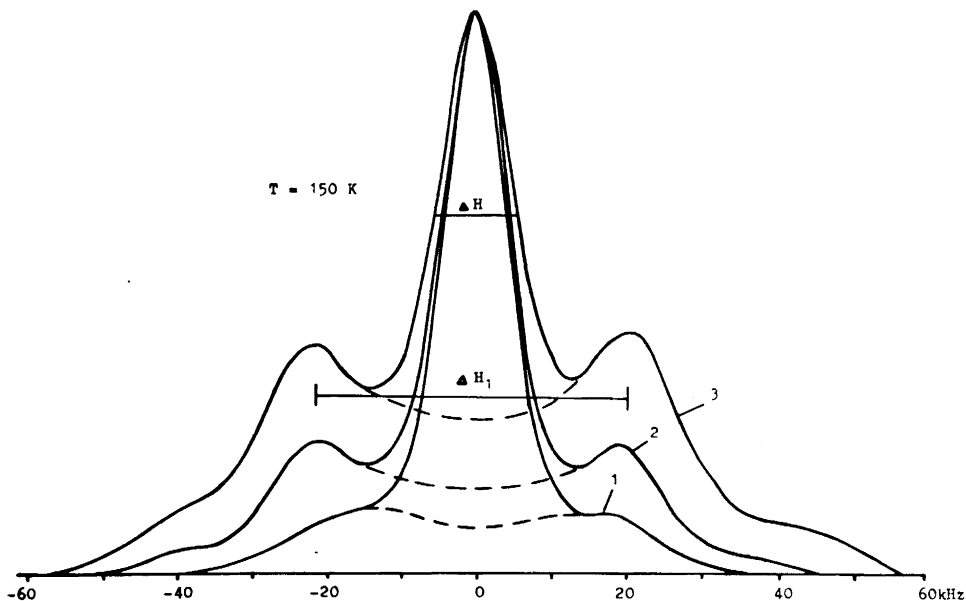


Fig. 5. ^1H NMR spectra of albite glasses with the varying water content, 1 - $X_{\text{H}_2\text{O}}^m = 0.34$; 2 - $X_{\text{H}_2\text{O}}^m = 0.503$; 3 - $X_{\text{H}_2\text{O}}^m = 0.581$. The spectra are normalized relative to the central peak intensity: ΔH , line width of the central peak; ΔH_1 , Peake doublet splitting (kHz)

Table 3. Experimental conditions and composition of water-albite glasses for ^1H NMR study

N n/n	Temperature $T^\circ\text{C}$	Pressure P, bar	H_2O , wt%	Mole fraction of components	
				$X_{\text{H}_2\text{O}}^m$	X_{Ab}^m
1	1250	1	-	-	1.0
2	1200	500	3.42	0.340	0.660
3	1200	2000	6.55	0.503	0.497
4	1100	5000	8.83	0.581	0.419

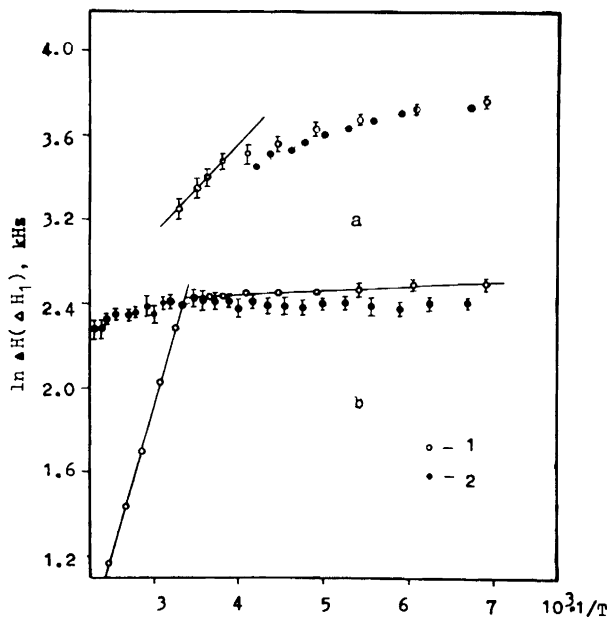


Fig. 6. Temperature dependence of the Peake doublet splitting, a, and line width of the central peak, b, in the ^1H NMR spectra of hydrous albite glasses: 1 - $X_{\text{H}_2\text{O}}^m = 0.581$; 2 - $X_{\text{H}_2\text{O}}^m = 0.503$.

glasses, possibly to the threshold value, part of the protons will form hydrogen bonds in water clusters (Zavelsky and Bezmen 1990). The weak absorption bands at $2800\text{--}2300\text{ cm}^{-1}$ in the IR and Raman spectra of the aluminosilicate hydrous glasses are often attributed to hydrogen bonds (McMillan and Remmele 1986).

For all water contents of the glasses, the doublet disappears gradually with increasing temperature (Figs. 4, 6). The most plausible explanation here is the distribution of the isotropic rotation barrier for isolated water molecules within the albite amorphous matrix. Due to such distribution, the number of molecules that pass into the isotropic rotation state increases with increasing temperature. As is known (Abraham 1961), the separation of the Peake doublet is zero averaged in this case, and the signal from water molecules in the state of free isotropic rotation merges with the central peak.

The NMR spectra for ^{23}Na and ^{27}Al contain only central transitions $-1/2 \rightarrow +1/2$. At room temperature, the signals appear as singlets $9.5 \pm 0.2\text{ kHz}$ and $5.5 \pm 0.2\text{ kHz}$ wide, respectively. The dissolution of water in the albite glass affects only the ^{23}Na peak: at $X_{\text{H}_2\text{O}}^m = 0.503$, the peak shrinks to $8.0 \pm 0.2\text{ kHz}$. The ^{27}Al spectrum remains unchanged within the error limit, to suggest the interaction of water with the sodium ions and the absence of direct links with the aluminium ions. The preferential interaction of water with sodium has long been suggested from thermodynamic calculations (Zharikov 1969).

System $\text{NaAlSi}_3\text{O}_8\text{--H}_2\text{O--H}_2$

Spectra of H_2 -bearing glasses are similar to those of hydrous glasses. Over the entire compositional range up to pure hydrogen they also contain OH groups and molecular water (Fig. 7). In the spectrum of glass formed

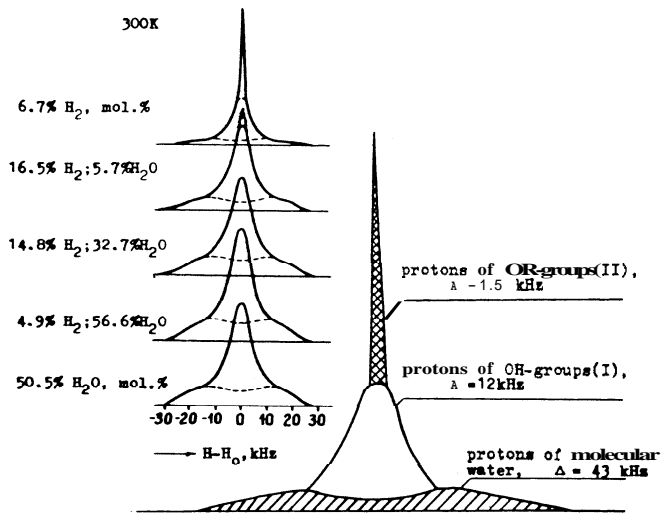


Fig. 7. ^1H NMR spectra of albite glasses containing H_2O and H_2 (the weight charge is 120 mg)

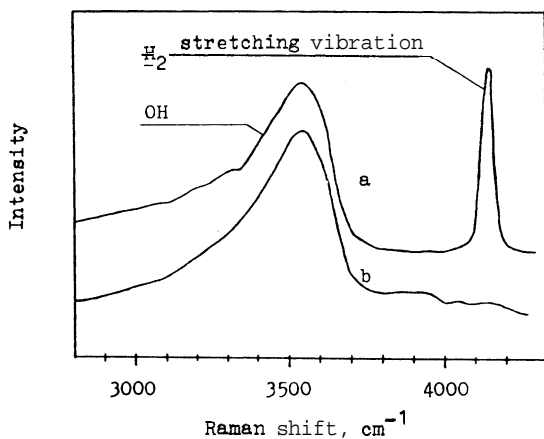


Fig. 8. Raman-spectra of albite hydrogenous glasses: $a - X_{\text{H}_2\text{O}}^{\text{I}} = 0.15$. $T = 1400^\circ\text{C}$, $P = 25$ kbar (Luth et al. 1987); $b - X_{\text{H}_2\text{O}}^{\text{I}} = 0.5$, $T = 1200^\circ\text{C}$, $P = 2$ kbar (our data)

with $X_{\text{H}_2}^{\text{v}} > 0.4$ there is a new shoulder as a narrow singlet with a width at half-maximum peak height of 1.5 kHz. This signal can not be attributed to gaseous hydrogen contained in the bubbles (200 Hz). This peak also seems to be due to OH groups but such as where the protons are more widely separated and interact but weakly with the nuclei of other elements (^{23}Na and ^{27}Al) and are therefore more labile. At the same time, ^1H NMR spectra contain no bands attributable to hydrogen present as discrete H_2 molecules which are statistically distributed in the matrix. No absorption band attributable to the presence of $\text{H}-\text{H}$ vibrations from the dissolved molecular hydrogen (at 4123 cm^{-1}) was observed in Raman spectra either, although Luth et al. (1987; Fig. 8) reported such a band for hydrogen-bearing albite glasses formed at 15–20 kbar, 1400°C under the iron-wustite buffer ($X_{\text{H}_2}^{\text{v}} = 0.18\text{--}0.23$). This may be due to pressure because according to the hydrogen isothermal solubility data, at least at low pressures (5 kbar), hydrogen is dis-

sociated in albite melts (Zharikov et al. 1988). This process is believed to result from reducing reactions, with some of the ions in the framework passing into lower valency states.

X-ray photo-electronic spectroscopy data

The mechanism of the reducing process is disclosed by the X-ray photo-electronic spectroscopy. The principal results (Fig. 9) are fairly consistent. The comparison of the $\text{Si}2\text{p}$ electron spectra of hydrogen-rich and hydrogen-free glasses is particularly interesting. An additional band at 99 eV is observed in the spectrum of hydrogen-rich albite glasses. This band corresponds to the known Si^0 spectra (Nefedov 1984). Note also a sharp shift in the maximum of the $\text{Si}2\text{p}$ band: from 103 eV in the albite glass to 102.3 in the albite-hydrogen glass. The shift is much more conspicuous than that resulting from the addition of water. The $\text{Al}2\text{s}$ electron spectrum also displaces toward lower energies (0.7 eV). The $\text{O}1\text{s}$ electron spectra contain an additional band in the spectra of hydrous glasses at 536.5 eV, which we have never observed for water-albite glasses with different H_2O content and which seems to correspond to OH-groups of other type detected in the NMR spectra (Fig. 7). The major band (532.5 eV) is seen to displace towards higher energies

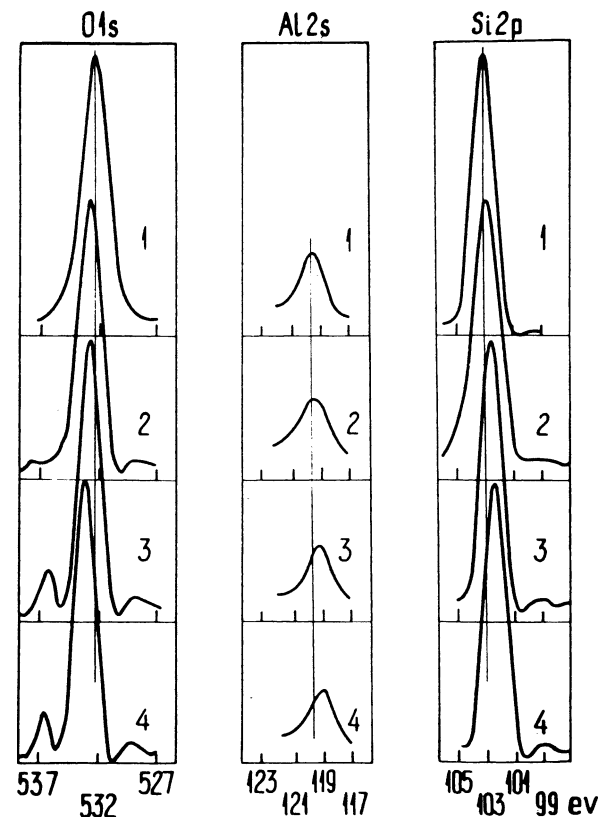


Fig. 9. X-ray photo-electronic spectra of glasses in the system albite- H_2O - H_2 . Glass samples shown are 1. ($X_{\text{Al}_2\text{O}_3}^{\text{m}} = 1$); 2. ($X_{\text{Al}_2\text{O}_3}^{\text{m}} = 0.712$; $X_{\text{H}_2\text{O}}^{\text{m}} = 0.288$); 3. ($X_{\text{Al}_2\text{O}_3}^{\text{m}} = 0.605$; $X_{\text{H}_2\text{O}}^{\text{m}} = 0.231$; $X_{\text{H}_2}^{\text{m}} = 0.164$); 4. ($X_{\text{Al}_2\text{O}_3}^{\text{m}} = 0.933$; $X_{\text{H}_2}^{\text{m}} = 0.067$). Peaks are discussed in detail in the text

consecutively from albite to hydrous albite and hydrogen-albite glasses.

Discussion

The contribution of inclusions to the possible mistakes in the analytical data on the solubility in the melts has been discussed at great length (Persikov 1984; McMilland and Holloway 1987). ^1H NMR spectra (Fig. 7) are characteristic of solid-state NMR powder patterns. Thus water and hydrogen are present not in the form of liquid-like "pools" or gas inclusions in any detectable amounts in the glasses after 48 h duration, but rather in forms such as anisotropically constrained OH and H_2O species. We have applied NMR-spectroscopy not only to study optimum conditions for approaching equilibrium, but also as an independent method for controlling analytical data. Figure 10 shows the results of comparing the relative integrated intensities (area) of NMR spectra with chromatographic data. There is a good agreement between these data.

The non-additive behaviour of volatile components during their combined melting in silicate melt is well recognized. One has at one's disposal data on the increasing solubility of H_2O in the presence of acid components B_2O_3 (Pichavant 1987) and HF (Sorapure and Hamilton 1984) both in the melt and fluid. It was shown that the addition of water to the system $\text{NaAlSi}_3\text{O}_8\text{--CO}$, results in the increase of CO_2 solubility (Mysen 1976; Shylobreeva 1984). Similar results have been obtained in this paper, for hydrogen in particular, its maximum solubility of 0.21 ± 0.005 wt% was attained at $X_{\text{H}_2\text{O}}^v = 0.4$. On the one hand this effect definitely is attributed to the chemical interaction of gases in the melt;

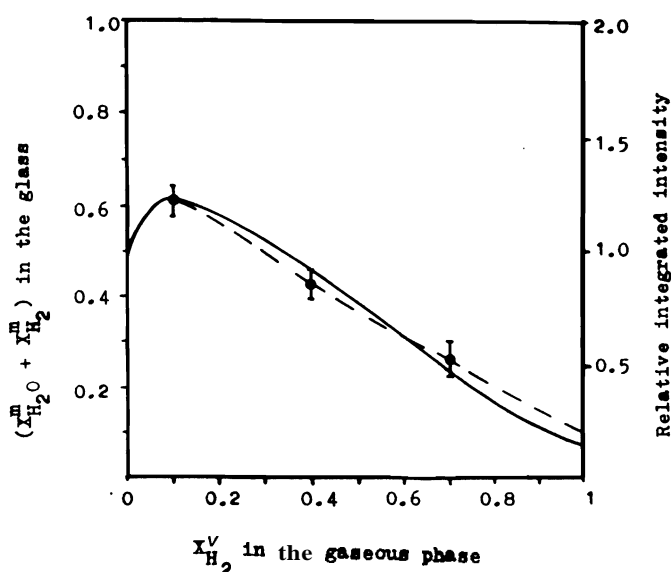


Fig. 10. Comparison gas chromatography analytical data, *solid line*, and relative integrated intensities, *area* of ^1H NMR spectra, *dashed line*. Spectra were obtained with 300 K temperature. The charge weight was 120 mg. The intensities of ^1H NMR spectra are normalized relative to the intensity of hydrous albite spectrum

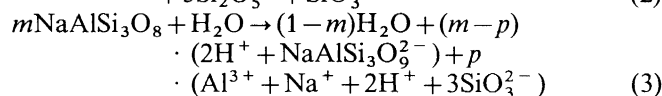
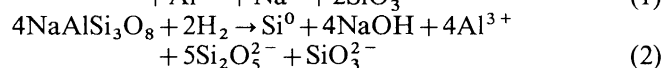
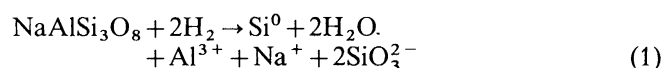
on the other hand it can be explained by the alteration of the melt composition itself, because water dissolves in hydrogen-saturated melts, while hydrogen dissolves in water-saturated melts. One should not forget about the important role of the reduction processes, which lead to the increasing basicity of the melt and to a corresponding increase in water solubility. In any case, shifting of Si2p; Al2s; O1s bands in the X-ray photo-electron spectra (Fig. 9), resulting from the addition of water and hydrogen to the melt, coincides with the trend towards a more basic mineral in the sequence quartz-plagioclase-pyroxene-forsterite. These reveal different ratios of bridging and non-bridging oxygen nuclei (Epelbaum et al. 1978). The shifting is more pronounced in the hydrogen-bearing spectra, which points directly to more intensive depolymerization processes in melts.

By using Raman (Mysen and Virgo 1986), IR spectroscopy (Stolper 1982; Epelbaum 1984) and NMR (Bartholomew and Schreurs 1980; Farnan et al. 1987; Eckert et al. 1988) it was found that water dissolves in aluminosilicate melts as molecular H_2O and as OH-groups. The interaction mechanism of water-hydrogen fluids with the aluminosilicate melt, determined by direct physical methods, provides insight into the somewhat paradoxical water generation which was also detected in earlier IR and Raman spectra of hydrogen and methane-bearing glasses (Luth et al. 1987; Taylor and Green 1987). The introduced material indicates that interaction between albite melt and hydrogen-bearing fluid leads to a reduction of Si and to the formation of three types of protons, which constitute the OH groups and water molecules. We expected Si to become di-valent, so that its corresponding band should be found at 100–100.5 eV (Nefedov 1984). However, there was no evidence of such band in the spectra (Fig. 9). It remains unclear so far, whether Si^0 was formed as a result of high temperature in the melt or as a result of disproportionation during the quenching of Si^{2+} to Si^0 and Si^{4+} . However, optical observations of the hydrogen-bearing systems allow the conclusion that Si^0 does not form an independent phase, but is distributed statistically within the amorphous matrix.

The solubility patterns of the reduced gases within quenched silicate glasses do not correspond usually to their patterns in the gas phase. Infra-red spectroscopy has not revealed C-H oscillations within methane-rich glasses (Taylor and Green 1987). There was also no evidence of C–O oscillations of hydrogen mono-oxides in the rhyolite glasses, obtained under the pressure of CO–CO, gas mixtures (Fogel 1990). In this work we have not determined H-H oscillations within hydrogen-bearing glasses, moreover there were no signs of N–H oscillations in Raman and NMR spectra of the albite glasses enriched in ammonia (unpubl. data). At the same time considerable concentrations of hydrogen, carbon and nitrogen were observed in the melts. Probably, the study of actual solubility forms could be resolved by studying quenching phenomenon. Infra-red spectroscopy has indicated that the quenching of rhyolite glasses could result in a change in the concentration of the relative OH group by as much as 30% on quench

in water-rich (> 5 wt% H₂O) glasses (Zhang et al. 1990). Our data suggest that the narrow band in NMR spectra, which is attributed to the OH group of the second type (Fig. 7), disappears gradually even when hydrogen-bearing samples are exposed to room temperature. That is why we had to determine the forms of fluid solubility immediately after the quenching. At the present time, due to certain methodological difficulties, it is not possible to study the state of the dissolved fluid in the melt under high temperatures and pressures. However the precise experimental conditions (temperature, pressure, quenching time) allow one to compare the results at least approximately.

If one considers quenching experiments together with the data introduced in this paper, then one can present schematically the interactions of water-hydrogen fluid in the following way:



The first reaction is the reduction of Si⁴⁺ to Si⁰ with the formation of water molecules. Second – the reduction of Si cation results in the oxidation of hydrogen to OH-groups, which are connected with sodium cations. The third reaction describes the interaction of water with albite, which leads to depolymerisation as a result of destruction of the Si–O–Si(Al) bonds and due to melting of the SiOH groups within glasses (written in the dissociation form). Apparently, in the actual situation, all of these reactions take place, which explains the presence of three forms of proton in the glass. Another important point is that these reactions account for depolymerization, which is reflected directly in the X-ray photo-electron spectra by a pronounced shifting of the peaks.

Concluding remarks

1. Under the pressure of water-hydrogen fluids at 1200° C and at 2 kbar, with an increasing amount of hydrogen within mixtures, water solubility first increases, attaining its maximum value (9.19 wt%) at $X_{\text{H}_2}^v = 0.1$, and then drops. The hydrogen solubility curve also shows a maximum value at $X_{\text{H}_2}^v = 0.42$, when hydrogen concentration approaches 0.206 wt%.

2. By using ¹H NMR four forms of protons have been revealed in the H₂O–H₂-bearing albite glasses. One of them can be identified easily, these are the protons of isolated water molecules which are represented by doublet in spectra. The second form of the protons is a wide (10–13 kHz) central band, which is attributed to the OH groups, coordinated with sodium and silicon nuclei. The third form is present in highly hydrogen enriched glasses and is interpreted in spectra as a more narrow central-component line (1.5 kHz). Most probably, this can be

referred to the OH groups, which have less developed bonds with the nuclei of other elements. The fourth form of the protons is interpreted as a very narrow peak (200 Hz) within non-equilibrium samples which trapped water in inclusions.

In our experimental runs there was no evidence of the peaks of structurally bonded molecular hydrogen.

3. Additional bonds of 99 eV and 536.5 eV were determined in the X-ray photo-electron spectra of the H₂-bearing glasses. These are attributed to the zero-valent Si2p electrons and O1s electrons of the OH groups, which are represented in NMR spectra as a more narrow central peak (1.5 kHz). A more remarkable shifting of the O1s, Al2s and Si2p bands within hydrogen-bearing glasses as compared to the barren and water-albite glasses allows us to conclude that hydrogen dissolution causes more depolymerization of melts than water.

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References

- Abraham A (1961) The principles of nuclear magnetism. Clarendon Press, Oxford
- Bartholomew RF, Schzeuz JWH (1980) Wide-line NMR study of protons in hydrosilicate glasses of different water content. *J Non-cryst Solids* 38/39: 679–684
- Bezmen NI (1989) High pressure gas media apparatus for controlling fugacity of hydrogen-bearing fluids systems. In: Gaur VK, Gupta AK (eds) Proc 1st Indo-Soviet Workshop Experimental Mineralogy and Petrology. Delhi, December 1987, pp 9–15
- Bezmen NI, Zharikov VA, Zavelsky VO, Koshemchuk SK, Suk NI (1990) The system of albite-hydrogen-water: the solubility of fluid species (1200° C, 2 kbar). *Geokhimiya* 5: 640–648
- Bohlen SR, Boettcher AL, Wall VJ (1982) The system albite–H₂O–CO₂: a model for melting and activities of water at high pressures. *Am Mineral* 67: 451–462
- Burnham CW (1979) The importance of volatile components. In: Yoder HS (ed) The evolution of igneous rocks: fiftieth anniversary perspectives. Princeton Univ Press, Princeton, pp 439–482
- Eckert H, Yesinowski JP, Silver LA, Stolper EM (1988) Water in silicate glasses: quantitation and structural studies by ¹H solid echo and MAS-NMR methods. *J Phys Chem* 92: 2055–2064
- Epelbaum MB (1980) Silicate melts with fluid components. Nauka Publ, Moscow
- Epelbaum MB (1984) On relation of various forms of water in water-albite glass. In: Zharikov VA, Fed'kin VP (eds) Ocherki physiko-khimicheskoi petrologii 12, pp 72–78
- Epelbaum MB, Chichagov AV, Nemoshkalenko VV, Aleshin VG, Moiseyenko EP (1978) Means of minerals basicity determination by oxygen X-ray photo-electronic spectra. In: Zharikov VA, Fed'kin VP (eds) Ocherki physiko-khimicheskoi petrologii 7, pp 204–209
- Farnan I, Kohn SC, Dupree K (1987) A study of the structural role of water in hydrous silicate glass using cross-polarisation magic angle spinning NMR. *Geochim Cosmochim Acta* 51: 2869–2874
- Fogel RA (1990) One solubility of C–O gases in rhyolite melt (abstract). In: VM Goldschmidt Conference Abstracts Baltimore, p 46
- Green DH (1990) The role of oxidation-reduction and C–H–O fluids in determining melting conditions and magma composi-

- tion in the upper mantle. In: Gaur VK (ed) Proc Indian Acad Sci Earth Planet Sci 99: 153–165
- Holloway JR, Jakobsson S (1986) Volatile solubilities in magmas: transport of volatiles from mantles to planet surfaces. Proc 16th Lunar and Planet Sci Conf Part 2. J Geophys Res 91: 505–508
- Kadik AA (1990) Redox state of the upper mantle. In: Gaur VK (ed) Proc Indian Acad Sci Earth Planet Sci 99: 141–152
- Kadik AA, Lebedev EB, Khitarov NI (1971) Water in magmatic melts. Nauka Publ, Moscow
- Koshemchuk SK, Tikhomirova VI (1984) Application of a CHN analyser for determining the H_2O^+ , H_2O^- , CO_2 contents of microcharges of minerals and rocks. Geokhimiya 7: 1083–1087
- Luth RW, Boettcher AL (1986) Hydrogen and the melting of silicates. Am Mineral 71: 264–276
- Luth RW, Mysen BO, Virgo D (1987) Raman spectroscopic study of the solubility behavior of H_2 in the system $Na_2O-Al_2O_3-SiO_2-H_2$. Am Mineral 72: 481–486
- Marakushev AA, Perchuk LL (1972) Origin and evolution of transmagmatic and metamorphic fluids. In: 1st International Geochim Congress Book 1: Metamorphism and metasomatism. Nauka Press, Moscow, pp 3–14
- McMillan PI, Holloway JR (1987) Water solubility in aluminosilicate melts. Contrib Mineral Petrol 97: 320–332
- McMillan PI, Remmele RL (1986) Hydroxyl sites in SiO_2 glass: a note on infrared and Raman spectra. Am Mineral 71: 772–778
- Melnik YuP (1978) Thermodynamic properties of gases in deep-seated petrogenesis. Naukova Dumka Publ, Kiev
- Mysen BO (1976) The role of volatiles in silicate melts: solubility of carbon dioxide and water in feldspar, pyroxene and feldspathoid melts to 30 kbar and 1625° C. Am J Sci 276: 969–996
- Mysen BO, Virgo D (1986) Volatiles in silicate melts at high pressure and temperature. 2: Water in melts along the join $NaAlIO_3-SiO_2$ and a comparison of solubility mechanism of water and fluorine. Chem Geol 57: 333–358
- Nefedov VI (1984) X-ray electron spectroscopy of chemical compounds. Khimiya Publ, Moscow
- Persikov EdS (1984) Viscosity of magmatic melts. Nauka Publ, Moscow
- Persikov EdS, Bukhtiyarov PG, Chekhmir AS (1986) Interaction of hydrogen with magmatic melts. In: The role of experiments in solving major geological problems. Nauka Publ, Moscow, pp 48–69
- Persikov EdS, Epelbaum MB (1978) Experimental set-up for studying the viscosity and density of magmatic melts at high pressures. In: Ivanov IP, Litvin YiA (eds) Experiment and equipment for high gas-media and solid-media pressure. Nauka Publ, Moscow, pp 94–98
- Pichavant M (1987) Effects of B and H_2O on liquidus phase relations in the haplogranite system at 1 kbar. Am Mineral 72: 1056–1070
- Shylobreeva SN (1984) Carbon dioxide solubility in basic and acidic melts during its release from magmas in volcanic regions. PhD Thesis, GEOKHI Inst, Moscow
- Silver LA, Stolper EM (1989) Water in albite glasses. J Petrol 30: 667–709
- Sorapure R, Hamilton DL (1984) The solubility of water in melts of albite composition with varying additions of fluorine. Prog Exp Petrol 6th Prog Rep Res NERC, NERC Publ Ser D, 13, Cambridge, UK, pp 92–100
- Stolper E (1982) Water in silicate glasses: an infrared spectroscopic study. Contrib Mineral Petrol 81: 1–17
- Taylor WR, Green DH (1987) The petrogenetic role of methane: effect on liquidus phase relations and the solubility mechanism of reduced C–H volatiles. In: Mysen BO (ed) Magmatic processes: physico-chemical principles No 1, pp 121–137
- The hydrogen bond (1976) Schuster P, Zundel G, Sandorfy C (eds) Amsterdam, North Holland, vol 1–3
- Zarajskii GP (1989) Zoning and condition of the metasomatic rocks formation. Nauka Publ, Moscow
- Zavelsky VO, Bezmen NI (1990) Water in albite glass (NMR study) Geokhimiya 8: 1120–1126
- Zhang Y, Stolper EM, Ihinger PD (1990) Reaction kinetics of $H_2O+O=2OH$ and its equilibrium (abstract). In: VM Goldschmidt Conference Abstracts, Baltimore, p 94
- Zharikov VA (1969) Regime of components in melts and magmatic replacement. In: Korjinskii DS (ed) Problems of petrology and genetic mineralogy, vol 1. Nauka Publ, Moscow, pp 62–71
- Zharikov VA, Persikov EdS, Bukhtiyarov PG, Koshemchuk SK (1988) Isothermal (1300° C) solubility of hydrogen in albite melt ($NaAlSi_3O_8$) at high pressures. Dokl Akad Nauk 300: 953–957
- Welhan JA, Graig H (1979) Methane and hydrogen in East Pacific Rise hydrothermal fluids. Geophys Res Lett 6: 829–832

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