Interaction in the systems of fluid-melt-crystal

Bukhtiyarov P.G.¹, Persikov E.S.¹, Aranovich L.Ya.², Nekrasov A.N.¹, Kosova S.A.¹ Metalsilicate separation in basalt melts interacting with hydrogen under conditions bottom of the Earth's crust and upper mantle (experimental study).

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Abstract. The first results of an experimental study of the metal-silicate separation of a basaltic melt during interaction with hydrogen without crystallization of the melt at the boundary of the earth's crust with the upper mantle (T = 1400 °C, $P(H_2) = 1.2 - 2.7$ GPa) are presented. The experiments were carried out using a highpressure cylinder-piston type installation (IEM RAS) with original internal cells, in which the source of hydrogen was titanium hydride, which decomposed under the experimental parameters. It is characteristic that, in contrast to experiments in the hydrogen-magnesium basalt system at moderate hydrogen pressure (100 MPa), in experiments at high hydrogen pressure there is an almost complete reduction of iron oxides from the basalt melt, in which drops of metal (Fe) of the liquation structure are formed and wherein phosphorus is concentrated in the metal.

Keywords: basaltic melt, hydrogen, temperature, pressure, reducing conditions, native metal, crust-mantle boundary

The role of reduced fluid in the processes of formation of igneous rocks and melts, volcanism, ore formation and the formation of the Earth's core is an urgent fundamental problem of petrology and geochemistry. Thus, questions of the origin of the Earth and its structure, the formation of the core, the origin of magmas at various depth levels in different geological epochs, their evolution in the lithosphere, degassing of the Earth's interior, as well as native metal formation and ore formation in the earth's crust are increasingly associated with active participation in them hydrogen [Wood et al., 2006; Kadik, 2008; Oleynikov et al., 1985; Marakushev, 1995, etc.]. Due to its fundamental scientific significance and relevance, our research is currently being continued. The paper presents the first results of an experimental study of the interaction of basalt melt with hydrogen without crystallization of the melt at the boundary of the earth's crust and upper mantle (T = $1400 \text{ }^{\circ}\text{C}$, $P(H_2) = 1.2 - 2.7$ GPa). The experiments were carried out using a high-solid-phase pressure installation of the cylinder-piston type (IEM RAS). The experiments were carried out in molybdenum ampoules with a diameter of 4 mm. The source of hydrogen was titanium hydride, which decomposed under the experimental parameters. Titanium hydride was separated from the substance by a thin molybdenum bridge with small holes. In the experiments, internal cells of 1.2 and 2.7 GPa were used (Fig. 1).



Fig. 1. The scheme of high pressure cells: (a) - by 1.2 GPa; (b) - by 2.7 GPa

Exposure time of experiments is 90 min, followed by isobaric hardening. After releasing the pressure in the installation and complete cooling, the ampoule with the sample was removed from the cell for subsequent analysis of the phases formed during the experiment. The chemical composition of the phases obtained in the experiments was determined using a digital electron X-ray microscope CamScan MV2300 (VEGA TS 5130 MM), with an attachment for energy-dispersive microanalysis INCA Energy 450 and WDS Oxford INCA Wave 700. Analyzes were carried out at an accelerating voltage of 20 kV with a beam current of up to 400 pA and spectrum collection time 50 -100 sec.

The results of chemical analysis of quenched glasses are presented in Table. 1. It also presents an analysis of the original magnesian basalt of the Northern eruption of the Tolbachik volcano, eruption 1975-1976, Kamchatka [Fedotov et al., 1984] and the structural and chemical parameters (100NBO/T) of the original basalt and basaltic glass (average composition) after experiments under hydrogen pressure. As can be seen, as a result of the interaction of basalt with hydrogen, acidification of the melt occurs from 49.5 wt. % SiO₂ up to 53.16 and 57.93 wt. % (respectively, for experiments at 1.2 and 2.7 GPa). In this case, almost complete reduction of iron oxides from the basalt melt occurs, in which drops of metal with a liquation structure of various sizes are formed (Fig. 2).

The results of the chemical analysis of the metal phase in Table. 2. As can be seen, the metal phase consists mainly of iron and phosphorus from the melt is concentrated in it.

Table 1. Chemical composition (wt.%) and structural-chemical parameter (100NBO/T) of the original basalt and basalt glass (average composition) after experiments under hydrogen pressure.

Oxides	№12CP*	№27CP**	Compound original basalt ***
SiO ₂	53.16	57.93	49.5
Al_2O_3	14.24	19.50	13.18
Fe_2O_3	н.о.	н.о.	3.18
FeO	0.87	0.01	6.85
MgO	9.77	5.21	9.98
CaO	14.12	6.72	12.34
Na ₂ O	2.73	6.02	2.18
K_2O	1.09	2.76	0.93
TiO ₂	3.03	1.04	1.01
P_2O_5	0.07	0.00	0.25
H ₂ O-	0.73	0.81	0.29
Sum	99.81	100.00	99.69
100NBO/T	77	63	84





Fig. 2. Scattered electron scanning (BSE) micrographs of sample quenching products after experiments on the interaction of basalt melt with hydrogen at high pressures. (a) - run N_{2} 12CP, P (H₂) = 1.2 GPa, T = 1400 °C, experiment duration 1.5 hours, then isobaric hardening (white color - Fe metal alloy, composition - see. Table 2, dark gray color - basalt glass, composition - see Table 1). (b) - run N_{2} 27CP, P(H₂) = 2.7 GPa, T = 1400 °C, experiment duration 1.5 hours, then isobaric hardening (white color - Fe metal alloy, composition - see Table 2, light gray color - residual glass, composition - see Table 1).

Table 2. Chemical compositions (mass %) of metal phases in basalt melts (quenched samples) after experiments under hydrogen pressure

Components	№ 12CP	№ 27CP	
Fe	98.32	98.27	Note:
Mg	0,01	0.24	1. The results presented in the table are the average of 4
Ti	0.12	0.09	measurements.
О	0.40	0.8	2. The concentrations of all impurity elements (Si, Ca, Ti) in metal
Si	0.10	0.14	phases are determined approximately, since these values are within
Ca	0.05	0.13	the limits of analytical errors.
Р	1.00	0.62	
Sum	100.79	100.29	

Thus, as a result of the interaction of hydrogen with magnesian basalt, the initially homogeneous basaltic melt becomes heterogeneous. The following phases are formed in the melt: melts that are more polymerized and richer (relative to the initial composition) in silica with a certain amount of dissolved water; separation of metal with liquation texture, in which phosphorus is concentrated from the melt. It is characteristic that in this case almost complete reduction of iron oxides in the basalt melt occurs (Tables 1 and 2).

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Khodorevskaya L.I., Kosova S.A., Spivak A.V., Safonov O.G., Zakharchenko E.S. Experimental study of partial melting garnet-

two-mica schist with CO₂, CO₂-H₂O fluid at 500 MPa and 900°C. *UDC 552.13*

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Abstract. CO₂ is the major component of fluids under conditions of granulite and amphibolite facies metamorphism in the lower and middle continental crust. Its sources can be both mantle magmas at the base of the crust (external sources) and graphite and carbonates in the protolith (internal sources). This paper presents preliminary results of experiments on the interaction of garnet-twomica schist with CO₂ and CO₂-H₂O fluids at 900°C and 500 MPa, simulating the effect of a fluid from an external source. The experimental products include the initial quartz, garnet, apatite and ilmenite, and newly formed products of peritectic melting reactions: potassium feldspar, spinel, sillimanite, orthoamphibole, coexisting with a peraluminous alkaline-calcic rhyolitic melt. In the Raman spectra of the melt, characteristic bands of silicate glasses, quartz, pyroxene and a wide band of OH⁻ were identified, but no signs of dissolved carbon in forms of CO₂ or $CO_3^{2^2}$ were detected. The Raman spectra of gas bubbles in glasses contain peaks of CO₂, N₂ and quartz. However, the density of CO₂ in the bubbles in experiments with CO₂ fluid 0.68 \pm 0.02 g/cm³ indicates that, probably, CO₂ was dissolved in the melt and separated just during nonisobaric guenching. A noticeably higher CO₂ density, 0.85- 1.00 ± 0.05 g/cm³, in experiments with H₂O-CO₂ fluid indicates that the CO₂-rich fluid coexisted with the melt under experimental conditions.

Keywords: garnet-two-micas schist, dehydration melting, graphite, granitoid melts, carbon dioxide fluid, inclusions, Raman spectra, experiment.

Introduction. The coexistence of inclusions containing CO_2 and/or carbonate phases and graphite with inclusions of silicate melts in migmatite and granulite minerals (Cesare et al., 2007, 2015; Bartoli, Cesare, 2020; Ferrero, 2021 and others) clearly demonstrate the connection between granite formation and CO_2 -rich fluids in areas of high-temperature metamorphism. Sources of CO_2 can be either mantle magmas at the base of the crust (external sources) or graphite and carbonates in the protolith (internal sources). This paper presents the results of experiments on the interaction of garnet-

bimica schist with CO_2 and CO_2 -H₂O fluids at 900°C and 500 MPa, simulating the interaction of metapelite with fluid coming from an external source.

Technique and methodology of experiments The experiments were carried out using a twoampulle method in high gas pressure installations with internal heating (gas bombs) at 900°C and 500 MPa. 25-40 mg of shale powder was placed in an internal vertical ampoule with a diameter of 3 mm and a height of 5-10 mm. The shale consisted of muscovite (43%), quartz (30%), biotite (13%), garnet (10%), $\sim 1.5\%$ apatite and $\sim 1.5\%$ ilmenite (the mineral and chemical composition of the rock is presented in the work of Mityaev et al., 2022). The upper part of the ampoule was squeezed, but not brewed. The source of fluid with $X_{CO2} = 1.0$ was the equilibrium calcite + quartz = wollastonite + $CO_2(1)$ (Ogasawara et al., 1983). Therefore, a mixture of quartz, calcite, wollastonite in ratios close to stoichiometric in reaction (1), or a mixture of calcite and quartz, was placed in an external ampoule with a diameter of 5 mm and a height of 40-50 mm. In addition, experiments were carried out on the interaction of shale with H_2O - CO_2 fluid with X_{CO2} = 0.5, the source of which was oxalic acid. The results of experiments with CO₂ and H₂O- CO₂ fluids were compared with the results of experiments on dehydration melting of shale (without excess fluid) at the same P-T parameters. Experimental and analytical methods are presented in the article by L.I. Khodorevskov et al. (2023). Gas bubbles in glasses were detected in transmitted light under the surface of thin plates using a Nikon ECLIPSE LV100N POL microscope. The Raman spectra of bubbles and melts were measured in backscattering geometry on a setup SpectraPro-2500i that included an Acton spectrometer with a CCD Pixis2K detector cooled to -70°C and an Olympus microscope. A continuouswave solid-state single-mode laser with a wavelength of 532 nm and diode pumping was used. The laser beam was focused onto the sample using an Olympus 50' lens into a spot with a diameter of \sim 5 mm. The laser emission line in the scattered beam was suppressed using an optical super-notch filter with an optical density of OD=6 and a bandwidth of ~160 cm-1, and the excitation intensity directly in front of the high-pressure chamber was ~ 0.7 mW. The spectrum accumulation time was 360 sec (120 sec \times 3). Raman spectra were processed using the Fityk 1.3.1 and Origin2021 software packages.

Experimental results. The products of experiments on partial melting of metapelite in the presence of CO₂ and CO₂-H₂O fluids contain quartz, garnet, apatite, ilmenite, preserved from the original rock, while biotite and muscovite are absent. The experimental products contain quenched melt (Gl), the amount of which is 50 - 60 vol. %. The glasses contain isometric or elongated gas bubbles, which represent a fluid phase that coexisted with the melt under experimental conditions or separated during non-isobaric quenching. The newly formed crystalline phases are hercynite-magnetite spinel (Spl), potassium feldspar (Kfs), sillimanite (Sil). Kfs plates and Sil crystals up to 20 µm in size are enclosed in the melt. Spinel is sometimes located in the form of borders around garnet grains, which acquire uneven edges in contact with the melt. But the bulk of spinel is randomly distributed throughout the sample (Fig. 1). The average composition of spinel in experiments at $X_{CO2} = 1$ and in experiments at $X_{CO2} = 0.5$: $(Fe^{2+}_{0.87}Mg_{0.13})(Fe^{3+}_{0.70-0.90}Al_{1.3-1.1})O_4$. The ratio of $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ in spinel in all experiments is close, 0.45-0.50, and is somewhat different from the composition of spinel in the products of the experiment without excess fluid $(Fe^{2+}_{0.77}Mg_{0.20})(Fe^{3+}_{0.40}Al_{1.6})O_4$, $Fe^{3+}/(Fe^{3+} + Fe^{2+}) =$ 0.34. In ilmenite the ratio is $Fe^{3+}/(Fe^{3+}+Fe^{2+}) = 0.5$ -0.7.

The compositions of the melts correspond to high-alumina, alkali-calcareous and alkaline varieties of S-type granites (Frost et al., 2001; Chappell et al., 2012). Both in experiments without CO₂ and with $X_{CO2} \approx 1$, the melts contain 73-75 wt. % SiO₂, and 13-16 wt. % Al₂O₃ (in terms of anhydrous residue). However, in experiments at $X_{CO2} = 0.5$, the melts contain 68-70 wt. % SiO₂, which indicates a high degree of rock melting in the presence of H₂Ocontaining fluid. The Al₂O₃ content in the melts varies from 13-15 wt. % in experiments without excess fluid and in experiments with $X_{CO2}=1$ to $16 \pm$ 1 wt. % in experiments at $X_{CO2}=0.5$.

Raman spectroscopy

Quenched melts

In order to identify carbon-containing components in the melts from experiments D19, D21 ($X_{CO2} = 1$) and experiment D20 ($X_{CO2} = 0.5$), Raman spectra were studied in the range 120 - 4000 cm-1 (Fig. 1).





Fig. 1. Representative Raman spectra of quenched melts from samples D19, D20 and D21. Q^2-Q^4 , D - characteristic bands of silicate glasses, Qtz - quartz, Pyr - pyroxene.

The spectra of quenched melts contain broad bands in the regions of 400-700 and 800-1300 cm^{-1} , characteristic of the Raman spectra of aluminosilicate glasses (shaded areas in Fig. 1). Intense bands in the low-frequency part of the spectrum with a maximum around 480 and 580 cm⁻¹ are associated with stretching and bending vibrations of Si-O-Si(Al) bonds (McKeown et al., 1984, McMillan et al., 1992). The broad bands at \Box 920 and 1115 cm⁻¹ are due to vibrations of non-bridging bonds in structural units Q^2 and Q^3 , respectively (McMillan, 1984, Zakaznova-Herzog et al., 2007). In addition, the Raman spectra of all samples contain a combination of broad vibrational bands of OH groups 3450-3650 cm⁻¹ (Frezzotti et al., 2012). However, the glasses did not show any evidence of dissolved carbon in the form of CO_2 or CO_3^{2-} .

Gas bubbles in melt quenching products

In the Raman spectra of gas bubbles in glass, along with the characteristic peaks of $CO_2 \sim 1284.4$ and ~ 1388.8 cm⁻¹ (Fermi dyads), there are peaks of N₂, quartz and OH- groups (Fig. 2).

Using the equation from the work of H. Wang et al. (Wang et al., 2011), the density (ρ CO₂) in the bubbles was calculated from the distance between the peaks in the Fermi dyad. It turned out to be almost the same 0.68±0.02 g/cm³ in all samples from experiments with the initial fluid CO₂. In experiments with the initial fluid represented by H₂O-CO₂, the density of CO₂ was noticeably higher, 0.85-1.00±0.05 g/cm³.

Conclusions

Experiments demonstrate that at 900°C and 500 MPa in the presence of fluid CO_2 or CO_2 -H₂O

Fig. 2. Raman spectrum of gas bubbles in glasses of samples D19 - D21 with characteristic peaks of CO_2 - Fermi dyads (shaded area in Fig. 2).

(external sources of CO₂), partial melting of plagioclase-free garnet-bimica (with Qtz, Ap, Ilm) schist occurs with the formation of melts of rhyolitic composition. There are no signs of dissolved carbonate-containing compounds in the form of CO₂ or CO_3^{2-} in the melts. However, the reduced density of CO₂ bubbles present in glasses from experiments with CO₂ fluid suggests that this fluid was largely dissolved in the melt and separated from it only during the process of non-isobaric quenching, simulating the rise and cooling of the melt in the crust. The high density of CO₂ in bubbles in a system with H₂O-CO₂ fluid is apparently associated with an increase in the H₂O content in the melt, which is accompanied by a decrease in the solubility of CO_2 in it (e.g. Ni, Keppler, 2013) and the formation of free CO₂ fluid with a density corresponding to P-T parameters of the experiment. The bubbles obtained in the experiments indicate that C-O-H fluids are preserved during anatexis up to conditions of high and ultra-high (>900°C) temperatures.

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Korzhinskaya V.S., Kotelnikov A.R., Suk N.I., Van K.V. Experimental investigations of solubility of $Zr_{0.5}Hf_{0.5}SiO_4$ solid solution in silicate melts (T = 800°, 1000°C, P – 400 MPa). UDC 550.89

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Abstract. Research on the solubility of the Zr_{0.5}Hf_{0.5}SiO₄ solid solution in an aluminosilicate melt at temperatures of 800°C and 1000°C for a pressure of 400 MPa in the presence of water has been continued. The duration of the experiments was 12 days for 800°C and 5 days for 1000°C. The starting material was fused glass of granite composition of different agaiticity (1.10 - 2.05), as well as a solid solution of the composition Zr_{0.5}Hf_{0.5}SiO₄, synthesized by the solution-melt method. The composition of the samples after the experiments was determined by electron probe X-ray spectral analysis. It was found that with increasing pressure from 200 MPa to 400 MPa for both temperatures, solubility of $Zr_{0.5}Hf_{0.5}SiO_4$ decreases at close agpaitic content. It is noted that the agpaiticity of the melt has a stronger effect on the solubility of the Zr_{0.5}Hf_{0.5}SiO₄ solid solution than pressure and temperature

Keywords: silicate melt; solid solution; experiment; solubility

Experimental data are presented on the solubility of the Zr0.5Hf0.5SiO4 solid solution in an aluminosilicate melt for temperatures of 800° and 1000°C and a pressure of 400 MPa. Experiments was carried out in a high gas pressure vessel (HGPV-10000) in the presence of water. The duration of the experiments was 12 days for 800°C and 5 days for 1000°C. The starting material was fused glass of granite composition of different agpaiticity (Kagp = (Na+K)/Al): 0.95 – 2.05, as well as a solid solution of composition Zr0.5Hf0.5Si04, synthesized by the solution-melt method (Kotelnikov et al., 2023). The composition of the samples after the experiments was determined by electron probe X-ray spectral analysis.

To clarify the effect of agpaiticity on the solubility of Zr0.5Hf0.5SiO4 (ZrcHfn), pre-fused aluminosilicate glasses with different agpaiticity with coefficients Kagp= (Na+K)/Al: 0.95; 1.10; 1.19; 1.51; 1.75 and 2.05 were prepared. To assess the solubility (ZrcHfn) in an aluminosilicate melt, we used a method for measuring the diffusion profile of the ZrO2 content in tempered glass from the crystal boundary, described previously (Kotelnikov et al., 2019). Using a similar method, the solubility of the Zr0.5Hf0.5SiO4 solid solution in an aluminosilicate melt was studied. The experiments were carried out in gold (800°C) and platinum (1000°C) ampoules 3x0.1x50 mm, into which 50 - 80 mg of granite glass and 5-7 mg of synthesized Zr0.5Hf0.5SiO4 solid solution were loaded. A certain amount of water was poured into the ampoules (see Tables 1 and 2). The ampoules were hermetically sealed and placed in a "gas" bomb for the experiment. The compositions of all samples after the experiments were determined by electron probe X-ray spectral analysis (EPXRA) using a Tescan Vega II XMU scanning electron microscope (Tescan, Czech Republic), equipped with an INCA Energy 450 system for X-ray spectral microanalysis with energy-dispersive (INCAx-sight) and crystal- diffraction (INCA wave 700) X-ray spectrometers (Oxford Instruments, England) and the INCA Energy+ software platform.

Table 1 presents the results of experiments on the solubility of Zr_{0.5}Hf_{0.5}SiO₄ in a melt with different agaiticity at $T = 800^{\circ}C$, P = 400 MPa, and Fig. 1a shows the dependence of the solubility of Zr_{0.5}Hf_{0.5}SiO₄ in an aluminosilicate melt on again again (Kagp = (Na+K)/AI) in the presence of water. It has been established that as Kagp increases from 0.98 to 1.78, the content of $\sum (ZrO_2 + HfO_2)$ in glass increases on average from 0.21 wt.% (for Kagp = 0.98) to 4.20 wt.% (for Kagp = 1.78). The glass composition in wt.% after the experiment is as follows: Na₂O - 6.51%; Al₂O₃ - 12.25%; SiO₂ -61.23%; K₂O - 6.75%; CaO - 0.09%; TiO₂ - 0.05%; (for Kagp = 1.36). After the experiments, the agpaiticity of the melt decreased slightly compared to the initial one, which can be explained by the partial

redistribution of alkalis into the fluid phase.

Table 2 presents the results of experiments on the solubility of $Zr_{0.5}Hf_{0.5}SiO_4$, in a melt with different agpaiticity at T = 1000°C, P = 400 MPa, and **Fig. 1b** shows the dependence of the solubility of $Zr_{0.5}Hf_{0.5}SiO_4$ in an aluminosilicate melt on agpaiticity (Kagp = (Na+K)/Al) in the presence of water (duration of experiments - 5 days). As can be seen from Fig. 1b, the content of $\sum (ZrO_2 + HfO_2)$ in glass increases from 0.39 wt. % Kagp = 0.93 to 3.40 wt. % (Kagp = 1.51). At the same time, Kagp also decreases after experience. Glass composition in wt. % for Kagp = 1.30 is as follows: Na₂O - 6.25%; Al₂O₃ - 12.97%; SiO₂ - 60.41%; K₂O - 6.11%; CaO - 0.13%; TiO₂ - 0.07%;

In Fig. 2 the results of the solubility of ZrcHfn in an aluminosilicate melt for two temperatures 800° and 1000° C at the same pressure 400 MPa are presented for comparison. The graph shows that with increasing temperature at similar agpaitic values, the solubility of the solid solution increases slightly. Thus, for 1000° C at Kagp = 0.93, the solubility of ZrcHfn is 0.39 wt.%, and for 800° C at Kagp = 0.98 it is 0.21 wt.%.

Nº exp.	Weight, mg	Solution, mg	ZrO _{2,} wt.%	HfO₂, wt.%	ZrO ₂ +HfO ₂ , wt.%	Kagp before/exp. Kagp after/exp
ZrcHfn-17	50.29gr.+7.24 Zrc _{0.5} Hfn _{0.5}	$H_2O - 49.30$	0.05	0.16	0.21	Kagp bef/ex = 0.95
						Kagp aft/ex = 0.98
ZrcHfn-18	54.24gr.+6.95 Zrc _{0.5} Hfn _{0.5}	H ₂ O - 48.18	0.08	0.22	0.30	Kagp bef/ex = 1.10
						Kagp aft/ex = 1.06
ZrcHfn-19	52.19gr.+7.29 Zrc _{0.5} Hfn _{0.5}	H ₂ O – 46.09	0.63	0.75	1.38	Kagp bef/ex = 1.19
						Kagp aft/ex = 1.27
ZrcHfn-20	51.01gr.+7.48 Zrc _{0.5} Hfn _{0.5}	H ₂ O – 49.58	0.68	1.11	1.76	Kagp bef/ex = 1.51
						Kagp aft/ex = 1.36
ZrcHfn-21	60.08gr.+7.02 Zrc _{0.5} Hfn _{0.5}	$H_2O - 50.00$	1.31	1.66	2.97	Kagp bef/ex = 1.75
						Kagp aft/ex = 1.61
ZrcHfn-22	54.24gr.+6.95 Zrc _{0.5} Hfn _{0.5}	H ₂ O - 50.78	1.74	2.46	4.20	Kagp bef/ex = 2.05
						Kagp aft/ex = 1.78

Table 1. Experiments on the solubility of $Zr_{0.5}Hf_{0.5}SiO_4$ in a melt with different agaiticity at T = 800°C, 400 MPa

Note. gr. – granite glass.

№ exp.	Weight, mg	Solution, mg	ZrO _{2,} wt.%	HfO₂, wt.%	ZrO ₂ +HfO ₂ , wt.%	Kagp before/exp. Kagp after/exp.
ZrcHfn-23	55.91gr.+5.82 Zrc _{0.5} Hfn _{0.5}	H ₂ O – 37.56	0.11	0.28	0.39	Kagp bef/ex = 0.95 Kagp aft/ex = 0.93
ZrcHfn-24	52.04gr.+5.82 Zrc _{0.5} Hfn _{0.5}	H ₂ O - 49.28	0.35	0.77	1.12	Kagp $aft/ex = 0.00$ Kagp bef/ex = 1.19 Kagp aft/ex = 1.13
ZrcHfn-25	57.27gr.+7.43 Zrc _{0.5} Hfn _{0.5}	H ₂ O – 50.56	0.88	1.11	1.99	Kagp bef/ex = 1.51 Kagp sft/ex = 1.20
ZrcHfn-26	63.49gr.+6.99 Zrc _{0.5} Hfn _{0.5}	H ₂ O - 49.81	1.42	1.98	3.40	Kagp $at / ex = 1.50$ Kagp bef/ex = 2.05 Kagp aft/ex = 1.51

Table 2. Experiments on the solubility of $Zr_{0.5}Hf_{0.5}SiO_4$ in a melt with different agaiticity at T = 1000°C, 400 MPa



Fig. 1a. Dependence of the solubility of the $Zrc_{0.5}Hfn_{0.5}$ in an aluminosilicate melt on agaiticity (Kagp = (Na+K)/Al) in the presence of water (T=800°C, P = 400 MPa, duration of experiments - 12 days).

Fig. 1b. Dependence of the solubility of the $Zrc_{0.5}Hfn_{0.5}$ in an aluminosilicate melt on agaiticity (Kagp = (Na+K)/Al) in the presence of water (T=1000°C, P = 400 MPa, duration of experiments - 5 days).



Fig. 2. Solubility curves of the $Zrc_{0.5}Hfn_{0.5}$ solid solutions in aluminosilicate melt depending on agpaiticity (Kagp = (Na+K)/Al) in the presence of water for temperatures of 800°C and 1000°C at a pressure P = 400 MPa

As can be seen from **Fig. 2**, with increasing temperature at a pressure of 400 MPa, the solubility of the ZrcHfn solid solution increases, although less than at P = 200 MPa (Kotelnikov et al., 2023).

Figs. 3a and 3b show for comparison the solubility curves of the solid solution (ZrcHfn) at pressures of 200 and 400 MPa for T = 800 °C (Fig. 3a) and 1000 °C (Fig. 3b). As we see, in the region of low Kagp values (from 0.95 to 1.20), the solubility (ZrcHfn) changes little with increasing pressure for both temperatures. But already in the region of high agpaitic contents, the solubility of the solid solution (ZrcHfn) is 2-4 orders of magnitude lower at a pressure of 400 MPa. Thus, it can be argued that with increasing pressure from 200 to 400 MPa, the solubility of the solid solution decreases. As a result of the studies, it was established that the agpaiticity of these minerals than pressure and temperature.



Fig 3a. Curves of the solubility of the $Zrc_{0.5}Hfn_{0.5}$ solid solutions in aluminosilicate melt as a function of againizity (Kagp= (Na+K)/Al) in the presence of water for T = 800°C at pressures of 200 and 400 MPa.

Fig 3b. Curves of the solubility of the $Zrc_{0.5}Hfn_{0.5}$ solid solutions in aluminosilicate melt as a function of againizity (Kagp= (Na+K)/Al in the presence of water for T = 1000°C at pressures of 200 and 400 MPa.

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Persikov E.S.¹, Bukhtiyarov P.G.¹, Aranovich L.Ya.^{1,2}, Shaposhnikova O.Yu.¹, Nekrasov A.N.¹ Features of crystallization of magnesian basalt melt during interaction with hydrogen at the boundary of the Earth's crust with the upper mantle (premilinary results).

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Abstract. This report presents the first results of an experimental study of the features of crystallization of basaltic melt during interaction with hydrogen at the boundary of the earth's crust with the upper mantle (T = 1200 - 1450 °C, P(H₂) = 1.2 - 2.7 GPa). The experiments were carried out using a high-pressure cylinder-piston type installation (IEM RAS), equipped with an original internal cell in which the source of hydrogen was titanium hydride, which decomposed under the experimental parameters. It is characteristic that, in contrast to experiments on the crystallization of basalt melt in the same hydrogen-magnesian basalt system at moderate hydrogen pressure

(100 MPa), in experiments at high hydrogen pressure almost complete reduction of iron oxides occurs. It is likely that their absence in the melts in the present experiments is primarily due to the high H₂ pressure, since it is known that the activity of a(FeO, melt) is inversely proportional to $f(H_2)$. This is an interesting result, because, in essence, it limits the power of the Earth's primary hydrogen atmosphere.

Keywords: basaltic melt, hydrogen, pressure, temperature, native metal, crystallization, reducing conditions, crust-mantle boundary

The role of hydrogen, the most common element of our Galaxy, in natural processes is extremely diverse and in recent years has attracted increasing attention from geologists and geochemists. Among other important problems of magma differentiation, the formation of native metals and ore formation processes in the Earth's crust are increasingly associated with the active participation of hydrogen (Bird et al., 1981; Ryabov et al., 1985; Oleinikov et al., 1985; Marakushev, 1995; Levashov and Okrugin, 1984; etc.). According to Yakut geologists who have studied in detail the intrusions of traps on the Siberian platform with a large-scale manifestation of native iron, the formation of native iron is based on the fluid-magmatic interaction of magma matter with reducing fluid components, mainly of hydrogen composition. All trap intrusions with iron manifestations are formed by a melt bearing signs of deep pre-chamber evolution (anorthosite tendency of magmatic differentiation). In material terms, this phenomenon is fixed in the obligatory appearance of rock-forming minerals in magmatites of pre-chamber paragenesis, which are represented by anorthitebitovnite (An95-76) and forsterite-chrysolite (Fa1228). The listed minerals record the reducing conditions and barophilicity of the situation in the mantle intermediate hearth, which, in their opinion, existed at P = 12-15 Kbar and T = 1450-1550 $^{\circ}$ C (Tomshin et al., 2023). This report presents the first results of an experimental study of the crystallization features of a basalt melt in interaction with hydrogen at the boundary of the Earth's crust from the upper mantle (T = 1200 - 1450 °C, P(H₂) = 1.2 - 2.7 GPa). The experiments were carried out using a highpressure cylinder-piston type installation (IEM RAS) equipped with an original internal cell (Fig. 1), in which the hydrogen source was titanium hydride, which decomposed under the experimental parameters.

Natural samples of magnesian basalt from the northern breakthrough of the Tolbachik volcano (Kamchatka) were used as the initial sample in the experiments. The chemical composition of the phases obtained in the experiments (Tables 1, 2) was determined using a CamScan MV2300 digital electron X-ray microscope (VEGA TS 5130 MM), with an attachment for energy dispersion microanalysis INCA Energy 450 and WDS Oxford INCA Wave 700. The analyses were carried out at an accelerating voltage of 20 kV with a beam current of up to 400 pA and a spectrum set time of 50-100 seconds

The methodology of the experiments is given in the caption to Fig. 2 and in the notes to Table 1.



Fig. 1. Scheme of a high-pressure cell for experiments at a hydrogen pressure of 1.2 GPa.

Table 1. Chemical composition (wt. %) and structural chemical parameter (100NBO/T) the initial basalt, residual basalt glass (medium composition) and the crystals formed after experiments under hydrogen pressure.

Components	1	2	3	4	5
SiO ₂	55.67	52.25	43.0	45.68	49.5
Al_2O_3	18.18	13.75	0.61	10.0	13.18
Fe ₂ O ₃	0.00	0.00	0.00	0.00	3.18
FeO	0.0	0.1	0.25	0.11	6.85
MnO	0.04	0.34	0.12	0.14	0.15
MgO	5.27	9.83	54.68	10.7	9.98
CaO	9.5	15.05	0.42	21.42	12.34
Na ₂ O	3.56	3.1	0.2	2.13	2.18
K ₂ O	2.95	1.07	0.0	0.0	0.93
TiO ₂	4.71	4.49	0.42	9.82	1.01
P_2O_5	0.2	nd.	nd	nd	0.25
H_2O+	nd	nd	nd	nd	nd
H ₂ O-	0.5	nd	nd	0.0	0.29
NiO	nd	nd	nd	0.0	nd
Co ₃ O ₄	nd	nd	nd	0.0	nd
Sum	100.58	99.98	99.7	100	99.84
100NBO/T	36	73	372	109	83

Note: The water content is determined by the Karl-Fischer titration method. 1 - Residual glass, run No 2CP_K experiment with magnesian basalt melt: $P(H_2) = 1.2$ GPa, T = 1400 °C, exposure time 1.5 hours, then temperature reduction to 1200 °C in isobaric mode, exposure time 1.5 hours (crystallization), and then isobaric quenching. 2 - Pyroxenes, run No 12CP_K. 3 - Olivines. Run No 27CP_K. 4 - Pyroxenes, run No 27CP_K. 5 - is the magnesian basalt of the northern breakthrough of the Tolbachik volcano (Persikov et al., 2019).

Table 2. Chemica	al compositions (wt.	%) of metal p	phases in basa	lt melts (quer	nched samples)	after experiments	under
hydrogen pressur	e.	,	-		- /	-	

Components	№12 СР-К	№ 27 СР-К
Fe	98.51	98.72
Mg	0.05	0.05
Ti	0.5	0.3
0	0.91	1.2
Si	0.6	0.16
Ca	0.04	0.03
Al	0.3	0.3
Sum	100.91	100.76

Note. 1. The results presented in the table are the average values of 7 measurements. 2. The concentrations of all impurity elements (Si, Ca, Mg) in metallic phases are determined approximately, since these values are within the limits of analytical errors.



(b)

Fig. 2. Raster micrographs in scattered reflected electrons (BSE) of quenching products of samples after experiments on interaction and crystallization of basalt melt at high hydrogen pressures. (a) - run No 12CP_K, experiment with melts of the initial magnesian basalt, P (H₂) = 1.2 GPa, T = 1400 °C, exposure time 1.5 hours, then temperature reduction to 1200 °C in isobaric mode, exposure 1.5 hours (crystallization), and then isobaric quenching (white color – Fe metal alloy, (p. 1,2,3 composition - see Table 2; dark gray color-basalt glass, p. 6, composition-see Table 1; light gray color- pyroxene crystals, vol. 4, 5 - composition-see See table 1). (b) run No 27CP_K, experiment on crystallization of magnesian basalt, $P(H_2) = 2.7$ GPa, T = 1400 °C, duration of the experiment 1.5 hours, then temperature reduction to 1200 °C in isobaric mode, exposure 2 hours (crystallization) and then isobaric quenching (white color – Fe metal alloy, p. 1-3, composition - see Table 2: light gray color-residual glass t. 8-11, composition-see table 1; dark gray color- crystals: olivine, p. 4-7, clinopyroxene, p. 12-17.

The obtained new experimental data on the crystallization of basalt melts at a temperature of 1200 °C and hydrogen pressures (1.2 - 2.7 GPa) make it possible to understand the possible role of hydrogen in the processes occurring in basalt melts at the boundary of the Earth's crust and upper mantle under reducing conditions ($f(O_2) = 10^{-14} - 10^{-15}$). It has been established that the following phases are formed during crystallization under hydrogen pressure in a basalt melt: 1) more polymerized residual melts; 2) H₂O dissolved in the melt; 3) small releases of molten metal (Fe) of the liquation structure (Fig.2) formed at a temperature much lower than the melting

point of Fe; 4) low ferrous olivines, clinopyroxenes (Fig. 2 and Tables 1 and 2). It is characteristic that, unlike experiments on the crystallization of a basalt melt in the same hydrogen-magnesia basalt system at a moderate hydrogen pressure of 100 MPa (Persikov et al., 2019), in experiments at high hydrogen pressure, almost complete reduction of iron oxides occurs. It is likely that their absence in the melts in these experiments is primarily due to the high pressure of H_2 , since it is known that the activity of a(FeO, melt) is inversely proportional to $f(H_2)$. This is an interesting result, because, in fact, it limits the power of the Earth's primary hydrogen atmosphere.

(a)

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Rusak A.A.¹, Shchekina T.I.², Zinovieva N.G.², Bychkov A.Y.² Distribution of rare earth elements, scandium, yttrium and lithium between melt and aqueous fluid at 800°C, 1 and 2 kbar. *UDC 552.13*

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Abstract. The distribution of rare earth elements (REE), scandium, yttrium and lithium between aluminosilicate (L) and aluminofluoride (LF) melts and aqueous fluid (FI) at 800°C, 1 and 2 kbar was experimentally studied. It is shown that all rare earth elements are predominantly distributed in favor of the aluminum fluoride melt. The most depleted phase in REE, Sc, Y and Li is aqueous fluid. The lithium concentration in the aqueous fluid is 1–2 orders of magnitude lower than in the aluminosilicate and salt phases. Lithium partition coefficients (KDLi(FI/L))

between aqueous fluid and aluminosilicate melt are 0,0009 – 0,04 at 800°C and 2 kbar. The characteristics of the REE spectra in these phases are similar to each other, but in experiments with water content in the system of 2,44 and 11,11 wt. % at 2 kbar, maxima are observed for praseodymium and neodymium. There are also differences in the distribution of vttrium, scandium and lithium between the aqueous fluid and the aluminosilicate melt. Yttrium separation coefficients decrease compared to rare earth elements with increasing water concentration from 2,44 to 4,94 wt. % at 800°C and 2 kbar. The scandium separation coefficients increase for all experiments at water contents from 2,44 to 12,89 wt. %, with the exception of the experiment with 4,94 wt. %. There is a slight increase in the separation coefficients between the aqueous fluid and the aluminosilicate melt from light REE to heavy REE. Thus, it can be argued that the agueous fluid phase in the model granite system Si-Al-Na-K-Li-F-O-H with different water contents from 2 to 13 wt. %, is characterized by the lowest concentrations of REE, Sc, Y and Li, while the salt phase separated from the aluminosilicate melt at 800°C accumulates the largest amount of REE with coefficients significantly greater than one (KDREE(LF/L) >> 1). It is assumed that it is the salt melt, rich in alkali elements and fluorine and separated at the last stages of differentiation of the granite melt, that is a concentrator of rare earth elements.

Keywords: aluminosilicate melt, aluminofluoride (salt) melt, aqueous fluid, separation coefficient, rare earth elements, scandium, yttrium, lithium, experiment

Introduction. Since the last century, many researchers have assumed that salt melts play an important role in the formation of ore deposits (Spurr, 1933; Smith, 1948; Fersman, 1960; Ermakov, 1960; Dolomanova, 1966). Such melts are found in nature in the form of inclusions in minerals of rocks and various veins (Ermakov, Dolgov, 1979; Roeder, 1981; Reif, 1984; Reif, 2004; Peretyazhko, Savina, 2010). In a number of them, significant concentrations of ore components were determined. Such fluid melts are most likely of magmatic nature. At later of differentiation the stages of aluminosilicate melts, fluid melts can be separated from magma, concentrating ore and rare components, according to the mechanism of liquid immiscibility (Grigoriev, Dolomanova, 1964; Dolomanova, 1966; Kogarko, 1967: Marakushev, 1979: Marakushev et al., 1983; Gramenitskiy et al., 2005; Shchekina et al., 2020; Rusak et al. (in press)). The works (Gramenitskiy et al., 2005; Alferyeva et al., 2011; Shchekina et al., 2013) show that one of the possible REE concentrators can be considered a salt melt separated from a fluorine-rich leucocratic aluminosilicate melt. The study of silicate-salt systems began with experiments in dry conditions at atmospheric pressure. In the first studies of the melting of albite and granite in the presence of HF and water vapor (Wyllie, Tuttle, 1961), no silicatesalt immiscibility was found, as well as in the work (Koster van Gross, Wyllie, 1965) in the system

 $NaAlSi_{3}O_{8} - NaF - H_{2}O$. For the first time in the work of L.N. Kogarko studied the region of immiscibility between silicate and fluoride melts in the Na₂O-Al₂O₃-SiO₂-NaF system. The fluoride melt was close in composition to cryolite (Na_3AlF_6) (Kogarko, 1967). She suggested that the presence of liquid immiscibility indicates the possibility of separation of fluoride melts during the accumulation of fluorine at the last stages of differentiation of granitic magmas and the possibility of the formation of cryolite bodies in a number of deposits, for example, Ivigtut (South Greenland). Regions of liquid immiscibility were discovered in the systems albite-lithium fluoride, albite-sodium chloride, albitepotassium chloride (Delitsyn, Melentyev, 1972). Experimental studies of artificial systems silicatesalt of fluoride composition (Kogarko, Krigman, 1981) and granite-alkali fluorides-H₂O (Gluck, Trufanova, 1977; Kovalenko, 1977; Kovalenko, 1979) showed that the process of crystallization of granite melt is accompanied by the manifestation of liquid immiscibility between aluminosilicate and salt fluoride melts. The influence of fluorine and alkali elements (Na, K, Li) on phase relationships in granites was studied and it was shown that the presence of lithium in granite melt expands the region of silicate-salt immiscibility (Trufanova, Gluck, 1986). It should be noted that the addition of Li to a granitic system in the absence of fluorine also leads to the appearance of immiscibility, but the separated salt melts do not have an aluminofluoride composition, but a meta- or disilicate type Li₂Si₂O₅ 1986). (Trufanova, Gluck, In the works (Gramenitskiy et al., 1989; 1993; 2005; Devyatova et al., 2007), the region of immiscibility of aluminosilicate and aluminofluoride melts in the model granite system Si-Al-Na-F-O-H was identified at a temperature of 800°C and a pressure of 1 kbar and the influence of lithium on phase relationships was studied. The above studies were confirmed in the works of Veksler et al. (2005; 2012) in dry conditions at 1100 and 1200°C at atmospheric pressure and in the presence of an aqueous fluid at 700 and 800°C and 1 kbar. In the Si-Al-Na-Li-F-O-H system was studied in more detail at 800°C and 1 kbar, which showed that the inclusion of lithium in the system increases the region of existence of the alkali-aluminofluoride salt melt and reduces the area of cryolite crystallization, which confirmed the results of previous researchers (Alferyeva et al., 2011). A vast region of Li-containing alkalialuminofluoride melt, in equilibrium with the aluminosilicate melt, was identified. The region of immiscibility in the presence of Li includes a wide range of compositions of the granite system, close to real rocks.

The purpose and objectives of the work. In this work, the goal was to study the distribution of rare earth elements (REE), scandium, yttrium and lithium between aluminosilicate (L) and aluminofluoride (LF) melts and aqueous fluid (Fl) at 800°C, 1 and 2 kbar. In this regard, the following tasks were solved are 1) conduct experiments on a high gas pressure installation (HGP) at the Institute of Experimental Mineralogy RAS at a temperature of 800°C and a pressure of 1 and 2 kbar with a water content of 2 to 13 wt. %; 2) study phase relationships in a model granite system; 3) study the distribution of rare earth elements and lithium between the aqueous fluid and the aluminosilicate melt at given TP parameters.

Methodology. For the experiments, the reference composition of an aluminosilicate melt was chosen, close in composition to the granite eutectic quartzalbite-orthoclase at 690°C, 1 kbar H₂O, 1 wt. % F (Manning, 1981) and containing 1,5 wt. % Li. The ratio of the atomic quantities of the main elements was Si:Al:(Na+K+Li) = 70:15:15. The ratio of alkaline elements was Na:K:Li = 7.5:2.5:5. An aluminofluoride component (corresponding in stoichiometry to the compound (Na,K,Li)₃AlF₆) was added to the silicate composition in an amount that was sufficient to saturate the aluminosilicate melt and isolate a separate aluminofluoride phase. The water content in the system ranged from 2 to 13 wt. %. Dried gel SiO₂, NaF, LiF, AlF₃, Al₂O₃, K₂SiF₆ were used as initial reagents. Rare earth elements, as well as Sc and Y, were introduced into the system in the form of oxides in an amount of 0,5 wt. % of the element. All starting substances were mixed in a jasper mortar in an alcohol atmosphere, dried in an oven, and placed in platinum ampoules with a diameter of 3 mm, a wall thickness of 0,2 mm and a height of 25-30 mm. The required amount of distilled water was added to each ampoule. The ampoules were welded using electric arc welding with a carbon rod. The experiments were carried out on an UVGD installation with internal heating at a temperature of 800°C and a pressure of 1 and 2 kbar at the IEM RAS (Chernogolovka). The temperature measurement error was $\pm 5^{\circ}$ C, pressure ± 10 bar. The oxygen volatility corresponded to the NNO buffer. The hardening speed was 150-200 degrees per minute. The duration of the experiments was 6-7 days. The experiment was considered successful if the difference in the mass of the ampoule before and after the experiment did not exceed 0,001 g. To study the aqueous fluid, the ampoules were opened, gas and aqueous fluid were released from them, we placed all the contents in test tubes, into which distilled water was poured in an amount of 40–50 ml. The test tubes were kept in an ultrasonic bath to better separate the crystalline phases and quenching products of the aqueous fluid from the walls of the ampoules. Then an aliquot of 10 ml was taken from these tubes, this solution was passed through a filter, and the resulting solution was placed in a smaller tube. The filtered solution was filled with a mixture of nitric and hydrochloric acids, and then the resulting solution was analyzed by ICP MS. Platinum ampoules and samples were washed on a filter with distilled water and dried. The samples were then examined under binoculars. Most often, the sample consisted of transparent white silicate glass and round white precipitates (globules) of the salt phase included in it. Some of the samples were placed in a checker for further study on a microprobe, and from the remaining material, glass and globules of the salt phase were selected with the highest possible purity to undergo the same acid treatment procedure as for the aqueous fluid phase, for analysis by ICP MS. The study of the sample structure, phase morphology and chemical composition was carried out using a scanning electron microscope Jeol JSM-6480LV (Japan) with energy-dispersive Oxford X-MaxN and INCAWave-500 crystal diffraction (Oxford Instrument Ltd., UK) spectrometers in the laboratory of local methods studies of matter at the Department of Petrology, Faculty of Geology, Moscow State University. Shooting conditions: 20kV, 0,7nA. The accuracy of the assessment of the main elements in the composition of the synthesized phases was 2-5 rel. %, instrument error when measuring fluorine $\pm 1\%$ of the concentration of the element. Some samples were studied using a Superprobe JXA-8230 electron probe microanalyzer (Japan). Samples were analyzed in defocused beam mode (up to 10 µm) at 10 kV and 10 nA to prevent glass destruction. At the peak and background intensity measurement time (30/15 s), the measurement dispersion of Si, Al and O was 0.8 rel. %, K – 1.5 rel. %, Na – 2 rel. %, and F -2 rel. %. REE determination was carried out at 20 kV and 30 nA. Their detection limit did not exceed 0,01%. The determination of REE, yttrium, scandium and lithium was carried out by mass spectrometry with inductively coupled plasma Element-2 in the laboratory of experimental geochemistry of the Faculty of Geology of Moscow State University. The detection limits of elements ranged from 0,01 ng/g for heavy and medium-weight elements, increasing to 1 ng/g for light elements. The measurement error was 1-3 rel. %. The samples were also analyzed by laser ablation at the ASIC of the Institute of Applied Mathematics and Mathematics of the Russian Academy Sciences. Measurements of were performed on an X Series II quadrupole inductively coupled plasma mass spectrometer (Thermo Scientific, USA) with a UP266 MACRO laser ablation attachment (New Wave Research, USA). The description of the operating parameters is described in detail in the article (Shchekina et al.,

2020). Element detection limits for REE range from 1×10^{-7} to 1×10^{-6} wt. %; relatively high detection limit for Sc 2×10^{-4} wt. %, which is due to polyatomic interferences.

Results and discussions of the work. As a result of the experiments carried out at a temperature of 800° C and a pressure of 1 and 2 kbar, an aluminosilicate melt (L), an aluminofluoride (salt) melt (LF) and an aqueous fluid are in equilibrium, with a water content of ~ 10 wt. % (Fig. 1).



Fig. 1. Round salt globules (LF) in porous aluminosilicate glass (L). T = 800°C, P = 2 kbar, 4.94 wt. % H₂O. Image in BSE.

Tempering products are aluminosilicate glass, into which small quenching phases (<10 μ m) of aluminofluoride composition and large salt globules from 20 to 1000 μ m in diameter are immersed. The amount of salt phase by volume is 20-25%. A clear boundary is preserved between the two melts, but near the phase contact the aluminosilicate glass is depleted in quenching phases.

The salt globule is represented by a polyphase aggregate of small crystals of lithium, sodium and potassium fluorides and aluminofluorides ranging in size from 2 to 7 microns. REE fluorides also crystallize within the salt globule, forming small white clusters in the BSE around the alkali fluorides. but they often form thin rims at the interface between the aluminosilicate glass and the salt globules. Sometimes we found aluminosilicate glass captured by a salt globule, which indicates the liquid state of the phases before quenching the sample. Aluminosilicate glass and salt globules contain pores, which characterize the loss of water from the melt during the quenching process. In experimental glasses with a low initial water content (2,06 wt. %), the number of pores is less than 1%. In experimental glasses containing 13,27 wt. %, pores $<< 1 \ \mu m$ in size are observed, forming garlands around crystalline fluoride precipitates. The chemical composition and distribution of major and rare earth elements, scandium, yttrium and lithium between aluminosilicate and aluminofluoride (salt) melts at 800°C, 1 and 2 kbar and different water contents are shown in (Shchekina et al., 2020). In this work, it was established that all REE are predominantly

 $\begin{array}{c} 0.1 \\ 0.01 \\ 0.001 \\ 0.001 \\ 0.0001 \\ 0.0001 \\ 0.0001 \\ 0.0001 \\ 0.00001 \\ La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y Sc Li \\ \end{array}$

The lithium concentration in the aqueous fluid is 1-2 orders of magnitude lower than in the aluminosilicate and aluminofluoride phases. Lithium partition coefficients (KDLi(Fl/L)) between aqueous fluid and aluminosilicate melt are 0,0009 - 0,04 at 800°C and 2 kbar. The characters of the REE spectra in these phases are similar to each other, but in experiments with water content in the system of 2,44 and 11,11 wt. % at 2 kbar, maxima are observed for praseodymium and neodymium. There are also differences in the distribution of yttrium, scandium and lithium between the aqueous fluid and the aluminosilicate melt. Yttrium separation coefficients decrease compared to REE with increasing water concentration from 2,44 to 4,94 wt. % at 800°C and 2 kbar. The scandium separation coefficients increase for all experiments at water contents from 2,44 to 12,89 wt. %, with the exception of the experiment with 4,94 wt. %. There is a slight increase in the separation coefficients between the aqueous fluid and the aluminosilicate melt from light REE to heavy REE.

Conclusions. The aqueous fluid is the most depleted phase with respect to all the rare elements studied are lithium, REE, yttrium and scandium. Of all the elements in aqueous fluid, neodymium, scandium and lithium accumulate best; these elements show the highest values relative to all other elements. The most enriched phase in REE, yttrium and lithium is the salt aluminofluoride melt.

Sources of financing. The work was carried out with the support of the state task of the Geochemical Institute of the Russian Academy of Sciences and on the state budget topic "Regimes of petrogenesis of the Earth's internal geospheres" of the Geological Faculty of Lomonosov Moscow State University. distributed in favor of the molten salt. The most depleted phase in REE, Sc, Y and Li is aqueous fluid (Fig. 2).

Fig. 2. Distribution $(KD_{REE,Y,Sc,Y}(Fl/L))$ of rare earth elements and lithium between aqueous fluid and aluminosilicate melt at 800°C and 2 kbar with different water content in the system: 1-2,44 wt. %, 2 – 4,94 wt. %, 3 – 11,11 wt. %, 4 – 12,89 wt. %, 1a and 4a – data on the content of REE, Y, Sc and Li in L, obtained by laser ablation.

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Safonov O.G., Khodorevskaya L.I., Spivak A.V., Kosova S.A., Viryus A.A., Zakharchenko E.S. Possible sources of CO₂ in hightemperature metamorphism. Experimental studies. UDC 552.13

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Abstract: The CO₂ balance in the continental crust involves both external and internal sources. External sources are usually associated with the degassing of upper mantle basic magmas accumulating at the base of the crust. Internal sources of CO₂ are associated with the initial presence of carbon-bearing minerals (first of all, carbonates and graphite) in the pre-metamorphic protolith. The paper presents the results of experimental testing of two models at 900°C and 500 MPa. The "external source" model was reproduced in experiments on the interaction of garnet-twomica schist with a fluid, in which X_{CO2} was 0.5 and 1.0. The "internal source" was modeled by the formation of CO₂ in situ due to oxidation of graphite added to the schist during the reduction of Fe in Fe-Mg minerals (mostly, in biotite and ilmenite). In both cases, partial melting of the rock occurs. CO₂ partially dissolves in melts in the form of Ca, Mg, Kcarbonate complexes and exists as a free fluid phase in gas bubbles in glass.

Keywords: CO₂, fluid, metamorphism, garnet-two-mica metapelite, carbon, granitoid melts, Raman spectra, experiment.

Introduction Mineral associations of rocks of high-temperature metamorphic complexes and accompanying granitoids at the middle and lower levels of the continental crust were formed under conditions of reduced water activity (Newton et al., 1980). It is caused by the presence of CO_2 and/or salt components in fluids, which are responsible for the immiscibility between the water-salt and watercarbon dioxide components of the fluids. The widespread findings of CO₂ inclusions in minerals of rocks of granulite complexes (including ultra-hightemperature ones) substantiated the "carbon dioxide model" (Newton et al., 1980), according to which fluids rich in CO₂ come from the lower crust during the degassing of basaltic magmas. CO₂ can be

transported by granitoid magmas formed by partial melting of crustal rocks. However, the low solubility of CO₂ in acidic-medium melts leads to its separation and interaction with the host rocks, which stimulates the formation of typical "anhydrous" associations of high-temperature metamorphic rocks (granulites) in them. However, numerous data (for example, variations in the carbon isotopic composition of fluid inclusions in minerals) (Nicoli et al., 2022 and others) show that in addition to external sources of CO₂, there are internal sources that are associated with the initial presence of carbon-containing minerals (primarily carbonates and graphite) in the protolite. One of the internal mechanisms of CO₂ generation is due to the oxidation of graphite in rocks during their metamorphism and partial melting. The reaction $C + O_2 = CO_2$ (1) requires the presence of free oxygen, which exists in extremely small quantities in the fluid phase of natural systems (Hollister, 1988; Cesare et al., 2005). The oxygen necessary for the oxidation of graphite can be obtained through the reduction of Fe^{3+} to Fe^{2+} in Fe-Mg minerals. CO_2 can also be formed in situ by the reaction $2C + 2H_2O = CO_2 + CH_4$ (2) (Touret, 1971; Whitney, 1992). Among the rock-forming minerals of metamorphic rocks, the leading concentrators of Fe^{3+} and H_2O are micas (especially biotite). They can as the most promising material for serve implementing coupled reactions (1) and (2). Decomposition and/or peritectic melting of micas makes it possible to provoke the formation of CO₂

due to the reaction $2Fe_2O_3$ (in biotite) + C \rightarrow 4FeO (in Fe-Mg silicates) + CO₂ (3) in graphite-bearing rocks in situ without the influence of external sources in a wide P-T range conditions.

This paper shows the results of experiments on the partial melting of garnet-two-mica schist at 900°C and 500 MPa with the participation of CO_2 fluid, formed both from an internal source and supplied from the outside (external source). Details of experimental and analytical research methods are presented in the article by L.I. Khodorevskaya et al. (2024).

Experimental results Internal CO_2 source. In the experiment, CO_2 in garnet-mica slate was generated, presumably, according to reactions (1) – (3) from graphite thoroughly mixed in various proportions with 25–40 mg of shale in gold ampoules, which were kept at experimental parameters.

External CO₂ source. The experiments were carried out using a two-ampule method. The powder of the original shale was placed in the inner ampoule, and a mixture of quartz, calcite and wollastonite was placed in the outer ampoule in the stoichiometry of the reaction calcite + quartz = wollastonite + CO₂, generating CO₂ fluid with $X_{CO2} = 1.0$ (Ogasawara et al., 1983). Experiments were also carried out with H₂O-CO₂ fluid with $X_{CO2} = 0.5$, which was set with oxalic acid. The resulting fluid (CO₂ or H₂O-CO₂) from the outer ampoule penetrated into the inner one and reacted with the shale.





Fig. 1. BSE photographs of experimental products: a – in a system containing graphite; b – in a system with free CO₂.



Fig. 2. Variations in the $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio in ilmenite (1), orthoamphibole (2) and spinel (3): a - in the MC system, b - in the MCO₂ system.

The phase compositions of the products of experiments on partial melting of metapelite with an internal source of CO₂ - graphite (metapelitegraphite, hereinafter MC) and with an external source of fluid CO_2 or H_2O-CO_2 (metapelite- CO_2 , hereinafter MCO₂) are close. Quartz (Qtz), garnet (Grt), apatite (Ap), and ilmenite (Ilm) from the original metapelite are preserved after the experiments, while biotite and muscovite are absent. The newly formed crystalline phases are hercynitemagnetite spinel (Spl), orthoamphibole (OAmph), sillimanite (Sil) and potassium feldspar (Kfs) (Fig. 1). The products of all experiments contain guenched melt (Gl), the amount of which in both series of experiments is close and amounts to 50-60 vol. %.

The differences between the two series of experiments primarily consist in variations in the composition of Fe-Mg minerals. In the MC system, with an increase in the graphite content in the starting mixtures of ilmenite, spinel, and orthoamphibole, the $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio noticeably decreases (Fig. 2a). This indicates an increase in reducing conditions in the ampoules due to reaction (3), while the released oxygen oxidizes graphite according to reaction (1). In the MCO2 system, the $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio in minerals in equilibrium with CO_2 or H_2O-CO_2 fluids increases slightly (Fig. 2b), indicating more oxidizing conditions.

Melts are formed during peritectic melting of biotite, muscovite in the presence of quartz: Bt + Ms + $Qz \rightarrow Kfs + Spl + OAmph + Sil + Gl.$ In both systems, the SiO₂ – (Na₂O + K₂O) ratios in the resulting melts correspond to rhyolites. According to the A/CNK - A/NK ratio, the melts belong to high-alumina alkali-calcareous S-type granites. Only when the graphite content is >17 wt.% in the MC system, the melts correspond to I-type alkaline granites (Frost et al., 2001; Clemens et al., 2011; Chappell et al., 2012).

Raman spectroscopy

Raman spectroscopy was used to identify carboncontaining components in the melt quenching products. The glasses contain gas bubbles 2-30 microns in size. They represent a fluid phase that either coexisted with the melt at the P-T parameters of the experiments, or are separated during nonisobaric quenching in a high gas pressure apparatus (Khodorevskaya et al., 2024). The composition of the bubbles was also studied using Raman spectroscopy.

MC system (internal CO_2 source). In the Raman spectra of quenched melts, against the background of broad bands of aluminosilicate glass, there is usually a quartz band at 464 cm^{-1} and bands at 457-457 and 513-514 cm⁻¹, corresponding to potassium feldspar (Freeman et al., 2008). The spectra of all samples contain bands of varying intensities of symmetrical stretching vibrations in the CO_3^{-2} groups. In contacts with residual graphite in glasses, independent carbonate phases were identified: calcite (main peak $\square 1085 \text{ cm}^{-1}$), double carbonate K₂Ca(CO₃)₂- (doublet 1082 and 1066 cm⁻¹; Arefiev et al., 2018), magnesite (peak $\square 1095 \text{ cm}^{-1}$). But there are no signs of CO₂ in the Raman spectra of glasses. The Raman spectra of gas bubbles show bands of N₂, OH- and CO₂ groups. The density ρCO_2 , calculated using the equation (Wang et al., 2011), varies between 0.86 - 0.60 g/cm³. The maximum values of ρCO_2 are close to the value of 0.87 g/cm³ of free CO₂ at experimental parameters of 900°C and 500 MPa (Shmulovich, Shmonov, 1978). Bubbles with such a density apparently reflect CO₂ fluid that coexisted with the melt under the experimental parameters. Lower values of ρCO_2 (up to 0.60 g/cm³) correspond to bubbles separated from the melt during decompression during non-isobaric quenching. These data suggest that CO₂ formed from graphite formed both carbonate complexes in the granitic melt and accumulated in the equilibrium fluid. So, under natural conditions, CO_2 transport to the upper crust can occur both in the form of a fluid phase and together with the melt. This conclusion is confirmed by the findings of fluid inclusions with carbonates in the minerals of granulites and accompanying granitoids (Carvalho et al., 2019; Safonov et al., 2020).

MCO₂ system (external CO₂ source) In contrast to the MS system, no bands of CO₂ and carbonates were observed in the spectra of glasses in the presence of an external source of CO₂. The Raman spectra of bubbles contain peaks of CO₂, N₂, quartz, and OH- groups. The density of CO₂ in bubbles of 0.66 - 0.70 g/cm³ is noticeably lower than the density of pure CO₂ at the experimental parameters. This indicates that CO₂ was released from the melt during decompression. In the metapelite-H₂O-CO₂ system, ρCO_2 in bubbles has higher values of 0.85-1.00±0.05 g/cm³. Apparently, this is due to an increase in the H₂O content in the melt, a decrease in the solubility of CO_2 in it (e.g. Ni, Keppler, 2013) and the accumulation of CO_2 in a free fluid with a density corresponding to the P-T parameters of the experiment.

Conclusions

Melting processes involving carbon-containing components in complex associations depend on whether the carbon-containing components are present in the substrate (internal source) or enter this substrate from the outside (external source). They will also depend on the mineral composition of the substrate, for example the ratio of hydrous minerals and feldspar + quartz. The influence of an external or internal source will probably be manifested in the nature of CO_2 transport, either with or through the melt. The influence of an external or internal CO_2 source will probably be manifested in solidus temperatures.

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Shchekina T.I.¹, Kotelnikov A.R.² Alferyeva Ya.O.¹, Zinovieva N.G.¹ Modeling of the interaction between granite melt and dolomite at 700°C, $P_{H2O} = 1$ kbar and 800°C, $P_{H2O} = 4.5$ kbar in the presence of fluorine. *UDC 552.113*

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Absract. The contact interaction between F-containing granite melt and Mg-Ca carbonate in the presence of aqueous fluid at temperatures of 700°C and 1 kbar and 800°C and 4.5 kbar and a water content of 10 wt.% was experimentally studied. As a result of the experiment, a clear skarn zoning was discovered in both cases, the nature of which depended on temperature and pressure. In the endocontact zone at a pressure of 1 kbar, alkali feldspar was formed, the next zone was composed of mullite, the next by plagioclase, then amphibole. The exocontact zones consisted of wollastonite, calcite, Fphlogopite, fluorite and humite. As we moved away from the contact with the granite melt in subsequent zones of exocontact, the proportion of magnesium in the carbonate increased and the amount of silicates decreased. At 800°C and 4.5 kb, the type of zoning changed: clinopyroxene crystallized in the first endocontact zone, fluorphlogopite and humite crystallized in the second one, then fluorphlogopite and clinopyroxene. In the exocontact zones, carbonates predominated, but silicates humite, fluorphlogopite were also present. During the interaction, there was active diffusion of fluorine, sodium and potassium and a less active transfer of Al and Si from the silicate melt to the carbonate rock and the movement of Mg and Ca from it towards the silicate melt. As a result of the experiment, new types of columns of interaction between aluminosilicate melt and dolomite in the presence of fluorine at different temperatures and pressures created by water and carbon dioxide were obtained, simulating the formation of magnesian skarns of the magmatic stage.

Keywords: interaction, skarn zoning, diffusion, fluorinecontaining aluminosilicate melt, dolomite

A feature of magnesian skarns is the possibility of their formation in nature at the magmatic stage (Khitarov et al., 1962; Shabynin, 1973; Zaraisky et al., 1986; Pertsev, 1998), in contrast to calcareous ones, for which skarns of the magmatic stage are rare (Bogomolov, 1970; Alferyeva et al., 2020, 2024). The purpose of the experiments was to identify the nature of the interaction of two contrast media (aluminosilicate melt and dolomite) in the presence of fluorine. The experiments were carried out at a temperature of 700°C, 1 kbar and 800°C, 4.5 kbar and a water content of 10 wt.% in a high gas pressure at the Institute of Experimental installation Experiments RAS. To diagnose phases and determine their composition in relation to rockforming elements, fluorine and oxygen, a Jeol JSM-6480LV scanning electron microscope (Jeol, Japan) with Oxford X-MaxN energy-dispersive an

spectrometer (Oxford Instrument Ltd., UK), purchased at the expense of Development programs of Moscow University, and on a probe microanalyzer Superprobe JXA-8230 (Jeol, Japan) in the laboratory of local research methods of the Department of Petrology and Volcanology, Faculty of Geology, Moscow State University.

As a result of the experiment conducted at 1 kbar, 7 zones were discovered (Fig. 1 a), differing in mineral composition and structure. In the endocontact zone directly at the boundary with carbonates, a rim of alkali feldspar 25-50 µm wide was formed (Fig. 1 a), then (inside a crack that apparently appeared during hardening of the sample), an endocontact zone followed, composed of needleshaped aggregates of mullite crystals 20-50 µm wide. The next two endocontate zones consisted of a zone of melt and potassium-containing plagioclase up to 30 µm wide and then a zone of magnesian (K,Na) alkaline and fluorine-containing amphibole with a thickness of 20 µm - 40 µm. The contacts between these zones are very clear. Then the exoskarn zones follow, the first of which is composed of calcite with a low MgO content (0.22 wt.%), along the edges of the grains wollastonite develops (Fig. 1 a). interaction, a zone of MgCa-pyroxene is observed with an appoximately equal ratio of Ca and Mg (at.%), within which humite precipitation is observed. In this zone, isolated areas of wollastonitecarbonate composition are observed. Wollastonite forms elongated prismatic crystals up to 100 µm in length and 40 µm in width. The carbonate also appears in the form of elongated crystals and contains Ca>>Mg. The thickness of this zone is about 800 µm. The last zone of the exoskarn part of the column consists mainly of CaMg carbonate in the form of prismatic crystals, but more often rounded segregations, within and between which humite segregations containing up to 6% fluorine are observed. It is humite that is a silicate that concentrates Mg in the original dolomite and F and Si in the granite melt. Below is the phase composition of the zones of the interaction column between granite melt and carbonate, obtained at 700°C and 1 kb.

Mineral composition of endoscarn:

 $L \parallel L + Fsp \parallel Mull \parallel Pl \parallel Amf \parallel F-Phl + Cpx + Gum + Flu \parallel \blacksquare$

Mineral composition of exoscarn by zones:

||| Woll + CaCc + Gum || Cpx + Woll + MgCaCc || CaMgCc + Gum

Distribution of elements in the zone of direct contact between granite and dolomite can be observed in Xrays along the K α lines of Si, F, Ca, Na. Mg, Al, K (at 15 kV, 20 nA).



Figure 1. Boundaries of enzo- and endocontact zones between quenched F-containing granite melt and dolomite: a – experiment 87, 700°C, 1 kbar, 10% H_2O ; b - experiment 7487, 800°C, 4.5 kbar, 10% H_2O .

The zoning that emerged under experimental conditions at 800°C and 4.5 kb (Fig. 1b) differs significantly from that formed in the previous experiment conducted at 1 kb. In the endocontact zone in the marginal part of the granite glass, which was in direct contact with the carbonate rock, there is a zone of clinopyroxene of the diopside composition. which in the form of individual elongated grains also penetrates deep into the granite melt (Fig. 1b). In this pyroxene zone, small areas of alkaline F-containing amphibole are also observed. In the next endocontact zone, separated from the previous one by a small crack, predominantly fluorphlogopite crystallizes with small humite deposits. Closer to the carbonate part of the sample, a clinopyroxene subzone is observed. The width of the endocontact zones is 30-60 microns. The first exocontact zone is composed of Ca-carbonate and small deposits of humite and fluorphlogopite. It contains small grains of fluorite. Subsequent zones of the column are composed mainly of carbonate with a minor amount of humite. At first, the column material has a porous structure and F-phlogopite is found in it. Towards the end of the column the material becomes more dense, consisting only of carbonate richer in magnesium and a minor amount of humite. The thickness of the endoskarn zone is about 6 mm.

Mineral composition of endoscarn by zones:

L || L+Cpx || L+Cpx+Amf || F-Phl+Cpx+Gum+Flu || Mineral composition of exoscarn by zones: III CaCc+ Gum+F-Phl (porous zone) || CaMgCc+Gum
(dense zone)

A feature of the mineral composition of the samples in all experiments was the appearance of plagioclase, clinopyroxene, alkali amphibole, and phlogopite in the endocontact zone, and the appearance of wollastonite, Ca- or Ca-Mg carbonates, humite, and fluorite in the exocontact zone. This indicates active mutual diffusion of the elements: F, Si, Al, Na, K from the aluminosilicate melt into the carbonate rock, and Ca and Mg in the opposite direction. The fluorine content in the silicate melt decreases significantly after the experiment compared to the initial one from 1.5 to 0.3 wt.%. In carbonate rock, fluorine is detected by the appearance of fluorine-containing minerals of the humite group instead of forsterite (in systems without fluorine) and fluorphlogopite in the zones of interaction of granite melt with dolomite. The fluorine content in humite was 7-8 wt.%.

Conclusion. As a result of the experiment, new types of interaction columns between aluminosilicate melt and dolomite, which arise in the presence of fluorine, were obtained. The mineral composition in the zones of metasomatic columns depends on temperature and pressure: at 700°C, 1 kbar the first zones are composed of feldspars, at 800°C, 4.5 - clinopyroxene. This fact indicates a more intense mutual diffusion of components at higher parameters, carried out through the penetration and transfer of components in the composition of aqueous carbon

Legend: L – granite melt, tempered in the form of glass; Amf—alkaline amphibole; Gum – humite; Cpx – clinopyroxene (diopside); F-Phl -fluorphlogopite; Flu – fluorite; CaCc and CaMgCc are essentially calcium and calcium-magnesium carbonate, respectively; Woll – wollastonite; The black line is the conditional boundary of the endo- (to the left of the border) and exocontact (to the right of the border) zones.

dioxide fluid. Particularly high mobility during the interaction of granite melt with dolomite is exhibited by F, Ca, Mg, Si and, to a lesser extent, Na, K and Al.

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Suk N.I.¹, Damdinov B.B.², Kotelnikov A.R.¹, Damdinova L.B.³, Khubanov V.B.³ Solubility of phenakite in aluminosilicate melts. *UDC* 550.89:549.08

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Abstract. The solubility of phenakite (Be_2SiO_4) in aluminosilicate melts was experimentally studied at T = 1000 and 1100°C and P = 1 and 4 kbar under dry conditions and in the presence of 10 wt. % H₂O. The starting material was fused glass of granitic composition of different agpaiticity (1–2.5), as well as natural phenakite. It has been established that the solubility of phenakite depends on the composition of the aluminosilicate melt, increasing with its agpaitic content ((Na+K)/Al), and in water-containing melts the solubility of BeO is higher than in dry ones. An increase in solubility with increasing pressure is also observed. The experimental data obtained support the model of beryllium concentration in residual alkaline water-containing melts.

Keywords: phenacite, aluminosilicate melt, experiment

To study the dependence of the solubility of phenakite (Be₂SiO₄) on TP-parameters, a series of experiments were carried out at T=1000 and 1100°C and P=1 and 4 kbar under dry conditions and in the presence of 10 wt. % H₂O. The experiments were carried out on a high gas pressure vessel. The duration of the experiments was 5 days. The starting material was glass of granite composition of different agaiticity (1–2.5), previously melted in platinum crucibles at T=1250°C in a KO-14 furnace for 12 hours, as well as natural phenakite. The composition of the samples after the experiments was determined by electron probe X-ray spectral analysis, the beryllium content was determined by laser ablation mass spectrometry.



Fig. 1. Aluminosilicate glass with phenakite crystals (dark) after the experiment at $T=1100^{\circ}C$, P=1 kbar (sample Be-4).

As a result of the experiments, glass with phenakite crystals was obtained (Fig. 1). The composition of the glass was determined near the crystals. It was found that the solubility of phenakite depends on the composition of the aluminosilicate melt, increasing with its agpaitic content ($K_{agp}=(Na+K)/Al$) (Fig. 2). An increase in solubility with increasing pressure is also observed. It was noted that the BeO content in water-containing melts is higher than in dry melts (Fig. 2). At constant

pressure, an increase in temperature does not noticeably affect the solubility of phenacite in dry melts with K_{agp} less than 1.5 for P = 1 kbar and less than 2 for P = 4 kbar. In more alkaline melts with K_{agp} greater than 1.5-2, an increase in the BeO content in the melt is observed (Fig. 3) with increasing temperature, this is especially evident in water-containing systems.

In alkaline melts with an agpaitic coefficient greater than 1.5, drop-shaped and worm-shaped secretions and small crystals of presumably beryllium oxide or hydroxide formed around phenakite crystals were observed (Fig. 4). Figure 4a shows the complete decomposition of a phenakite crystal. This may indicate intensive removal of silica from phenakite. The experimental data obtained support the concentration of beryllium in residual alkaline watercontaining melts. Moreover, the beryllium content in these residual melts can be quite high, allowing the formation of large beryllium deposits due to its extraction with fluids from relatively small-volume magmatic bodies. These melts are formed during heterogenization phenomena in fluid-magmatic systems associated with decompression during the evolution of granitic melts.

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Fig. 2. Dependence of phenakite solubility in aluminosilicate melt (wt.%): $a - at T=1000^{\circ}C$; $b - at T=1100^{\circ}C$. (1 – in a water-containing system, 2 – in a dry system at P=1 kbar; 3 – in a dry system, 4 – in a water-containing system at P=4 kbar).



Fig. 3. Dependence of phenakite solubility in aluminosilicate melt (wt.%): a - at P=1 kbar; b - at P=4 kbar. (1 - in a dry system, 2 - in a water-containing system at T=1000°C; 3 - in a dry system, 4 - in a water-containing system at T=1100°C).



Fig. 4. Drop-shaped and worm-shaped secretions and small crystals of presumably beryllium oxide or hydroxide formed around phenakite crystals in alkaline hydrous aluminosilicate melts. $a - ample Be-11 (T=1100^{\circ}C, P=4 kbar), b - ample Be-18 (T=1000^{\circ}C, P=4 kbar).$

Suk N.I., Kotelnikov A.R. Experimental study of cassiterite solubility in aluminasilicate melts. UDC 550.89:549.08

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Abstract. The solubility of cassiterite (SnO₂) in aluminosilicate melts of various alkalinities was experimentally studied at T = 900°C and P = 2 kbar under dry conditions and in the presence of 10 wt. % H₂O. The starting material was fused glass of granitic composition of different agaiticity (1-2.5), as well as natural cassiterite. It was found that the solubility of cassiterite depends on the composition of the aluminosilicate melt, increasing with increasing its agpaitic content ((Na+K)/Al). At the same time, the SnO2 content in the water-containing melt is higher than in the dry one. With the initial agpaiticity of glass from ~1.5 to ~2, in dry systems an aureole with a thickness of 20 to 500 µm with increased alkalinity and a content of 6.8 to 22 wt.% SnO₂ is formed around cassiterite crystals. When the initial agpaiticity of the glass is ~2.5, the formation of crystals is observed, the composition of which corresponds to the theoretical formula (K,Na)₂(Sn,Si)₄O₉.

Keywords: cassiterite, aluminosilicate melt, experiment

The solubility of cassiterite (SnO_2) in aluminosilicate melts of various alkalinities was experimentally studied at T = 900°C and P = 2 kbar under dry conditions and in the presence of 10 wt.% H₂O. The experiments were carried out on a high gas pressure vessel. The duration of the experiments was 10 days. The starting material was melted glass of granitic composition of different agaiticity (1– 2.5), as well as natural cassiterite. The composition of the samples after the experiments was determined by electron probe X-ray spectral analysis.

As a result of the experiment, a column of glass with cassiterite crystals was obtained (Fig. 1).

To assess the solubility of cassiterite in an aluminosilicate melt, a metod to measure the diffusion profile of the SnO₂ content in tempered glass from the crystal boundary was used. Figure 2 shows an example of the measured diffusion profile of SnO₂ distribution during the dissolution of cassiterite in a granite melt. It was found that at a distance of ~200-250 μ m from the crystal, the SnO₂ content in the glass remains constant and then begins to decrease. This gives grounds to accept these maximum values as the solubility of SnO₂ in the melt.

It was found that the solubility of cassiterite depends on the composition of the aluminosilicate melt, increasing with increasing its agpaitic content ((Na+K)/Al). At the same time, the SnO₂ content in the water-containing melt is higher than in the dry melt (Fig. 3). No dependence of cassiterite solubility on pressure was found.

With an initial agpaiticity of glass from ~1.5 to ~2, in dry systems an aureole with a thickness of 20 to 500 μ m with increased alkalinity and a content of 6.8 to 22 wt.% SnO₂ is formed around cassiterite crystals (Fig. 4). Within the border in the sample Sn-4, the formation of feldspar crystals is observed (Fig. 4a). At an initial agpaiticity of glass of ~2.5, the formation of crystals around the cassiterite crystals is observed (Fig. 5), the composition of which corresponds to the theoretical formula (K,Na)₂(Sn,Si)₄O₉.

The work was supported by the FMUF-2022-0004 program.



Fig. 1. Experimental sample obtained in a watercontaining experiment at T=900°C, P=4 kbar (sample Sn-13).



Fig. 2. Diffusion profile of SnO_2 distribution (wt.%) during dissolution of cassiterite in granite melt.



Fig. 3. Dependence of cassiterite solubility on the composition of the aluminosilicate melt (wt.%). 1 - in a dry system, 2 - in a water-containing system at T = 900°C and P = 2 kbar; 3 - in a water-containing system, 4 - in a dry system at T = 900°C, P = 4 kbar.



Fig. 4. An aureole of glass with increased alkalinity, enriched with SnO_2 , around cassiterite crystals in dry systems at T = 900°C, P = 2 kbar. a – sample Sn-4. Within its boundaries, the formation of feldspar crystals is observed. b – sample Sn-3.



Fig. 5. Crystals formed around cassiterite crystals in dry systems. a – sample Sn-15, T=900°C, P=4 kbar; b – sample Sn-9, T=900°C, P=2 kbar.