Interaction in the systems of fluid–melt–crystal

Chevychelov V.Yu. Study of solubility of natural pyrochlore in granitoid melts. First experimental results. UDC 550.42

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Abstract. The initial model glasses of SiO_2-Al_2O_3-Na_2O-K_2O composition with 0.64, 1.10, and 1.70 mole $Al_2O_3/(Na_2O+K_2O)$ ratios were melted from the gel mixtures. Then the obtained glasses were remelted with addition of 0.2 N HF solution and 1 wt% LiF and 0.5 wt% CaO. Pyrochlore $(Ca_{1.1}Na_{0.8}Ce_{0.05}La_{0.05})(Nb_{1.8}Ti_{0.2})O_{5.9}F_{1.1}$ from the Vishnevogorsky niobium deposit was used in our experiments. The experiments were conducted in IHPV facility at T=750°C, P=100 MPa and duration of 5 days. It is shown that at pyrochlore dissolution the Nb content in the melt is several times lower than at columbite dissolution and even significantly lower than at tantalite dissolution. Although the form of the dependence line of the Nb content versus the alkalinity-alumina of the melt remains the same: the maximum concentration of Nb in the alkaline melt and it decreases with increasing alumina content. The straight dependence line on the diagram in the range of mole $Al_2O_3/(CaO+Na_2O+K_2O)$=0.64-1.10 is almost parallel to those dependencies for columbite and tantalite. But with further increase in the alumina melt, pyrochlore becomes unstable and its composition begins to change in the near-contact marginal zone. Primarily Na_2O, then F and CaO are removed from it, and SiO_2, Al_2O_3 and probably K_2O are introduced in the mineral from the melt. With a change in the composition of the dissolved mineral, the slope of the dependence line on the graph changes from negative to near 0 or weakly positive. Thus, it has been experimentally shown that pyrochlore is unstable in enriched with alumina granite melts at T=750°C and P=100 MPa. At the same time pyrochlore can be crystallized with a higher probability from alkaline Ca-, Na-, F-rich residual magmatic melts than columbite-tantalite, since the significantly lower saturation concentration of the melt in Nb requires for the crystallization of pyrochlore.

Keywords: *solubility; pyrochlore; experiment; aluminosilicate melts; granitoids; niobium; fluorine; columbite; tantalite.*

The initial model glasses of SiO_2-Al_2O_3-Na_2O-K_2O composition with 0.64, 1.10, and 1.70 mole $Al_2O_3/(Na_2O+K_2O)$ ratios were melted from the gel mixtures. The melting was been carried out in Pt capsules in high-temperature furnace with silicon carbide heaters (KO-14) at atmospheric pressure and at temperature of 600 to 1350°C for ≈1.7 days (about 0.7 days at 1350°C). Then the obtained glasses were remelted with addition of 0.2 N HF solution and 1 wt% LiF and 0.5 wt% CaO. These experiments were conducted in the presence of Ni-NiO buffer in internally heated pressure vessel (IHPV) at T = 900-1000°C, P = 100 MPa, and the run duration was ≈6 hours. Pyrochlore $(Ca_{1.1}Na_{0.8}Ce_{0.05}La_{0.05})(Nb_{1.8}Ti_{0.2})O_{5.9}F_{1.1}$ from the Vishnevogorsky niobium deposit was used in our experiments. The powder of model aluminosilicate glass, at preparing experiments to determine the solubility of pyrochlore in granitoid melts, was loaded in Pt capsule, one enough large fragment of crystalline pyrochlore was placed in the center, 2-3 wt.% solution HF was added and then capsule was sealed. The experiments were conducted in IHPV facility at T=750°C, P=100 MPa and duration of 5 days.

Polished microsections for investigation by the method of local X-ray spectrometer analysis were made from the obtained glass samples. That analysis was carried out in the glass along profiles perpendicular to the boundary of the crystal. As result of processing the analyzes, the solubilities of pyrochlore in granitoid melts were calculated, namely the maximum Nb concentrations in the melts directly at the crystal boundary. The chemical compositions of granitoid melts after the experiments are shown in Table 1. The obtained results are compared with the data on the solubility of columbite and tantalite at the similar conditions.

Table 1. Chemical compositions (wt.%, normalized to 100%) of granitoid melts after experiments on pyrochlore dissolution.

	F	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	O = F	A/CNK*
Alkaline melt (initial A/NK ≈0.64)	0.31	7.21	11.62	75.43	5.01	0.42	0.53	0.64
Subnormal melt (initial A/NK ≈1.10)	0.54	5.82	15.83	73.51	4.11	0.19	0.91	1.10
Enriched with Al_2O_3 melt (initial A/NK ≈1.70)	1.17	4.79	17.85	72.43	3.32	0.44	1.97	1.45

* A/CNK - coefficient of alumina, mole ratio $Al_2O_3/(CaO+Na_2O+K_2O)$.

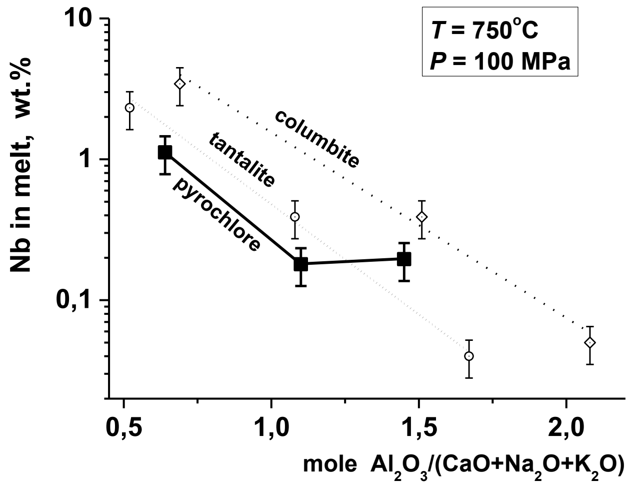

Fig. 1. The contents of Nb in aluminosilicate melts with different alkalinity-alumina at the dissolution of pyrochlore in the melt (as well as previous data on the dissolution of columbite and tantalite)

It is shown (Fig. 1) that at pyrochlore (it contains ≈67 wt.% Nb_2O_5) dissolution the Nb content in the melt is several times lower, than at columbite (≈58 wt.% Nb_2O_5) dissolution [Chevychelov et al., 2010; Chevychelov, 2013] and even significantly lower than at tantalite (≈38 wt.% Nb_2O_5) dissolution [Chevychelov, 2016]. Although the form of the dependence line of the Nb content versus the alkalinity-alumina of the melt remains the same: the maximum concentration of Nb in the alkaline melt and it decreases with increasing alumina content. The straight dependence line on the diagram in the range of mole $Al_2O_3/(CaO+Na_2O+K_2O)=0.64-1.10$ is almost parallel to those dependencies for columbite and tantalite. But with further increase in the alumina melt, pyrochlore becomes unstable and its composition begins to change in the near-contact marginal zone. Primarily Na_2O, then F and CaO are removed from it, and SiO_2, Al_2O_3 and probably K_2O are introduced in the mineral from the melt (Table 2).

Table 2. The chemical composition of pyrochlore after the experiments and the marginal zone of pyrochlore formed in enriched with alumina melt (wt%, normalized to 100%).

	F	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Nb_2O_5	Ce_2O_3	O = F
Pyrochlore	5.12	5.73	-	-	-	17.32	4.04	66.80	0.98	8.63
The modified marginal zone of pyrochlore at enriched with alumina melt	0.15	0.38	1.76	5.54	0.28	14.54	5.07	70.73	1.56	0.26

With a change in the composition of the dissolved mineral, the slope of the dependence line on the graph changes from negative to near 0 or weakly positive. Thus, it has been experimentally shown that pyrochlore is unstable in enriched with alumina granite melts at T=750°C and P=100 MPa. At the same time pyrochlore can be crystallized with a higher probability from alkaline Ca-, Na-, F-rich residual magmatic melts than columbite-tantalite, since the significantly lower saturation concentration of the melt in Nb requires for the crystallization of pyrochlore.

Acknowledgments. This study was financially supported by the RFBR, project № 18-05-01001A.

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Chevychelov V.Yu. Influence of fluorine on solubility of aqueous chloride fluid in rhyodacite melt. UDC 550.42

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Abstract. The solubility of H_2O-Cl-F-containing fluids of various concentrations (from 0 to 7M HCl and from 0 to 7M HF) in rhyodacite melt was studied experimentally. During preparation of the experiment powder of pre-synthesized homogeneous glass was loaded in Pt capsule, then initial solution filled in, and the capsule sealed. The experiments were carried out in internally heated pressure vessel (IHPV) at T= 1000°C and P= 200 MPa. The experiment duration was 5 days. The obtained glass samples were studied by local X-ray spectral microanalysis. The H_2O content of these glasses was evaluated using literature data. The contents of F and Cl in the fluid after the experiment were estimated by mass balance calculation. As a result, the influence of fluorine on the chlorine content in the rhyodacite melt and also influence of chlorine on the fluorine content in the same melt was estimated. It is shown that at Cl content in the fluid less than ≈20 wt.%, the F addition to the system reduces the Cl content in the melt. For example, at ≈10 wt.% Cl in the fluid, the Cl content in the melt decreases from ≈0.75 wt.% (the system does not contain F) to ≈0.65 wt.% (at 3*M* HCl+7*M* HF starting solution). It is also shown that at F content in the fluid about 2-4 wt.%, the Cl addition to the system decreases the F content in the melt. For example, at ≈4 wt.% F in the fluid (7*M* HF starting solution) about 1.71 wt.% F dissolves in the melt, and at Cl addition in the system (7*M* HF+7*M* HCl starting solution) the F content in the melt decreases to ≈1.35 wt.%.

Keywords: *experiment, solubility, fluorine, chlorine, aqueous fluid, rhyodacite melt, mutual influence of volatile components.*

The solubility of H_2O-Cl-F-containing fluids of various concentrations (from 0 to 7*M* HCl and from 0 to 7*M* HF) in rhyodacite melt was studied experimentally. During preparation of the experiment powder of pre-synthesized homogeneous glass was loaded in Pt capsule, then initial solution filled in, and the capsule sealed. The experiments were carried out in internally heated pressure vessel (IHPV) at T= 1000°C and P= 200 MPa. The experiment duration was 5 days. The obtained glass samples were studied by local X-ray spectral microanalysis. The H_2O content in these glasses was evaluated using literature data [Chevychelov et al., 2008]. The contents of F and Cl in the fluid after the experiment were estimated by mass balance calculation [Chevychelov, 2013].

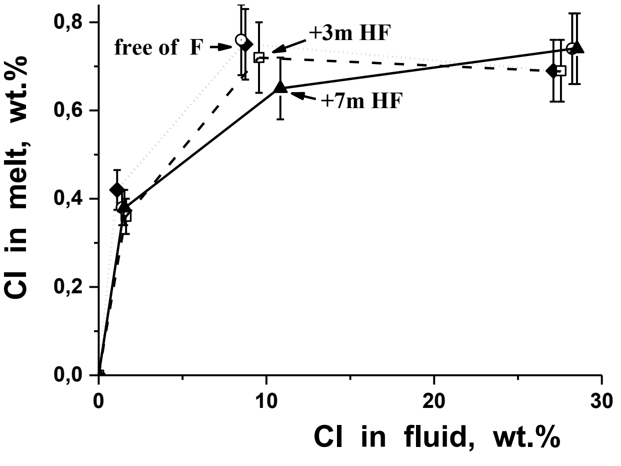

Fig. 1. Effect of fluorine additive in the system on the solubility of aqueous chloride fluid in the rhyodacite melt.

As a result, the influence of fluorine on the chlorine content in the rhyodacite melt and also influence of chlorine on the fluorine content in the same melt was estimated. It is shown in Fig. 1, that at Cl content in the fluid less than ≈20 wt.%, the F additive in the system reduces the Cl content in the melt. For example, at ≈10 wt.% Cl in the fluid, the Cl content in the melt decreases from ≈0.75 wt.% (3*M* HCl starting solution, the system does not contain F) to ≈0.65 wt.% (3*M* HCl + 7*M* HF starting solution). It is shown in Fig. 2, that at F content in the fluid about 2-4 wt.%, the Cl additive in the system decreases the F content in the melt. For example, at ≈4 wt.% F in the fluid (7*M* HF starting solution, free of Cl) about 1.71 wt.% F dissolves in the melt, and at Cl addition in the system (7*M* HF + 7*M* HCl starting solution) the F content in the melt decreases to ≈1.35 wt.%.

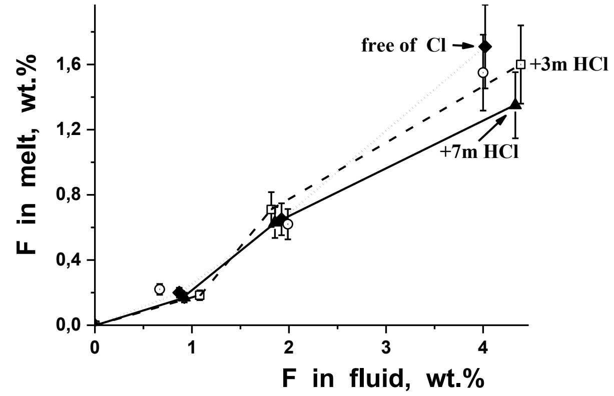

Fig. 2. Effect of chlorine additive in the system on the solubility of aqueous fluoride fluid in the rhyodacite melt.

Acknowledgments. This study was financially supported by the RFBR, project № 18-05-01001A.

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Khodorevskaya L.I., Varlamov D.A. Experimental study of amphibolite interaction with carbonate-alkaline fluid at 900°C and 6.5 kbar UDC 553.065.1

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Abstract. The results of studying the compositions of melts and mineral phases formed during the interaction of amphibolite (according to geochemical characteristics close to E-MORB) with H_2O-NaCl±CO_2 fluid at 5-7 kbar, 900°C are presented in article. The main phases after experiences are presented by amphibole and a quenching melt; the tiny crystals of Fe oxide with Ti impurity are sometimes noticeable. It is shown that increase in molar fractions of NaCl in an initial fluid leads to growth of contents of SiO_2 and (Na_2O+K_2O) in the resulting melts. Andesite-dacites, melted during the dehydration melting of amphibolite, are replaced by trachydacites and trachytes. The compositions of the melts, obtained both in the presence of the H_2O-NaCl fluid and the H_2O-NaCl-CO_2 fluid, are identical in the contents of the petrogenic components, however, among the mineral phases, a carbonate phase $(Ca_{0.25}Fe_{0.75})CO_3$ appears along with the amphibole. The results of the experiments are applicable to models of the formation of alkaline melts in oceanic crust rocks.

Keywords: *amphibolite, Na-K chlorides, melt, alkaline melt, carbonates, fluid interaction, metasomatism*

Lower crust chlorides, along with H_2O and CO_2, are the most important constituents of a fluid phase. Regardless of their genesis (juvenile chlorides or those associated with pore fluid remobilization) such fluids affect the mineral composition of rocks and are responsible for the composition of the melts produced. High salt concentrations in fluid contribute to changes in rock melting temperature (Aranovich, Newton, 1996 et al.), affect the compositions of co-existing phases, the solubility of rock-forming minerals and the transfer of rare-earth and trace elements (Newton, Manning, 2010 et al.).

The results of analysis of the compositions of melts and mineral phases, formed upon the interaction of amphibolites, geochemically similar to E-MORB, with the fluids H_2O–NaCl±CO_2 at a pressure of 6.5 kbar and a temperature of 900°C are reported. The composition of reference amphibolite (mas. %) was: SiO_2 – 47.59, TiO_2 – 1.37, Al_2O_3 – 13.39, FeO – 12.43, MnO – 0.06, MgO – 7.67, CaO – 11.21, Na_2O – 3.06, K_2O – 0.92, P_2O_5 – 0.49, Cl – 0.13, total 98.32 mas.%. The rock consists of 70-75 vol.% amphibole (SiO_2 – 40.80, TiO_2 – 2.17, Al_2O_3 – 11.47, FeO – 17.22, MnO – 0.19, MgO – 9.57, CaO – 11.25, Na_2O – 2.62, K_2O – 1.46, Cl – 0.80, H_2O (loss on ignition) – 1.8, total – 99.35 mas.%), and 25-30 vol.% plagioclase An_{46} (SiO_2 – 56.61, TiO_2 – 0.04, Al_2O_3 – 26.51, CaO – 9.46, Na_2O – 6.40, K_2O – 0.08, total – 99.10 mas.%). The composition of the initial fluid phase was preset by the varying ratio of salt NaCl (c.p.), distilled water and oxalic acid $H_2C_2O_4 \times 2H_2O$ (c.p.) and H_2O. A weighed quantity 25–40 mg of reference amphibolite was placed into a vertically positioned ampoule (5 mm in diameter and 50 mm in height). NaCl and $H_2C_2O_4 \times 2H_2O$, H_2O were then poured into the ampoule. 10-20-fold excess of fluid relative to a mineral sample was created in the ampoule to be able to diagnose the number of newly-formed phases. Upon filling, the ampoules were weighed, sealed, overturned and shaken vigorously for a more uniform solution-rock distribution. The experiments were carried in gold ampoules to avoid losses of iron in walls of ampoules. Oxygen fugacity was not controlled and was assumed to be close to the buffer Ni-NiO (Helz, 1976). The experiments were conducted in apparatuses with gas pressure and internal heating (gas bombs) at the Institute of Experimental Mineralogy, RAS. The experiments were carried out for 4 days, and then hardening was done. The temperature controlling and measuring error was ±7°, the pressure measurement error was ±10 MPa, and the hardening rate was 100°/min. After the experiments the ampoules were opened, solid sample was extracted from the ampoule and washed with distilled water. Each sample was then placed into a container, embodied into epoxy glue, polished and analyzed by a method for local X-ray microprobe analysis using a CamScan MV2300 (VEGA TS 5130MM) scanning electron microscope equipped with an INCA-350 Energy dispersion X-ray spectrometer (Laboratory of Electron Microscopy and Microanalysis, IEM, RAS). The time taken for spectrum collecting is 70 s for various phases.

Two series of experiments were conducted. The results of experiments on the interaction of amphibolites with one-phase fluid (water-salt, H_2O-NaCl) fluid, where X_{NaCl}=0.06-0.33, in L-series experiments and those with two-phase fluid (H_2O-NaCl-CO_2) in N-series experiments, are reported. The H_2O-NaCl±CO_2 ratio, preset in the initial fluid, is shown in Fig. 1.

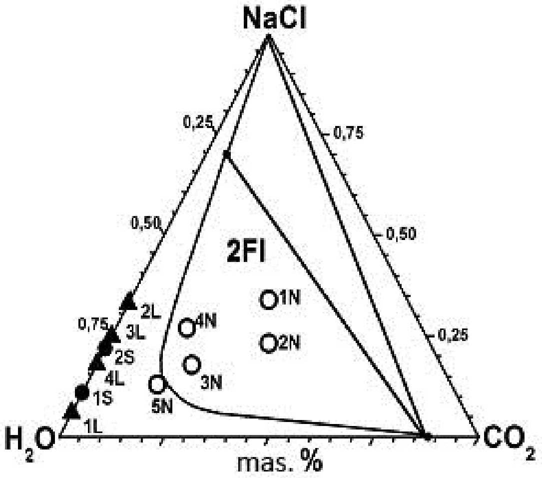

Fig. 1. The composition of the fluid phase preset in the experiment on a H_2O-CO_2-NaCl phase diagram (800°C and 9 kbar (Shmulovich, Graham, 2004). Triangles (L-series) and circles (N-series) in the figure are the numbers of experiments.

Major phases after L-series experiments (initial fluid is H_2O-NaCl) are amphibole, melt, biotite and Fe oxides. In N-series (initial fluid is H_2O-NaCl-CO_2), amphibole, melt and scarce biotite occur together with carbonates (Fig. 2).

At the preset parameters amphibole remained a major phase after the experiments. All amphiboles are in a Ca amphibole group, in which $(Ca+Na)_B > 1.50$ and $Na_B < 0.50$ are similar to pargasite (the position distribution of amphibole cations was assessed and Fe^{3+}/Fe^{2+} ratios were calculated under the program script described in (Schumahfeer, 1997). The iron content of the mineral is (f = FeO/(FeO+MgO) ≈ 0.1). The low Fe concentration of the mineral is due to preferential Fe redistribution relative to Mg into the fluid and/or melt and into carbonates in N-series. Figure 3 shows that L-series amphiboles display a higher Ca/(Ca+Na+K) ratio than N-series amphiboles which occurs due to the removal of part of Ca from amphibole into carbonates.

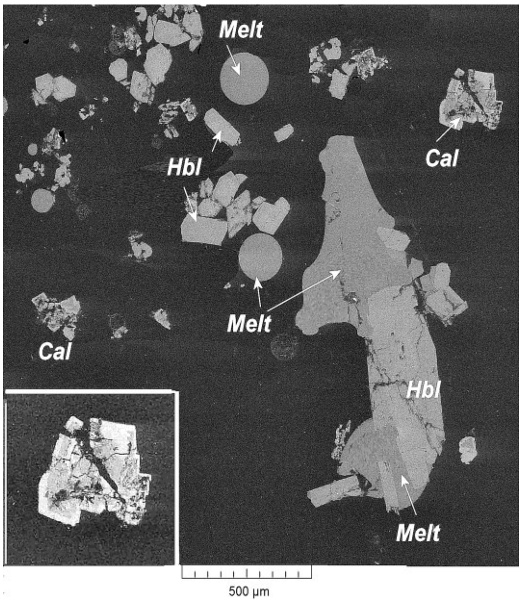

Fig. 2. Photographs of the products of experiment N-5 in inversely scattered electrons, Hbl = amphibole, Cal = carbonate, melt (Melt) around an amphibole crystal and its spherical shapes. The insert shows zonal carbonate.

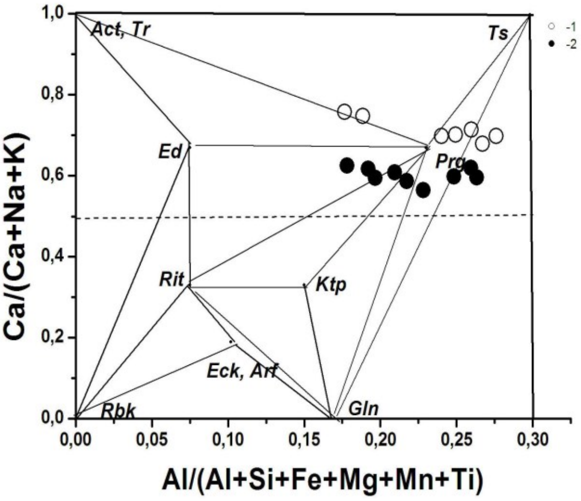

Fig. 3. Al/(Al + Si + Fe + Mg + Mn + Ti)–Ca/(Ca + Na+ K) ratio in amphiboles: 1 – experiments with the initial fluid H_2O-NaCl, 2 – those with the fluid H_2O-NaCl-CO_2

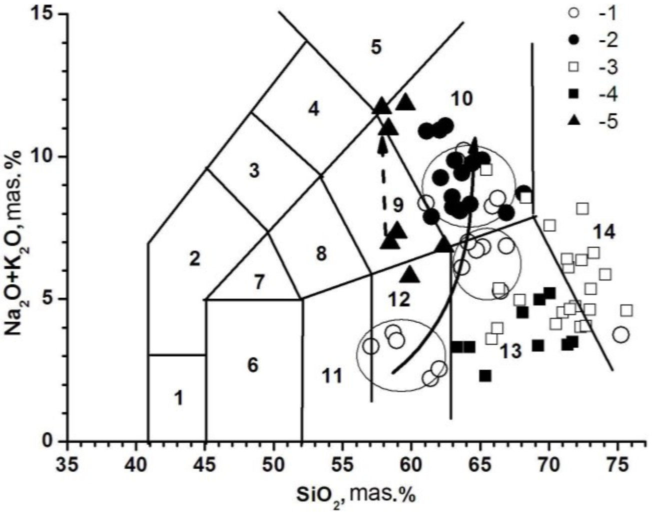

Fig. 4. SiO_2–(Na_2O+K_2O) ratio in the melts obtained in the experiments. *Fig. captions:* 1–2- L-and N-series experiments, respectively; 3–4 dehydration and water-saturated melting of metabasic rocks (Helz, 1976; Beard, Lofgren, 1991); 5–melting of alkaline basalt upon interaction with H_2O-CO_2 fluid (Kazuba, Wendlandt, 2000). *Numbers in Fig.4* show composition fields: 1–picrobasalt, 2–basanite and tephrite, 3–phonotephrite, 4–tephriphonolite, 5–phonolite, 6–basalt, 7–trachybasalt, 8–basaltic trachyandesite, 9 – trachyandesite, 10 – trachydacite and trachyte, 11 – basaltic andesite, 12 – andesite, 13 – dacite, 14 - rhyolite. Classification diagram (Le Bas et al., 1986).

In addition to amphiboles, scarce wonesite *(Mca)* – trioctahedral mica, structurally similar to phlogopite, in which K is almost entirely replaced by Na (with minor Ca impurity) (Spear et al., 1981) crystals were encountered after the experiments. The mineral contains 0 to 0.3–0,5 mas. % chlorine, TiO_2 = 0.20 f.u., $f \approx 0.05$-0.20. The melt, which flows around amphiboles and evolves along fractures in minerals in all the experiments, occurs together with *Hbl* and *Mca*. The melt also occurs in the form of spheres up to 200 µm in size. (Fig. 2). Such spheres are typically formed in experiments on alumosilicate melting in water-salt solutions because two liquids (melt and fluid) are not wettened (Newton & Manning, 2008). The chemical compositions of the spheres and intergranular melt are identical, suggesting that they were produced by incongruent amphibolite melting. SiO_2 concentration in such melts is 57-65 mas. %. Noticeable melt spheres occasionally encountered together with tiny (< 10 µm) drops either among amphiboles or on their surface. Such tiny drops are a hardening fluid, i.e., the precipitation of dissolved amphibole elements from a fluid phase upon hardening. This hardening fluid contains much higher SiO_2 concentrations (68-97 mas.%).

The SiO_2 – (Na_2O+K_2O) ratios in the melts, obtained in our experiments, are shown in Fig. 3.

It is clear from the figure that Na_2O+K_2O and SiO_2 concentration in the melts increases with increasing NaCl in the fluid (L-series, arrow in Fig. 4). Andesite-dacite, molten upon dehydration melting of amphibolites, is succeeded by trachydacite and trachyte. Melts, produced at a varying H_2O-CO_2-NaCl ratio (N-series), are in a trachydacite-trachyte field. All the melts are quartz-normative. According to (Kazuba, Wendlandt, 2000), melts produced by the interaction of alkaline basalt with fluid H_2O-CO_2 (X_{CO2}=0.22-0.49) at a temperature of 1025°C and a pressure of 7-10 kbar, are also in the trachyte field (triangles in Fig 4). Thus, Fig. 4 shows that melts, produced by partial metabasic rock melting in the presence of H_2O-NaCl±CO_2 fluids contain higher alkali concentrations and slightly lower SiO_2 concentrations than melts obtained upon the dehydration melting of metabasic rocks and upon melting with excess H_2O (Helz, 1976; Beard, Lofgren, 1991).

The Fe- Ca carbonates were encountered along with amphibole and melt in N-series experiments. Carbonates occur as well-defined rectangles, commonly 50 μm and lesser 200 μm in size. Carbonates are heterogeneous in composition: one can see in the inset in Fig. 2 that the mineral margins are lighter, suggesting that its margins contain more Fe (up to $FeCO_3$) than the grain centre. Carbonates in the middle of the grains are composed of $(Ca_{0.25}Fe_{0.75})CO_3$.

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Persikov E.S., Bukhtiyarov P.G., Nekrasov A.N. Kinetics of interaction of hydrogen with basalt melt.

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Abstract. Continuation of our early works, an experimental study of the kinetics and interaction mechanisms in the hydrogen-basalt melt system at a hydrogen pressure of 100 MPa and a temperature of 1250 oC was carried out. It has been established in kinetic experiments that, despite the high reduction potential of the H_2 - the melt system, the reactions of hydrogen oxidation and complete reduction of Fe, Ni, Co oxides in the melt do not go to the end. As a result, the initially homogeneous basaltic melt becomes heterogeneous, new phase is formed - small metal separations of different structures. This experimentally established fact fully agrees with the natural data on the findings of small amounts of the metallic phase, primarily iron and its alloys with nickel and cobalt, in magmatic rocks of different composition and genesis. It is characteristic that many features of inclusions of the metallic phase in igneous rocks (dimensions, morphostructure, composition) are well correlated with those observed in the experiments carried out.

***Keywords:** basalt, hydrogen, melting relations, kinetics, high temperature and pressure, crust, metals*

The role of hydrogen in natural processes is extremely diverse and in recent years has attracted increasing attention of petrologists and geochemists. In the course of our earlier studies (Persikov et al., 1986), an experimental study of the kinetics and interaction mechanisms in the hydrogen-basalt melt system at a hydrogen pressure of 100 MPa and a temperature of 1250 °C was carried out. The experiments have been done using an original high gas pressure apparatus with internal heater (IHPV). The apparatus includes a gas compression system (Ar), which creates a pressure in the (IHPV). A unique device is installed inside this (IHPV), which ensures experiments at high temperatures and hydrogen pressures (Persikov & Bukhtiyarov, 2002). The scheme of this device together with the scheme of the internal heater of a (IHPV) are shown in Fig. 1. The internal volumes of the reactor (5) with a molybdenum ampoule with a starting sample (6) and equalizer-separator (9) under the piston (10) were filled with hydrogen at a pressure of 10 MPa using a special system. The device assembled in this way, together with the internal heater (2), was placed inside the (IHPV) in such a way that the ampoule was in the gradientless temperature zone of the heater. Due to the displacement of the piston (10), the gas pressure (Ar) in the vessel during the experiment was always kept equal to the hydrogen pressure in the internal volume of the reactor (5). At the beginning of the experiment, the argon pressure in the (IHPV) and, correspondingly, hydrogen in the reactor (5) was raised for one hour to the required value of 100 MPa.

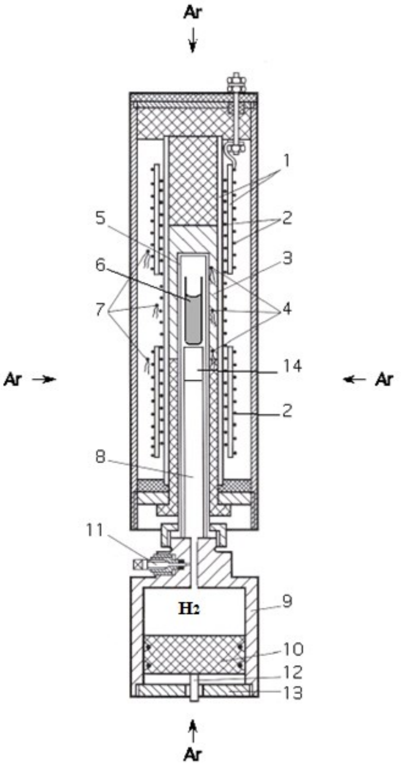


Fig. 1. Scheme of the original internal device (equalizer-separator) of a (IHPV)
1,3 - insulators; 2 - two sectional internal heater; 4 - measuring thermocouples; 5 - molybdenum reactor; 6 - Mo ampoule with a sample; 7 - control thermocouples; 8 - a stopper; 9 - shell equalizer-separator; 10 - the piston; 11 - the valve; 12 - piston position sensor; 13 - cover; 14 - Pt capsule with oxygen buffer.

Table. Chemical compositions (wt. %) and structural-chemical parameter (100NBO/T) of starting basalt and basalt glasses after experiments under hydrogen pressure.

Components	№ 2099*	№ 2100*	Starting basalt composition
	1 hour	5 hours	
SiO_2	53.27	53.59	51.52
Al_2O_3	14.09	13.74	13.87
FeO	5.66	6.91	8.37
MnO	0.31	0.32	0
MgO	10.02	9.58	9.68
CaO	12.26	11.57	12.15
Na_2O	2.41	2.44	2.48
K_2O	0.89	0.87	0.9
TiO_2	1.0	0.98	0.97
Sum	100	100.01	99.94
100NBO/T	78.3	79.3	85

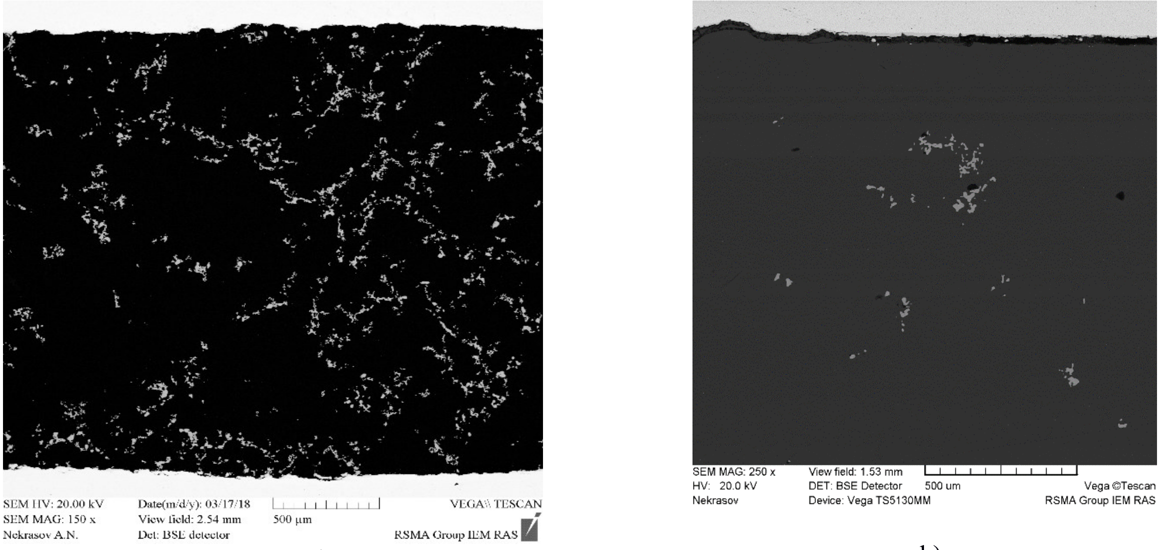
*Note:** - experiments with melts of the starting magnesian basalt (P (H_2) = 100 MPa, T = 1250 ^{oC}).

Further, the temperature of the experiment was raised to the required value of 1250 ° C. With these parameters, the samples were maintained in automatic mode for the necessary time of kinetic experiments (1 hour in the first series of experiments and 5 hours in the second). After that, the isobaric quenching was carried out with the internal heater of the unit switched off. At the same time, a sufficiently high melt quenching rate (~ 300 ° C / min) was achieved, which ensured the production of glasses. The error in measuring the temperature of the experiment was ± 5 ° C, and the hydrogen pressure ± 0.1% rel. After isobaric quenching, the device was removed from the vessel, Mo ampoule with the sample was extracted from the molybdenum reactor for the subsequent microprobe analysis of the phases formed in the melt during the experiment. As starting samples used powdered in an agate mortar powder magnesian basalt of the Great Fissure Eruption 1975-1976, Volcano Tolbachik in Kamchatka (Big ..., 1984). The chemical compositions of the starting sample and the glasses obtained in the experiments were determined using an X-ray microprobe analyzer (see Table).

The compositions of melts obtained in experiments with hydrogen are compared with the composition of natural magnesian basalt (see Table). The comparison criterion is not the concentrations of the main rock-forming components of the melts, but the gross basicity of such melts, which is numerically determined by the structural-chemical parameter 100NBO/T, is the degree of depolymerization (percentage of broken bonds in the melt structure) or the basicity coefficient. This structural chemical parameter of the melts reflects correctly enough the basicity of magmatic melts and, accordingly, the peculiarities of the total chemical composition and structure of silicate and igneous melts, which was explained in detail earlier (Persikov et al., 1990; Persikov, 1991; Mysen, 1991; Persikov, Bukhtiyarov , 2009).

The main experimental features of the interaction of hydrogen with basalt melt are as follows:

1. It has been established in kinetic experiments that, despite the high reduction potential of the melt + H_2 system, the reactions of hydrogen oxidation and complete reduction of Fe oxides in the melt do not go to the end. As a result, the initially homogeneous basaltic melt becomes heterogeneous, and small metallic segregations of different structures are formed in it (Fig. 2a, 2b), and H_2O.



a) b)

Fig. 2. Grinds of magnesian basalt glasses after experiments.a) - experiment No. 2099, the duration of the experiment is 1 hour (the white color - metal phase, the black color - basalt glass, grey color – Mo ampoule); b) - experiment No. 2100, duration of the experiment 5 hours (the white color - metal phase, the black color - basalt glass, the gray color – Mo ampoule).

These reactions can be represented schematically as follows:

$$Fe_3O_4 + H_2 \Rightarrow 3FeO + H_2O,\ FeO + H_2 \Rightarrow Fe + H_2O \qquad (1)$$

The stopping of reactions (1) in the basalt melt is also confirmed by the data given in the table when comparing the compositions of melts formed in kinetic experiments of different duration. Practically the reactions (1) are completed already in the hourly experience, because the concentration of iron oxide in the melt even slightly increases with a 5-hour experiment. Calculations performed on the basis of buffer equilibria showed that the stopping of reactions (1) in melts should occur with an increase in the oxygen potential to $f(O_2) \sim 10^{-12}$ MPa, which corresponds to a partial pressure of H_2O in the gas phase of ~ 5 MPa and a concentration of H_2O in melt ~ 3 mol. % at total pressure $P_{fl.} = P(O_2) + P(H_2) + P(H_2O) = 100$ MPa and T = 1250 °C. If we take into account that in the experiments the initial ratios of the partial pressures of H_2, O_2 and H_2O in the gas phase are completely different: $P(O_2) = 10^{-20}$ MPa, $P(H_2) = 100$ MPa, $P(H_2O) = 10^{-12}$ MPa, then it becomes obvious that the water formed in the melt during oxidation-reduction reactions (1) will diffuse into the gas phase, but at a much lower rate compared to the counter-diffusion of hydrogen.

2. It is also important to emphasize that melts after completion of reducing reactions with hydrogen become more acidic than the original melt, their basicity, and accordingly, 100NBO / T decrease mainly due to the loss of iron oxide (see the table).

3. The process of Fe separations of a liquid-like morphostructure (balls of different sizes, loops, spongy iron) is undoubtedly of a complex nature (Fig. 3).

Such Fe structures obviously do not indicate melting of iron under hydrogen pressure at temperatures of ~ 290 °C lower than the melting point of pure iron at atmospheric pressure. This seems not real. It is not excluded that such iron structures are formed by the formation of coalitions of reduced iron atoms due to surface tension forces in the basalt melt. It is likely that the wettability at the melt-metal interface also has a certain significance. This experimentally established fact fully agrees with the natural data on the findings of small amounts of the metallic phase, primarily iron and its alloys with nickel and cobalt, in magmatic rocks of different composition and genesis (Fig. 4a, 4b). It is characteristic that many features of the inclusions of the metallic phase in igneous rocks (size, morphostructure, composition) are well correlated with those observed in the experiments.

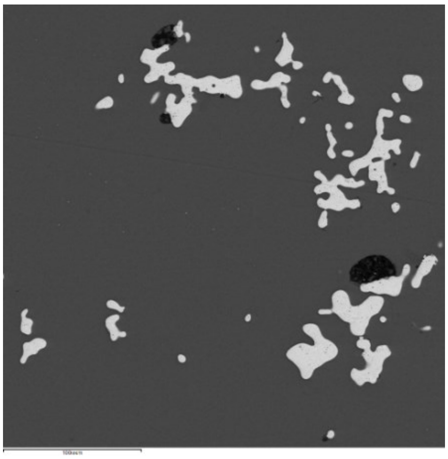
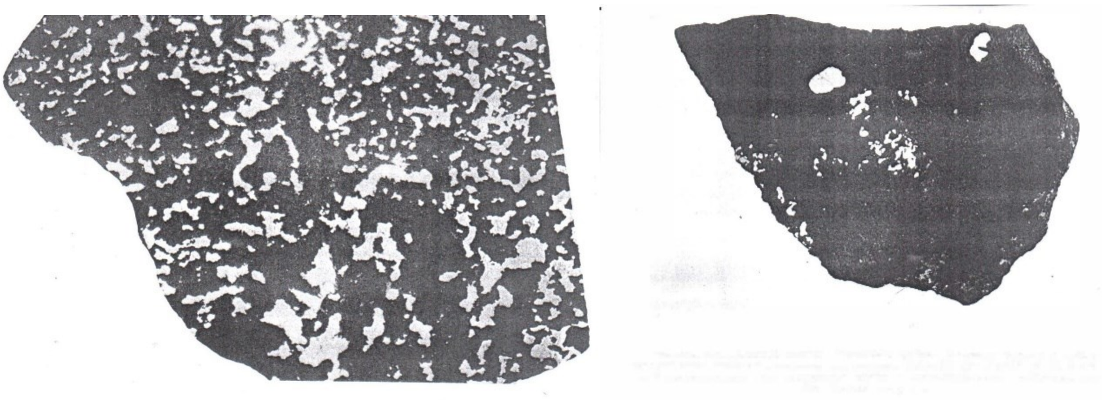


Fig. 3. Morphostructure of metallic iron in a basalt melt as the result of interaction with hydrogen (white color - metallic iron, black color - basalt glass, experiment No. 2100).



a **b**

Fig. 4. a - Disseminated ore of native iron in gabbro-dolerite, intrusion of mountain Ozernoy, natural size; b - Poor-grained ore of native iron in olivine-bearing gabbro-dolerite. The Khungtukun trap intrusion, the north of the Siberian platform. Sample-Hung-62, natures. led. (white color - native iron, black color - gabbro-dolerite) [Ryabov et al., 1985].

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