Mineral equilibria at high PT-parameters

Butvina V.G²., Smirnova M.D.¹, Safonov O.G.², Van K.V.² Experimental modeling of subsolidus parageneses of ultramafic lamprophyres of the Irkeneeva-Chadobets trough, South -Western Siberia, at high PT-parameters. UDC 552.13

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Abstract. Paper presents the results of experiments on Devonian ultramafic lamprophyres from the Ilbokich uplift, Erkeneeva-Chadobetskaya trough, South-Western margin of the Siberian craton (Kargin et al., 2016). The studied rocks characterize the diversity and complexity of the Devonian alkaline magmatism of the region, they are manifested in the form of a series of low-power (5-100 cm) dikes, which were found in the core of the well at the Ilbokich Gas-condensate field. The experiments were carried out on the "anvil with a hole" type installation NL-13T in IEM RAS at pressures of 4 and 5 GPa and temperatures of 1100 - 1500°C. The results of the experiments showed that at a pressure of 5 GPa, paragenesis is obtained, which differs from the natural association of minerals: in the experiments, the appearance of clinohumite is observed, there is no olivine in the products of experiments conducted at temperatures below 1500°C. At 4 GPa there is a mineral paragenesis similar to the natural one: mica-olivine-pyroxene rock with carbonate minerals in the bulk. In all experiments, the paragenesis and composition of minerals are identical, the only difference is in their ratio. Thus, the composition of paragenetic minerals obtained by melting natural aillikites at 4 GPa is more consistent with the paragenesis of natural samples, which may indicate P-T parameters of formation of natural Siberian aillikites under identical thermodynamic conditions.

Keywords: aillikites, alkaline-ultramafic lamprophyres, high-pressure experiment, experimental geochemistry, aillikites paragenesis, Chadobets uplift, Ilbokich uplift, Siberian craton

Introduction. This paper discusses results of experiments on partial melting of samples of aillikites from Ilbokich and Chadobets uplifts (SW Siberia) at 5 GPa and $1150 - 1500^{\circ}$ C and 4 GPa, $1450-1600^{\circ}$ C. Experiments allow us to determine the paragenesis, characteristic of a complex carbonate-silicate systems under different thermodynamic conditions and characterize the behavior of such associations in nature.

The object of study became ultramafic lamprophyre the South-Western margin of the Siberian craton, found on Ilbokich uplift in Irkineyevo-Chadobets trough. Lamprophyres form low-power dikes with a capacity of up to 1.5 m. They were also found in the core of the Ilbokich gas condensate field (Kargin et al., 2016). Using standard classification schemes, it is difficult to systematize

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rocks. However, according to classification scheme (Tappe et al., 2005), these rocks are classified as aillikites. They are characterized by a porphyritic an/or globular texture, are enriched in primary magmatic carbonates (up to 25 wt.% of bulk CO₂), show great variety of olivine xeno- and/or phenocrysts, and rare pyroxene phenocrysts. Groundmass is composed of carbonates, phlogopite, clinopyroxene, spinel, ilmenite, rutile, perovskite, Ti-garnet, and K-feldspar. Variety of mineral assemblages, their composition and morphology indicate multi-stage evolution of the rocks, which included early magmatic, late magmatic and autometasomatic stages. Experiments on the melting of these rocks will reveal mineral parageneses characteristic of different thermodynamic conditions and, in conjunction with petrological data, suggest the mechanism of formation of such rocks.

Petrologically studied samples from Ilbokich uplift and also from similar rocks of Chadobets uplift (Nosova et al., 2018). The studied rocks are characterized by porphyre and/or globular structure, enriched with magmatic carbonate (up to 25 wt.%) and phenocrysts of olivine, less commonly of pyroxene. The mineralogical composition of rocks indicates several stages of rock evolution, including late autometasomatic transformations. Therefore, it is very difficult to assess the conditions of rock formation, moreover, it is extremely difficult to identify unambiguously mineral parageneses of any stage. However, the identification of minerals characteristic of solidus paragenesis and PT parameters of rock crystallization is important for understanding the Genesis. To evaluate the thermodynamic parameters of aillikites was applied monomineral olivine thermometer (De Hoog, 2010) and evaluation of TP-parameters of other researchers (Tappe et al., 2006). Studies have shown that possible conditions for the formation of aillikites were 5 GPa and $1200-1400^{\circ}C$ (Smirnova et al., 2017). The PT conditions of the experiments were chosen according to these results.

Experimental methods. The experiments were carried out at 5 GPa and $1150 - 1500^{\circ}$ C and at 4 GPa and $1450 - 1550^{\circ}$ C (see table 1), and on the basis of the results of the experiments an experiment was conducted with the addition of oxalic acid at 5 GPa and 1350° C. The duration of the experiments ranged from 3 to 10 hours depending on the temperature (Fig.1).



Fig.1. Conditions and phases obtained as a result of the experiment.

Experiments were carried out with rock powder, as well as with the addition of 20% oxalic acid to the starting mixture. For experimental work, the least remodified by petrographic and geochemical data, as well as the most representative sample was selected. Sample IIb28 is characterized by idio - and subidiomorphic olivine phenocrysts (200-900mkm), partially or completely replaced by secondary minerals (serpentine, bowlingite). In olivines partially unchanged may remain up to 90% of the original grain, in such cases, as a rule, there is a concentric zoning. The bulk of the rock is represented by phlogopite, carbonate, garnet, Apatite, magnetite, spinel, and pseudomorphoses of ilmenite and rutile perovskite. Clinopyroxene with spotted zonality and xenomorphic amphibole are found as accessory minerals. Probably, some minerals, such as garnet, clinopyroxene and amphibole were formed at the late autometasomatic stages of rock crystallization.

The experiments were performed using a toroidal high-pressure anvil-with-hole type apparatus (NL-13T) at the Korzhinskii Institute of Experimental Mineralogy of Russian Academy of Sciences (IEM RAS), Chernogolovka (Litvin, 1991). The limestone high-pressure cell (working volume is 0.1-0.15 cm³) prepared individually for each run is equipped with a graphite heater of 8 mm in length, 7.5 mm in diameter, and 0.75 mm wall thickness. The capsule was placed in the center of the cell on the holders of pressed MgO and BN mixture made (MgO:BN=3:1). Pressurization of the cell was accomplished using the uni-axial compression of upper and lower anvils in a 500-ton hydraulic press. Pressure at room temperature was calibrated using bismuth phase transitions at 2.55 (Bi I – Bi II), 2.7, and 7.7 (Bi III – Bi V) GPa, as well as barium phase transition at 5.5 GPa. Run pressure was controlled to \pm 0.1 GPa. The current power setting control of temperature has been used. The temperature-current

power dependence of the cell was calibrated using a Pt₇₀Rh₃₀/Pt₉₄Rh₆ thermocouple without pressure correction. The cells were recalibrated after several runs to check the reproducibility of the temperaturecurrent power dependence. Run temperature was controlled within ±20°C using a MINITHERM-300.31 controller. This accuracy includes an error of the $Pt_{70}Rh_{30}/Pt_{94}Rh_{6}$ thermocouple used in calibration, self-accuracy of the controller, and an error resulted from the thermogradient in the cell. Experiments were quenched by shutting power off subsequently depressurized. and Microprobe analyses. Each run sample was embedded in epoxy and polished. After preliminary examination in reflected light, the microscopic features of run products and phase compositions Microprobe analyses of minerals were performed using CamScan MV2300 (VEGA TS 5130MM) electron microscope equipped with EDS INCA Energy 350 and Tescan VEGA-II XMU microscope equipped with EDS INCA Energy 450 and WDS Oxford INCA Wave 700 at the Korzhinskii Institute of Experimental Mineralogy, Chernogolovka, Russia. Analyses were performed at 20 kV accelerating voltage with a beam current up to 400 pA, spot size 115-150 nm and a zone of "excitation" with 3-4 µm diameter. Counting times was 100 s for all elements. The ZAF matrix correction was applied.

Experimental results. The mineral associations obtained in the experiments are shown in table. 1. They vary from clinohumite-garnet-pyroxene to olivine-mica. temperature Pressure and are responsible for the appearance of garnet, clinohumite/olivine, and the increase in CO₂ content is expected to form a large amount of Mg-Fe carbonate. The chemical compositions of the phases probably reflect less changes in the PT parameters (Fig. 2 - 4). The clinopyroxenes have patchy zoning (Fig.1) and wide spread of Fe/Mg ratio (Fig. 2).





Fig.2. Zoning in clinopyroxene: a) results of experiment 5 GPa and 1500° C; b) the natural sample Ilb28. Cpx- – clinopyroxene, Ol – olivine, Amph – amphibole.

Sample, conditions of	The main minerals	Secondary minerals
experiment		
Natural Ilb28 (starting composition)	Olivine, phlogopite, calcite	Clinopyroxene, garnet, ilmenite, perovskite, Ti-
4 GPa, 1450°C , 4h	Mica, clinopyroxene, olivine	Carbonate(?), sulfides, sphene
4 GPa, 1550°C, 4h	Olivine, carbonate, mica (?)	Sulfide, phlogopite (?)
5GPa, 1150°C, 10h	Garnet, clinohumite, clinopyroxene	Ilmenite, perovskite, mica
5 GPa, 1200°C, 10h	Clinopyroxene, clinohumite, mica	Spinel, perovskite, ilmenite, pyrite, apatite, calcite
5 GPa, 1300°C, 10h	Clinohumite, garnet, clinopyroxene	Ilmenite, perovskite, pyrite
5 GPa, 1500°C, 4h	Olivine, clinopyroxene, garnet	Mica, ilmenite, perovskite, pyrite
5GPa, 1350°C, 4h,	Mg-Fe-carbonates, micas	Sphene, sulfides
+20% ox.ac.		

Table 1. Mineral parageneses of natural and experimental samples.

The dependence of composition on temperature is not revealed. The garnets obtained in the experiments are characterized by a high content of Al, Ca (Fig. 3) and low Ti content. The compositions of clinohumite in different experiments: they are rich in F (up to 1.2 wt.%), TiO₂ (up to 2 wt.%) and contain 40-55 wt.% MgO. High concentrations of fluorine and titanium expand the stability field of clinohumite (Engi, Lindsley, 1980), and only at a temperature of 1500°C at 5 GPa clinohumite is replaced by olivine. Olivines are represented by two groups differing in Mg (88.4 – 89.4) and (93.0 – 94.6), but the differences in composition do not correlate with PT parameters of the experiments. On Fig. 4 it can be seen that clinohumites contain a greater amount of Ti, but this difference is not large, the content of Mg and Fe are similar.

Discussion. Mineral parageneses vary from clinohumite-garnet-pyroxene to olivine-mica. Pressure and temperature are responsible for the appearance of garnet, clinohumite/olivine, and the increase in CO_2 content stabilizes olivine and increases the contain Mg in carbonate. Chemical compositions of phases, and probably to a lesser extent, reflect changes to the PT settings. Clinopyroxenes almost always have a spotty zoning (Fig.2) and a wide spread of compositions in the Fe/Mg ratio (Fig.3-5).



Fig. 3. Classificatory triangle of pyroxenes.





Fig. 5. Contents of Mg, Ti, Fe (atm. %) in clinohumite and olivine.

As a result of melting of aillikites at 4 and 5 GPa of the identified mineral assemblages characteristic of various PT conditions, identified the main paragenesis of the system and the change in paragenesis, depending on the availability of water-carbonate fluid in the system, and revealed some regularities of variations of chemical compositions of minerals.

Thus, the results of the experiments showed that at a pressure of 5 GPa, paragenesis is obtained, which differs from the natural association of minerals: in the experiments, the appearance of clinohumite is observed, there is no olivine in the products of experiments conducted at temperatures below 1500^oC. In addition, experimental samples contain more clinopyroxene and garnet than natural samples. However, at 4 GPa there is a mineral paragenesis very similar to the natural one: micaolivine-pyroxene rock with carbonate minerals in the bulk. In all experiments, the paragenesis and composition of minerals are identical, the only difference is in their ratio. Thus, the composition of minerals obtained by melting aillikite at 4 GPA, more in line with the natural paragenesis of aillikite. This may indicate that the natural aillikite formed at identical P-T conditions.

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Butvina V.G.¹, Vorobey S.S.², Safonov O.G.¹, Varlamov D.A.¹ Experimental study of chromite-ilmenite-K₂CO₃-oxalic acid at 3,5 and 5 GPa. UDC: 552.13

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Abstract. In order to further study the effect of K-activity on the formation of K-Cr titanates and K silicate phases at pressures of 3.5 and 5 GPa, experiments on the interaction of the chromite-ilmenite system with K aqueous carbonate fluid were carried out at the NL-13T and NL-40 apparatus. As starting substances for experiments, natural chromite and natural ilmenite were used, which were mixed in ratios of 1:1 or 2:1 by weight. Previous results (Butvina et al., 2018) showed the possibility of crystallization of chromium priderite as a reaction product of high-chromium spinel and rutile with potassium aqueous carbonate fluid (melt) in the upper mantle. In particular, the obtained experimental data allow us to interpret the relationship between K-Crpriderite and carbonate-silicate inclusions in chromites of Bohemian garnet peridotites. In this paper, the dependence of the crystallization intensity and the appearance of K-Cr titanates on the amount of K₂CO₃ in the system is investigated. Based on the obtained experimental data, the reactions of mantle metasomatism describing the process of formation of K-Cr titanates are derived. In the experimental study of the reaction of chromite and ilmenite with aqueous potassium-carbonate fluid (melt) phases of the pair of titanates (priderite, vimengite and vimengite, mathiasite) - indicator minerals, mantle metasomatism, which directly confirms the possibility of formation of yimengite, mathiasite and K-Crpriderite and other titanates, the result of mantle

metasomatism of upper mantle peridotite under conditions of the highest activity of potassium (Safonov, Butvina, 2016).

Keywords: high T-P experiment, mantle metasomatism, K-Cr titanates, yimengite, priderite, mathiasite, indicator minerals, aqueous potassium-carbonate fluid

Introduction. Previous results (Butvina et al., 2018) showed the possibility of crystallization of chromium priderite as a reaction product of highchromium spinel and rutile with potassium aqueous carbonate fluid (melt) in the upper mantle. Experimental data from researchers (Foley et al., 1994; Konzett et al., 2005; Huggerty et al., 1983) point to a very wide area of existence of K-Ba titanates, confirming the possibility of coexistence of these phases with diamond in the subcontinent upper mantle in the areas of generation of kimberlites of groups I and II and lamproites. These minerals may be the leading concentrators of LILE and HFSE not only in the lithospheric mantle, but also in the asthenosphere, possibly to the depths of the transition zone (eg. Konzett et al., 2005).

However, it is obvious that not only temperature and pressure, but also specific chemical conditions are responsible for the stability of K-Ba-titanates. These minerals are formed when the ability to concentrate K and LILE in phlogopite and potassium richterite is exhausted. Formation of minerals of groups hawthorneite-yimengite, landsleit-mathiasite and priderite characterizes the highest degree of metasomatic changes in the conditions of high activity (concentration) of alkaline components, especially potassium in the fluids, noticeably larger than is necessary for the formation of phlogopite and potassium richterite (Safonov, Butvina, 2016). The formation of these minerals is usually associated with peridotite reactions with alkali-rich fluids (melts) with low SiO₂ activity (Konzett et al., 2013; Giuliani et al, 2012). The inclusion of such fluids found in the MARID Association of minerals (Konzett et al. 2014) - the closest to those associations in which K-Ba-titanates were identified. Thus, these minerals can be considered as indicators of the activity of highalkaline water-carbon dioxide fluids or salt melts in the mantle. However, there are no experimental or calculated data that would answer the question of how high the concentrations of alkali-salt components in fluids should be for the appearance of these minerals. In this paper an attempt is made to reproduce experimentally at P-T conditions of the upper mantle reaction of formation of priderite, vimengite and mathiasite involving aqueous potassium-carbonate fluid.

The experimental method and the starting mixture. The experiments were carried out at pressures of 3.5 and 5 GPa at the apparatus of NL-13T and NL-40 at the Korzhinsky Institute of Experimental Mineralogy RAS.

System spinel- K_2CO_3 , spinel-rutile- K_2CO_3 -oxalic acid (hereinafter ox.ac.), spinel-ilmenite- K_2CO_3 ox.ac. As the starting substances for the experiments we used natural chromite and synthetic TiO₂ powder or natural ilmenite, which were mixed in ratios of 1:1 or 2:1 by weight. Composition chromite (Mg_{0.49}-0.54Fe_{0.50-0.54}Mn_{0.01-0.02}Zn_{0.01-0.02})(Al_{0.17-0.20}Cr_{1.55}-

 $_{1.61}$ Fe_{0.10-0.22}Ti_{0.03-0.07})O₄ (see table.1) was selected from the xenolith of the garnet lherzolite of the kimberlite pipe Pionerskaya, Yakutia. Ilmenite of the composition Fe_{0.98}Mg_{0.01}Mn_{0.06}Ti_{0.93}Al_{0.01}Nb_{0.01}O₃, is xenocrysts from kimberlite pipe Udachnaya, Yakutia. As a fluid component, a mixture of K₂CO₃ and oxalic acid in different ratios was used (9:1; 7:3; 5:5; 3:7; 1:9) by weight. The mixture of chromite + TiO₂ was mixed with a "fluid" mixture in the ratios 4:1 and 9:1, and chromite + ilmenite – in the ratio 9:1 by weight. The experimental conditions are presented in table 1.

Discussion

*System spinel-ilmenite-K*₂*CO*₃*-ox.ac.*

Series of experiments B1, B1-1, B1-2, B1-3, B1-4 (at 5 GPa - see table.1) and M-0, M-1, M-2, M-3, M-4 (at 3.5 GPa-see table.1) was carried out at different K₂CO₃ relations: ox.ac. in the fluid for the study of the crystallization ability of K-Cr titanates from activity K in the system. It is seen (table.1) that the greatest number K in the system (9% K_2CO_3) To form the highest enriched titanates - priderite and yimengite (at 5 GPa) and yimengite and mathiasite (with 3.5 GPa), with 5 and 7 % K_2CO_3 priderite is not formed in the experiment, there is an intense formation of vimengite subidiomorphic and idiomorphic hexagonal shape with a size of 10-100 microns (fig.1), and also appears the titanate mathiasite, less than 5 % K₂CO₃ in the system titanates are not formed at both pressures. Experience B2 (see table.1) showed that 30% of ilmenite in the system is sufficient for the formation priderite and vimengite, i.e. experience B2 reproduces the full experience B1.

NºNº	Mineral composition,(mas .%)	Fluid, (mas.%)	Contains of fluid in the system, %	Time, h.	P, GPa	Synthesis of priderite, yimengite, mathiasite
Sp1	Spinel	K ₂ CO ₃	30	21	5	-,-,-
Sp2	Spinel: rutile (1:1)	K_2CO_3 :ox.ac. (9:1)	20	23	5	+,-,-
Al	Spinel: rutile (1:1)	K_2CO_3 :ox.ac. (9:1)	10	20	5	+,-,-
A2	Spinel: rutile (2:1)	K_2CO_3 :ox.ac. (9:1)	10	24	5	+,-,-
B1	Spinel: ilmenite (1:1)	K_2CO_3 :ox.ac. (9:1)	10	22	5	+,+,-
B1-1	Spinel: ilmenite (1:1)	K_2CO_3 :ox.ac. (7:3)	10	22	5	-,+,+
B1-2	Spinel: ilmenite (1:1)	K ₂ CO ₃ :ox.ac. (5:5)	10	22	5	-,+,-
B1-3	Spinel: ilmenite (1:1)	K ₂ CO ₃ :ox.ac. (3:7)	10	22	5	-,-,-
B1-4	Spinel: ilmenite (1:1)	K_2CO_3 :ox.ac. (1:9)	10	22	5	-,-,-
B2	Spinel: ilmenite (2:1)	K_2CO_3 :ox.ac. (9:1)	10	20	5	+,+,-
M-0	Spinel: ilmenite (1:1)	K_2CO_3 :ox.ac. (9:1)	10	8	3,5	-,+,+
M-1	Spinel: ilmenite (1:1)	K_2CO_3 :ox.ac. (7:3)	10	8	3,5	-,+,+
M-2	Spinel: ilmenite (1:1)	K ₂ CO ₃ :ox.ac. (5:5)	10	8	3,5	-,+,+
M-3	Spinel: ilmenite (1:1)	K ₂ CO ₃ :ox.ac. (3:7)	10	8	3,5	-,-,-
M-4	Spinel: ilmenite (1:1)	K_2CO_3 :ox.ac. (1:9)	10	8	3,5	-,-,-

System spinel-rutile-K $_2CO_3$ *- ox.ac.* Experiment Sp2 (table 2).

In this system, due to the fact that not enough Fe for the formation of yimengite formed priderite. It forms individual anhedral and subhedral grains, as well as tetragonal prisms and di-tetragonal dipyramids up to 40 μ m in size (fig. 2). Priderite also forms inclusions in rutile. The ratios of Fe (Fe²⁺+Fe³⁺), Ti and Cr in the priderite formulas synthesized in systems with rutile and ilmenite differ

little. In products of experiments, priderite is in paragenesis with newly formed chromite (table.2) which contains less Fe_2O_3 , Cr_2O_3 , more TiO_2 compared to the original. Based on the phase compositions of this experiment, we can record the following reaction of formation: K_2O + 5.786203TiO₂ + 0.459471O₂ + 1.103516Cr₂O₃ + 24.498376Chr2 = 1.169591 Pri + 9.452462 Chr + 14.568025Chr1.

Table 2. Representative analyses (f. e.) of compositions of paragenetic minerals (products) in experiments on the synthesis of K-Cr titanates at 5 GPa and 1200° C.

Runs			В	1			
Comp-t/Mineral	Yim	Pril	Ilm	Ilm1		llm2	Rt1
Ti	4,76	6,15	0,93	0,93		0,98	0,85
Cr	2,87	1,56	-	-		0,01	0,20
Fe ³⁺	0,25	0,15	0,08	8	0,03		-
Fe ²⁺	3,30	0,10	0,9	5		0,70	-
Al	0,35	0,06	0,02	2		-	-
K	1,01	1,77	-			-	-
Mg	0,47	0,06	0,04	4		0,28	-
№Exp.		Sp2			B1-1		
Comp-t/Mineral	Chr1	Chr2	Pri2	Yin	nl	Yim2	Ilm3
Ti	0,10	0,14	6,23	4,34		4,25	0,97
Cr	1,47	1,46	1,47	2,9)9	3,31	0,02
Fe ³⁺	0,02	-	0,11	0,11 0,68		0,42	0,04
Fe ²⁺	0,31	0,46	-	2,6	51	2,74	0,74
Al	0,31	0,26	0,13	0,6	59	0,66	-
K	-	-	1,71	1,0	00	1,01	-
Mg	0,79	0,68	0,12	0,6	57	0,67	0,23

System spinel-ilmenite- K_2CO_3 -ox.ac. Experiment B1 (table 1,2). The system components are Fe, Ti and K are sufficient for formation and priderite, and yimengite. The composition of yimengite obtained by the reaction of chromite and ilmenite with the fluid, form the trend, reflecting the isomorphism of $(Fe^{2+}+Fe^{3+})+Ti \leftrightarrow Cr$ if the constancy of the ratio $(Fe^{2+}+Fe^{3+})/Ti$. Yimengite is characterized by a relatively low content of Al₂O₃ and MgO. It contains up to 3.5 wt. % Nb₂O₅, despite the fact that coexisting with him priderite does not contain this component (table 2). Based on the compositions of the newly formed phases (table 2), can be composed of three exchange and K-Cr titanate formation reactions:

 $\begin{aligned} Rt1 &+ 0.105649 Chr + 0.124873 K_2 O + 0.210133 Ilm 1 \\ &= 0.114438 Pri1 + 0.046724 Yim + 0.025989 Cr_2 O_3 + \\ &0.127047 Ilm 2 \end{aligned}$

 $\begin{aligned} Rt1 &+ 0.142749 Chr + 0.168723 K_2 O + 0.298481 TiO_2 \\ &+ 0.283922 Ilm1 = 0.154624 Pri1 + 0.063131 Yim + \\ &0.171660 Ilm2 \end{aligned}$

 $\begin{array}{rl} 0.923197 Chr + 1.091184 K_2 O + 0.646730 Cr_2 O_3 + \\ 7.427572 Ti O_2 &+ 1.836211 Ilm 1 &= Pri 1 &+ \\ 0.408285 Yim + 1.110175 Ilm 2 & (3) \end{array}$

System spinel-ilmenite-K₂CO₃-ox.ac. Experiment B1-1 (table 1,2). Decrease of the ratio $K_2CO_3/(H_2O+CO_2)$ to 7/3 leads to disappearance of priderite, but yimengite actively forms as subhedral hexagonal crystals of 10-100 µm in size (fig. 1). Kpoor titatnate, mathiasite, appears along with vimengite. Yimengite only forms at $K_2CO_3/(H_2O+CO_2) = 5/5$. Using representative composition of phases in the run B1-1 products (table 2), a number of equilibria could be written to illustrate the formation of this titanate assemblage, for example:

5.29Chr + 9.87Ilm + 1.08K₂CO₃ + 7.61TiO₂ = Yim₁ + 1.14Yim₂ + 0.68Cr₂O₃ + 8.09Ilm₃



Fig.1. Products of the experiment B1-1 and B1-2 (Table 1) in the system chromite-ilmenite- K_2CO_3 - H_2O-CO_2 at 5 GPa and 1200°C: hexagonal crystals of yimengite.



Fig.2. Tetragonal crystals of priderite (run A, Table 1) in the system chromite-rutile-K₂CO₃-H₂O-CO₂ at 5 GPa and 1200°C.

Mineral equilibria at high PT-parameters

The equilibrium demonstrates formation of yimengite with variations of the ilmenite composition (it becomes more magnesian). The excess of Cr_2O_3 and TiO_2 demonstrates possible non-stoicheometry of titanates or formation of additional non-detectible oxides in the run products. No titanates are observed at lower $K_2CO_3/(H_2O+CO_2)$ ratios (table 1).

Conclusions. The dependence of crystallization intensity and appearance of K-Cr titanates on the amount of K₂CO₃ in the system was investigated. Based on the obtained experimental data, the reactions of mantle metasomatism describing the process of formation of K-Cr titanates are derived. In the experimental study of the reaction of chromite and ilmenite with aqueous potassium-carbonate fluid (melt) phases of the pair of titanates (piderite, vimengite and vimengite, mathiasite) - indicator minerals, mantle metasomatism, which directly confirms the possibility of formation of yimengite, mathiasite and K-Cr-priderite and other titanates, the result of mantle metasomatism of upper mantle peridotite under conditions of the highest activity of potassium (Safonov, Butvina, 2016).

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Fedkin V.V.¹, Shchipansky A.A.². Subduction initiation of the maksyutov eclogiteglaucophane schist complex (South Urals) UDC 549.6+552.16:552.48

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Abstract. The new geodynamic concept of the "Subduction initiation rule" (SIR) (Whattam and Stern, 2011) connects the processes of formation of collision zones of lithospheric plates with the formation of ophiolitic complexes, pre-arc basins and the processes of initiation of subduction (SI). This concept predicts that most ophiolites were formed during SI and the diagnostic chemostratigraphic progression for SIR ophiolites is from less to more HESE-depleted and LILE-enriched compositions. The Maksyutov eclogite-glaucophane highpressure complex in the Southern Urals (MC) is a unique object for studying the phenomenon of subduction initiation. The main reason is related to the fact that along with the diagnostic magmatic chemostratigraphic sequence of SI and ophiolites, the reconstructed HP-UHP subduction channel, which is the Maksyutov complex, was also discovered here. To understand the geodynamics of the SI process, this is of paramount importance, since the time of HP-UHP metamorphism of the MC coincides with the appearance of the Magnitogorsk intra-oceanic island arc in the early Devonian. In this work, on the basis of precision XRF and ICP MS, analyzes of bulk composition of representative samples of garnet-bearing mafic rocks of the MC attempted to identify the temporal, tectonic and geochemical features (indicators) of the SI process and assess their role in the geodynamic development of the complex. The issues of the chemical composition and genesis of the protoliths of the complex, the geodynamic setting of their source, the participation in the subduction process of the mantle-plume mechanism and crustal contamination, as well as the role and importance of boninite-bearing ophiolites in the subduction initiation of are considered.

Keywords: Maksyutov complex, Ural Mountains, UHP metamorphism, protolith, eclogite, subduction, XRF and ICP MS bulk-rock chemistry

A new geodynamical concept 'The subduction initiation rule' (SIR) recently introduced by **Whattam and Stern (2011)**, creates seductive prerequisites for revising a large amount of factual material on geology, geochemistry, petrology, geochronology and geodynamics of the Maksyutov eclogite-glaucophane schist HP/UHP complex in the Southern Urals. The subduction initiation rule considers the processes of subduction nucleation in conjunction with the formation of ophiolite complexes, the development of forearcs basins and allows to establish patterns of the subduction process based on geochemical indicators, to evaluate its parameters: temporal, spatial, petrological. The Maksyutov eclogite-glaucophane schist complex is a unique object for studying the phenomenon of subduction initiation, because along with the diagnostic magmatic chemostratigraphic sequence and ophiolites, the restored HP/UHP subduction channel, which is the Maksyutov complex, is found here, and the time of HP/UHP metamorphism of the Maksyutov complex coincides with the appearance of the Magnitogorsk intra-oceanic island arc in the early Devonian (**Brown et al., 2006; Puchkov, 2010).**

The more than 50-year history of studying the complex and a large amount of factual material accumulated over this time creates a good basis for testing new geodynamic ideas, analyzing the causes of the emergence and conditions for the development of subduction structures. The mineralogical criteria and characteristic phases of ultrahigh pressure are well known: quartz pseudomorphs in coesite, graphite cuboids after diamond, diamond microinclusions in garnet and other minerals. There are numerous publications reflecting various interpretations of the geodynamic conditions, age, geochemical composition of rocks, and PT conditions for the formation of the complex. Nevertheless, some geodynamic aspects of the development of the terrane remain controversial due to the complexity of the subduction process and the diversity of the geochemical characteristics of its rocks. In this paper, an attempt is made to identify the temporal, tectonic and geochemical features (indicators) of the process of subduction initiation and to evaluate, taking into account the new concept, their role in the geodynamic development of the complex. This work is carried out on the basis of precision analyzes of the bulk composition of representative samples of garnet-containing mafic rocks MC.

The Maksyutov complex is located in the zone of the Main Ural fault, in the junction zone of the East European Platform and the western margin of the Siberian Craton, at the boundary of the Riphean rocks of the Suvanyak complex in the west and the Kempirsai hyperbasite belt, as a part of the Magnitogorsk island arc, in the east. Three structuralmaterial (lithological-tectonic) units are distinguished within the complex (Lennykh et al., 1995, Beane, Leech, 2007):

(1) the lower "subcontinental" eclogiteglaucophane schist unit: glaucophane and feldsparmica schists, quartzites with lenses, boudins, bodies and interlayers of eclogites, Grt-Cpx and less often Ol-En rocks;

(2) upper metaophiolitic unit, consisting of rocks of the oceanic crust, associated graphite crystalline schists and metagreywacks, sometimes including bodies and lenses of serpentinites, marbles and metabasalt rocks;

(3) and an intermediate Yumaguzin unit metasedimentary rocks (quartzites and mica schists, without eclogite).

Of greatest petrological interest is the lower unit of the complex, in which, in addition to numerous lenses, bodies, boudins and layers of eclogitic rocks, there are described phases of ultrahigh pressure: diamond and coesite, as well as other mineralogical and petrological indicators of HP/UHP metamorphism: lawsonite associations, jadeite with quartz, olivine-enstatite ultramafites (Dobretsov et al., 1996; Lennykh et al., 1995; Beane, Connelly, 2000; Leech, Ernst, 2000; Valizer et al., 2015).

1. The chemical composition of the protolith. Previous works on the geochemistry of the rocks of the Maksyutov complex (Volkova et al., 2004; Beane and Sorensen, 2007; Valizer et al., 2015, Kovalev et al., 2015) have shown a wide variety of their bulk composition. Taking into account these data, 18 representative samples of mafic eclogites were analyzed by XRF and ICP MS, in the analytical laboratory of the University of Washington for rockforming, rare, scattered and rare-earth elements. For the main rock-forming components, most of the studied samples show a wide variation of compositions, but generally fall into the area of lowpotassium basalts with SiO₂ content of ~ 47-52 wt. %, And only one of them corresponds to basalt and esite with SiO₂ content of ~ 61 wt. % According to the Mg# = Mg/(Mg+Fe2+) index, mafic differences show strong fractionation in the range from 0.37 to 0.59-0.65. The calcium index Ca#=Ca/(Ca+ Na) of eclogitic rocks shows that the ratios of modal quantities of igneous clinopyroxene and plagioclase were approximately in equal proportions, around the mode of 50%. On the AFM diagram, Maksyutov eclogites form a single trend of the tholeitic and calc-alkaline series, including both depleted and enriched compositions. This emphasizes the origin of their protoliths from various mantle sources — N-MORB and OIB, respectively. However, a simple FeO*/MgO - SiO₂ diagram (Miyashiro, 1974) records changes in composition from tholeitic basalts to calc-alkaline basalts, basaltic andesites and andesites. It is extremely important to note that a shift in the composition occurs even in one eclogite block, 5 m \times 30 m, studied in detail by Volkova et al. (2004). However, this chemical pattern is more characteristic of volcanic island arc series or tectonic environments OIB, but not in MORB or BAAB (Zimmer et al., 2010). Bulk-rock composition does not show noticeable fractionation trends, and a variety of their composition does not allow identifying uniquely a single magmatic source of protolith. Thus, protoliths constituting HP/UHP mafic rocks of complex were originated either in

contrast plate-tectonic environments, or from a common source, but under the influence of metasomatic processes of variant degree.

2. Genesis of the protolith. Most of the analyzed eclogite rocks of the Maksyutov complex do not reveal coherent positive anomalies of Eu and Sr in the REE spectra characteristic of middle crust gabbro intrusions that have undergone metamorphism of the eclogite facies, which proves their origin through the transformation of basalt. The behavior of rare and scattered elements (Sr / Sr *, Eu / Eu *, Gdpm, (La / Sm) pm), normalized to the primitive mantle, also confirms the volcanogenic origin of protoliths from the basalt melt. The increased Sr/Sr* values relative to the Eu/Eu* values in the eclogites of the Maksyutov complex indicate that their protoliths originated from a volcanogenic igneous source in the setting of island arcs IAB, and not during the fractional crystallization of the intrusive rocks MORB (Niu and O'Hara, 2009). The bulk of the points on the Gdpm - MgO and (La/Sm)pm - MgO diagrams fall on the trend of fractional crystallization of MORB, or in the field of enriched mantle melts. The only exception is one sample (235/236) with the highest Mg#, 0.65 and Ca#, 0.57, which indicates the most primitive composition derived from a mantle melting column. The REE spectrum of this sample shows a well-pronounced positive Sr anomaly $(Sr/Sr^*=1.8)$, which is more characteristic of the IAB situation than for the MORB. In combination with the highest possible magnesia and calcium levels, this may indicate the cumulative nature of the original gabbro or diabase.

3. Sources of protolith. For a long time, it was believed that the Maksyutov complex was formed during the subduction of the continental margin of the East European Plate to the east (Beane and Connelly, 2000; Brown et al., 1998; Brown et al., 2006; Puchkov, 2010) when it collided with the Magnitogorsk volcanic arc. However, the distribution of high-charging small elements in the eclogites of the complex shows that their compositions show depleted (La/YbN ~0.5-1.5) and enriched (La/YbN \sim 2-4.7) differences, indicating the origin of their protoliths from different mantle sources: N-MORB and OIB, respectively. In addition, most of the eclogites MK was very unusual in geochemistry - the so-called Nb-enriched basalts (NEB). This factor is an indicator of the subduction of oceanic ridges and the interpretation of eclogites as sills and dyke bodies in a reef basin on the edge of a craton requires at least clarification.

On the MnO*10 - P_2O_5*10 - TiO₂ diagnostic diagram, the bulk composition of UHP MC rocks overlaps the fields of basalts of oceanic islands, island-arc tholeiites, N-MORB and E-MORB basalts. Practically at each studied site of the complex two

groups of samples are distinguished, the REE profiles of which are close to N-MORB or are clearly enriched relative to N-MORB with the elements LREE, MREE and HFSE. However, half of the samples of the first group that have similarities with N-MORB, detect negative Nb anomalies (Nb/Thpm=0.5-0.7 ppm), which indicates that they belong to the IAT plate-tectonic condition, and not to the N-MORB. In addition, many of them show positive Sr peaks, also typical of IAT. The second group of eclogites, with steeper REE spectra (La/Ybpm \sim 2-5), has negative Sr anomalies characteristic of MORB, and negative peaks of elements of the HFSE group: Nb, Zr, Ti, characteristic of the supersubduction zones (SSZ).

A very similar separation of REE spectra into two groups is also observed for high-Nb samples: (1) a group close to the OIB standard, with positive Nb anomalies, without signs of anomalous behavior of Zr and Ti, and (2) a group intermediate between OIB and E -MORB, with negative Nb peaks and weak Zr and Ti disturbances.

Thus, various geochemical indicators show at least the dual source of Maksyutov mafic eclogites' protoliths: the depleted basalts of the mid-oceanic ridges of the E-MORB type and the enriched basalts of the OIB oceanic islands and the subtle geochemical characteristics of their composition according to HFSE, rare and scattered elements allow to distinguish between the geodynamic features of sources of protolithic magmas.

4. The phenomena of the crustal contamination and the mantle-plume interaction make a certain contribution to the development of the subduction process, although perhaps to a lesser extent than the surrounding plate-tectonic situation. These processes are most clearly reflected in the ratios of high-field strength elements of the original rocks: TiO2 / Yb - Nb / Yb and Th / Yb - Nb / Yb, which were analyzed in detail by Pierce (2008). The compositions of Maksyutov eclogites are well interpreted by the interaction model of the OIB-type mantle-plume source and the MORB depleted mantle source. In the coordinates of TiO2 / Yb - Nb / Yb, the compositions of depleted mafic rocks lie within the MORB array, whereas enriched basalts, on the contrary, along the curve of polybaric melting from the deep garnet-bearing peridotite to much less deeper than spinel lherzolite mantle, being set the interval of baric conditions of possible magma generation for Maksyutov rocks from 3.5 to 1.5 GPa. The source of the mantle plumes - fragments of the Paleoproterozoic primitive mantle - could be deep magma chambers associated with hot spots. The presence of UHP ultramafic (Ol-En) rocks in the lithological-tectonic lower unit of complex structurally and spatially connected with eclogites (Valizer et al., 2015), confirms the participation of the ancient (Lower Cambrian - \geq 533 Ma) tectonic mantle-crust inclusions in the protolith substrate of the region.

5. Boninites as a sign of IP. Another important sign of the subduction initiation and mantle-crustal interaction is the occurrence of boninites or the ophiolite volcanites, a series of boninitic rocks that were formed in situ by partial melting of peridotite. In the structure of the South Ural Paleozoids, ophiolites are widely distributed, the composition of which rocks indicates that they were formed in a suprasubductive setting and belong to the boninite series. Such information is given for the Caledonian island-arc complex of the Sakmar zone, for the Buribay district in the west of the Magnitogorsk zone. The tectonic structure of the Maksyutov complex, the spatial connection and the temporal proximity of boninite-bearing ophiolites emphasize the influence of the activity of the mantle plume on the initiation of early Devonian subduction and indicate that Maksyutov ophiolites were formed in the suprasubduction environment.

6. Crustal contamination or contribution of a subduction component. The variable anomalies of Nb in the composition of the UHP rocks of the Maksyutov complex indicate both the absence of the crustal or subduction contamination (with Nb / ThN > 1) and its presence (with Nb / ThN < 1). The Th / Yb - Nb / Yb diagram is a sensitive indicator of crustal contamination (of contribution of the subduction component) to the petrogenesis of mafic volcanites (Pearce, 2008). The composition of eclogites of the Maksyutov complex for these components reveals another source of formation of protoliths. According to model calculations, most of the eclogite compositions, both depleted and enriched, fall into the MORB-OIB field, which, on the one hand, confirms their oceanic (not arc) identity, and on the other, determines the contribution of the subduction component, which ranges from 1 up to 4% and occurs due to the receipt of subduction material, not due to the mantle-crust interaction. This is probably due to the fact that the formation of the Early Devonian P-MORB range in the Southern Urals took place on the oceanic lithosphere, which underwent suprasubduction changes in Ordovician time (Ryazantsev et al., 2008).

Some conclusions and arguments.

The geochemistry of the basic eclogites of the Maksyutov complex shows that their protolith was tholeitic and sub-alkaline basalts, both enriched (of the OIB type) and depleted (of the N- and E-MORB types) with inherited signs of the subduction component and of subsequent metasomatic changes.

Most of the studied samples of eclogites of MK do not reveal coherent positive anomalies of Eu and

Sr, typical for intracrustal gabbro intrusions, which proves their origin through crystallization of basalt melt, and not transformation of crystalline gabbro.

Crustal contamination and an unusual (Nbenriched) composition of basalts are indicators of the subduction of oceanic ridges.

The presence of boninite-bearing ophiolites in the region implies participation in the subduction process of the mantle-plume mechanism, which developed in the supersubduction environment of the island-arc complex.

The geochemistry of the basic eclogites of the Maksyutov complex shows that the formation of their protoliths occurred with the participation of three different sources: the depleted mantle of the N-MORB type enriched by the OIB mantle, the inherited contribution of the subduction component, and possibly some mantle source.

As for the initiation of subduction, for its understanding of paramount importance:

1. A temporary combination of the formation of eclogites and ophiolites. The formation time of the HP-UHP channel and the metamorphism of the Maksyutov complex coincides with the appearance of the Magnitogorsk intra-oceanic island arc in the early Devonian;

2. Spatial combination. High-barreled (HP / UHP) subduction channel is actually combined with ophiolites into a single structural-tectonic terrane – the Maksyutov complex.

3. The necessary chemostratigraphic sequence is provided with a three-membered structure of MK: High-Pressure subcontinental part, with eclogites, the metaophiolitic upper unit consisting of oceanic crust rocks and flisch-like Yumaguzin metasedimentary sequence.

4. Finally, geochemical criteria for the composition of rocks that demonstrate various geodynamic settings of the complex formation in the process of its subduction.

Apparently, the most probable geodynamic settings, where processes of such mixing could be realized, could be pre-arc or back-arc areas of plate convergence, similar to those of the modern zone of convergence of the Pacific and Indo-Australian lithospheric plates.

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Khodorevskaya L.I. Experimental study of diopside-fluid H₂O-Na₂CO₃ interaction under pressure gradient conditions at 750°C.

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Abstract. High-temperature melanocratic metasomatism in basic rocks was simulated experimentally by transporting petrogenic components at a temperature of 750°C and a pressure of 500 MPa under pressure gradient conditions. Diopside (*Di*) in our experiments was a source of transported elements such as Si, Ca and Mg. The solution consisted of saturated Na₂CO₃. During the experiments under gradient conditions *Di* was partly dissolved and the dissolved components were redeposited as amphibole *Hbl*_S on the surface. Normalizing *Hbl*_S is accompanied by the removal of CaO and SiO₂. The experiments have shown that solutions containing Na and carbonate ions are not characteristic of basificate formation upon granitization.

Keywords: fluid , filtration, metasomatism, amphibole, granitization, basification.

The removal of Ca, Mg and Fe bases is essential for the construction of D.S. Korzhinsky's model of granitization which supplies alkalies and silica to host rocks. These elements are excessive for granite eutectics. As they are removed from host rocks, the rock approaches granite composition and is molten at corresponding P-T conditions. The components removed and redeposited are scattered or (less frequently) concentrated, giving rise to melanocratic metasomatic rocks called basificates. The addition and removal of components are largely controlled by the composition of the fluid phase which is filtered through the rock. The goal of the present study is to assess the transfer pattern of the above elements associated with the fluid $H_2O-Na_2CO_3$.

The directed flow of solution containing Ca, Mg, Fe, Si and Al under gradient conditions was reconstructed experimentally. Diopside (Di_{in}) was a source of the above elements, whose composition is given in table 1. Di_{in} was placed on the bottom of an ampoule. Saturated Na₂CO₃ (0.05-0.07 ml) solution was poured. A cylindrical amphibolite sample, prepared with regard for the internal diameter of the ampoule, was then inserted tightly into the ampoule. The amphibolite was a surface on which the elements removed from diopside were deposited. The amphibolite consisted of garnet, biotite, ilmenite and amphibole Hbl_{ucx} . (Table 1). The amphibole nomenclature, recalculation procedure of amphibole analyses to the crystal-chemical formula $AB_2C_5^{VI}T_8^{IV}O_{22}(OH)_2,$ and characteristics of isomorphism in the mineral follow recommendations by Leake et al. (1997). The distribution of cations between crystal chemical sites and the Fe3+/Fe2+ was calculated with the software of Schumaher (1997). corresponds The amphibolite to ferropargasite.

The distance between *Di* and the amphibolite was 15-20 mm, and they interacted only via a fluid phase. A thick-walled microchamber was mounted on the amphibolite. During the experiments an external pressure of 5 kbar spread into the lower portion of the ampoule because its walls are thin. Primary pressure in the upper portion of the ampoule was 1 atm because the walls of the microchamber are thick. Variations in pressure along the ampoule resulted in the directed flow of the solution between the ampoule walls and the sample (along the fractures in the samples, etc.) until the pressure in the upper and lower portions of the ampoule was levelled. These variations in pressure resulted in a small uncontrolled temperature gradient along the ampoule (throttling). Oxygen volatility in the experiments was not controlled because it was hard to fill the ampoules. The experiments were conducted for 240 h. The experimental temperature (750°C) was consistent with the conditions of formation of natural basificates upon granitization. A pressure of 400 MPa is typical of high-temperature metamorphic and metasomatic processes (Levitsky, 2005).

The composition of the initial phases and phases after the experiments are given in table 1.

	Di						Amphibolite			
Minerals	Initial	After the	After the experiments			Hbl Initial	After the	e experin	nents	
	Di _{in.}	Hbl_{Di}	Hbl_{Di}	Hbl _{Di} +Di	Di	Di	(Hbl _{in} .)	HblA	Hbl_S	Hbl_S
Component		7*	8	9	10	11				
SiO ₂	58.17	50.62	50.51	52.32	53.09	53.14	42.03	48.66	52.78	53.47
TiO ₂	0.39	0.64	0.63	0.47	0.42	0.06	0.37	0.32	0.23	0.52
Al ₂ O ₃	0.35	3.45	3.81	3.31	1.66	1.73	13.69	9.70	4.64	4.50
FeO	1.54	3.33	3.49	3.4	3.08	4.11	22.95	10.90	5.58	4.92
MnO	0.05	0.01	0.27	0.35	0.34	0	0.01	0.23	0.15	0.03
MgO	20.38	17.92	16.88	15.98	15.63	14.89	6.72	14.55	20.50	20.52
CaO	18.65	8.38	7.89	14.73	23.6	23.67	10.23	12.35	7.67	7.63
Na ₂ O	0.36	8.86	9.48	9.11	1.5	2.11	2.25	0.70	7.05	6.91
K ₂ O		0.01	0.02	0.01	0.03	0	0.57	0.71	0.07	0.06
Total	99.99	98.17	98.35	99.88	99.99	99.99	98.82	98.11	98.65	98.56
Mineral form	nulas		•							
0	6	22	22		6	6	22	22	22	22
	2.09	7.78	7.84		1.93	1.93	6.30	6.96	7.35	7.38
Ti	0.01	0.07	0.07		0.01	0.00	0.04	0.03	0.02	0.05
Al	0.01	0.62	0.70		0.07	0.07	2.42	1.63	0.77	0.73
Fe'''	0.00	0.00	0.00		0.17	0.22	0.58	0.18	0.41	0.50
Fe"	0.05	0.43	0.45		0.00	0.00	2.29	1.12	0.25	0.07
Mn	0.00	0.00	0.03		0.01	0.00	0	0.02	0.02	0
Mg	1.09	4.10	3.90		0.85	0.80	1.5	3.1	4.26	4.22
Са	0.72	1.38	1.31		0.92	0.92	1.64	1.89	1.14	1.13
Na	0.03	1.64	1.71		0.11	0.15	0.66	0.2	1.91	1.84
K		0.00	0.00	1		1	0.11	0.13	0.01	0.01
X(Mg)	0.96	0.43	0.45	1	0.99	1.00	0.4	0.73	0.95	0.98
Type Hbl		Rit	Rit	1			Fe-Prg	Ed	lg-Ktp	lg-Ktp

Table 1. The compositions of initial phases and phases after the experiments.

* The numbers of analyses 7 - 11 are consistent with the numbers in Fig.1.

During the experiment $Di_{in.}$, placed into the lower portion of the ampoule (Fig.1), was partly dissolved at the contact with the fluid and was altered to amphibole (Hbl_{Di}) (analyses 7-8 in Table 1). Away from the contact with the fluid, Hbl_{Di} is mixed with Di(analysis 9 in Table 1), and Hbl_{Di} is then replaced by Di, the composition of which is slightly different from the original (analyses 10-11 in Table 1). The bulk composition is generally redistributed from the least altered Di(analysis 11 in Fig.1) to the margin, which is in contact with the fluid (where Hbl_{Di} occurs, analysis 7 in Fig.1): the percentages of SiO₂, CaO and FeO decrease and those of Al₂O₃, MgO and Na₂O increase.



Fig. 1. Photo showing the amphibolite margin facing the fluid and altered original *Di*.

Mineral equilibria at high PT-parameters

Due to the gradient conditions created, partly dissolved Di components were transferred by the fluid phase (the direction of the arrows in Fig. 1) and redeposited as a rim on the amphibolite margin facing the fluid flow. In Fig.1, the rim formed is separated from the amphibolite by a dotted line. Furthermore, the elements dissolved in the fluid precipitated upon hardening as single spherical units (hardening fluid in Fig.1). The chemical composition of the fluid is: $SiO_2 - 76.66$, $TiO_2 - 0.35$, $Al_2O_3 - 0.35$ 3.20, FeO - 3.46, MnO - 0.03, MgO - 6.14, CaO -6.61, Na₂O - 3.06, K₂O - 0.13; total 99.99 mas. %.

The rim formed consists of amphibole Hbl_{S} Fig. 2b shows that the sizes and orientation of amphibole Hbl_A in the original amphibolite differ from those of Hbl_{S} formed in the rim (Fig. 2b). Hbl_{S} occurs as coarse crystals oriented along the direction of fluid filtration. Incompletely replaced Hbl_A from the amphibolites is locally encountered among Hbls. The compositions of the amphibole Hbl_A from the amphibolite after the experiments and the compositions of the amphibole in the rim of Hbl_s are shown in Table 1. Our analytical results indicate that the amphiboles in the amphibolites, affected by the fluid at preset P-T parameters, change in composition altering from original ferropargasite to edenite (Hblin. and Hbl_{A} in Table 1). The newly-formed Hbl_{S} in the amphibole rim is Ca-Na similar to magnesiocatophorite (Mg-*Ktp*, Table 1). This amphibole displays a higher Fe^{3+} / Fe^{2+} ratio and a lower percentage of Fe as compared to Hbl_{Di}

Original

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300 MKM

The compositions of Hbl_s produced by the

transfer and redeposition of the elements, are

100 мкм

for MgO is minimum. Therefore, MgO may be

generally similar to those of high-temperature alkaline amphiboles occurring in nature. Thus, as a result of the directed flow of solution triggered by a P-T gradient, the original diopside was recrystallized, partly altered to Ca-Na amphibole (Hbl_{Di}) and partly dissolved. Dissolved Di components were redeposited as a rim (Hbl_s) on the amphibolite. However, part of the dissolved components remained in the solution, which we could not analyze because of its small quantity. To assess the addition and removal of the components by solutions, a geochemically inert component, which is neither added nor removed by solutions, should be identified. In other words, an element, the concentration of which in the original *Di* is similar to that in the newly-formed Hbls, should be identified. The calculations $[i(_{Di}) - i(Hbl_s) / i(Hbl_s) \times 100\%$, where i is the oxide of the element] show that in the chemical compositions of Di and Hbl_{S} (analyses 1 and 3 in Table 1, respectively) a difference of $\approx 2 \%$

identified as an inert component. Field evidence shows that the processes accompanying granitization are associated with the removal of Fe, Ca and Mg from host rocks, their further dispersal or concentrated redeposition and the formation of basificates. Earlier studies (Khodorevskaya, 2019) have shown that largely aquatic fluid ± small-scale additions (Na, K)Cl contribute to the removal of Ca, Fe and Mg from host rocks. It is aquatic rather than acidified fluids which control the degree of removal of Ca, Fe and Mg that are responsible for the formation of basificates upon granitization. On addition of NaCl ($X_{NACl} \approx 0.1$) to the fluid, solutions carry out Fe and Mg from host rocks. Ca behaves like an inert component (Khodorevskaya, 2019). The experiments have shown that the presence of both Na ions and carbonate ions in solutions results in the removal of SiO₂ and CaO from rocks and the inertness of Mg. Such metasomatic alterations of host rocks are not characteristic of the formation of basificates upon granitization.



Fig. 3. SiO₂-normalized FeO, MgO, CaO and Al_2O_3 concentrations in Hbl_{Di} and $Hbl_{S.}$

Fig. 3 shows that SiO_2 and particularly CaO concentrations in Hbl_s (MgO-normalized) are lower than those in Hbl_{Di} . Consequently, part of Si and Ca is dissolved and Al_2O_3 and FeO in HBls increase slightly in comparison to Hbl_{Di} .

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Kovalskaya T.N., Varlamov D.A., Shapovalov Yu.B., Kotelnikov A.R., Kalinin G.M. The specification of amphibolization process in gabbroids of Tiksheozerskiy massif (by experimental data)

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Abstract: Experimentally studied the formation of alkaline amphibole rims around grains of clinopyroxene (diopsidehedenbergite-augite composition) encountered in the study of mineral characteristics Tiksheozerskiy masisif. Gabbro from Lukkylaisvaara massif was used as a starting material, because it is less susceptible to secondary changes, in contrast to Tiksheozerkiy massif. In the experiments with a concentration of KCI and KF 1 M was obtained amphiboles range pargasite-cataphoric, the composition closest to the natural. Keywords: amphibole,experiment, postmagmatic processes, alkaline massifs, gabbro

Within the Fenno-Scandinavian shield, the development of amphibolites in the main rocks is quite common (Khodorevskaya, Varlamov, 2018, Safonov et al., 2014), however, the alkaline nature of postmagmatic changes in the main rocks of the Tiksheozero massif is most interesting.

The central part of the massif is composed by olivinites, in places heavily serpentized and chloritized, interspersed with aluminum chromites, relics of olivine and clinopyroxene (fig. 1). The basic rocks are pyroxenites and gabbroids, which are also quite strongly modified. Pyroxenites are composed of clinopyroxene (diopside-hedenberigit and augite), phlogopite, and titanium magnet. In gabbroids, pyroxene of diopside-hedenbergite composition, plagioclase with an anortic component of 70-75%, amphibole of two generations, corresponding to pargasite and richterite-cataphorite, are also observed. The first amphibole forms independent grains, the second is found in rims around the clinopyroxene grains of the diopside-hedenbergite composition, which is probably the result of postmagmatic high-temperature alteration of the rocks of the massif. An example of the relationship between clinopyroxenes and amphiboles is shown in Fig.2. Within the same breed, amphiboles of different composition are found, which is a consequence of the change in the physicochemical conditions of rock formation and the potential of alkaline components.

The paragenetic analysis carried out earlier and geothermometers applied on its basis (Perchuk, 1970) made it possible to calculate the formation temperatures of amphibole parageneses. The formation temperatures of amphibole-pyroxene parageneses of the Tikshozero massif using clinopyroxene-amphibole, biotite-amphibole, and pyroxene-biotite geothermometers (Perchuk, Ryabchikov, 1976) are estimated at 710-980°C. It was not possible to estimate the formation pressure amphibole of rims using an amphibole geothermometer (Simakin, Shaposhnikova, 2017) because of the alkaline nature of amphiboles. The pressure values during the formation of the Tikshozero massif, based on the literature data (Metallogenia ... 2001), are estimated at 3-4 kbar. Therefore, to reconstruct the mechanism and conditions of the process of amphibolization of Tikshozero gabbroids, an attempt was made to experiment it with experimental parameters with parameters similar to those calculated. This method is described in detail in the work (Suk et al., 2007). The study of sodalite-containing parageneses in the rocks of the later phases of the formation of the Tiksheozero massif and the thermometry carried out using the data obtained showed that these

Component	Luckulais-	Tikshoozoro
Component	vaara	TIKSHEOZEIO
SiO ₂	49.27	47.13
TiO ₂	1.03	3.16
Al_2O_3	13.43	11.46
Cr_2O_3	0.13	0.18
FeO*	14.94	13.98
MnO	0.14	0.67
MgO	5.21	5.98
CaO	6.24	7.02
Na ₂ O	4.35	6.16
K ₂ O	1.81	3.86
Total	99.56	99.60

Table 1. The average composition (wt.%) of gabbroids

 from the Lukkulaisvaara and Tikshozersky massifs

associations were formed at a temperature of about 450 ° C (Ustinov et al., 2006). The anionic group in sodalite is represented only by the Cl- ion. These data make it possible to use KCl solution as a fluid in modeling the amphibolization process.

For the experiments, crushed gabbro of the Luckulaisvaara massif (Karelia) were used as starting materials, since the composition of the main rocks of the Lukkulysvaara massifs is similar in chemical composition to Tiksheozersky (Table 1), while they were significantly less subjected to secondary changes in contrast to the Tikshozero massif. The fluids used were KCl and KF solutions with concentrations of 0.5, 1 M, and 2 M, respectively. All experiments were carried out in high-pressure gas installations with internal heating UVGD-10000.

The starting materials were loaded into platinum ampoules of $\emptyset 5 \times 0.2 \times 50$ mm or $\emptyset 4 \times 0.1 \times 50$ mm, the required amount of fluid solution was added, weighed and brewed. The filled ampoules were loaded into the reactors of the plants, put into operation and maintained at the experimental parameters for 10 days.

First, the reaction mixture was heated to $1100 \degree C$ at 3 kbar, kept for 3 hours, then isobaric cooling to 850 ° C followed by aging for 10 days. In the course of the two series of experiments (with KF and KCl solutions with a concentration of 0.5 M, 1 M, 2 M), the following results were obtained: the products of the experiments were a fine-crystalline mass (Fig. 3, 4) of a greenish-gray color; individual crystallites.

Table 2. Compositions (wt.%) of Tikshozero amphiboles and synthesized amphiboles

Com-			Na	tural samples	Experimental samples			
ponent	pyroxenite	gabbro	gabbro	iolite-urtite	syenite carbonatite		Synthetic amphibole (1M KF)	Synthetic amphibole (1M KCl)
SiO ₂	44.08	41.33	43.27	49.10	40.21	51.91	47.18	46.12
TiO ₂	0.48	0.06	1.41	0.91	1.07	0.94	1.32	0.86
Al_2O_3	11.20	17.28	10.91	6.53	14.30	4.06	12.78	10.42
Cr_2O_3	-	-	-	-	-	-	-	-
FeO*	16.43	20.44	18.57	13.23	19.38	13.75	14.94	15.91
MnO	0.00	0.13	0.05	0.00	0.19	0.09	0.25	0.03
MgO	11.81	6.36	10.81	15.60	9.06	14.70	12.32	13.81
CaO	13.47	11.96	9.00	8.68	10.93	7.30	6.14	8.01
Na ₂ O	1.29	1.85	5.16	5.43	3.57	6.66	2.24	3.71
K_2O	1.24	0.58	0.81	0.52	1.30	0.59	1.83	1,13
Total	100.00	100.00	100.0 0	100.00	100.00	100.00	100.00	100.00



Fig. 1. Schematic position of the Tikshozero and Eletozero massifs.



Fig. 2. Natural amphibole rims around clinopyroxene.



Fig. 3. Products of experiments with 1 M KCl solution at a temperature of 850 $^\circ$ C and a pressure of 3 kbar.

Fig. 4. Products of experiments with 1 M KF solution at a temperature of 850 $^{\circ}$ C and a pressure of 3 kbar.

Experiments with 0.5 M KCl solution. Analysis of the products of experiments with a fluid concentration of 0.5 M KCl revealed no formation of alkaline amphiboles. In the interstitium between the newly formed clinopyroxene are fine grains of potassium feldspar

Experiments with 1M KCl solution. In experiments with such a salt concentration in the fluid, clinopyroxenes of diopside-hedenbergite and amphiboles were obtained in terms of their composition corresponding to richteritol cataphorite observed in Tiksheozero gabbroids (Fig.3, 4, Table 2). The size of the individual grains reaches 100 microns.

Experiments with 2M KCl solution. Among the products of this series of experiments, alkaline amphiboles, which differ greatly in composition and single grains of clinopyroxenes, were noted; titanomagnetite was found as an accessory mineral.

Experiments with 0.5M KF solution. As in the experiment with 0.5 M KCl as a fluid, no alkaline amphiboles were observed in this experiment. In the products of experience diagnosed with allocation of clinopyroxene and phlogopite. The crystallite size in the products of experience does not exceed 50 microns.

Experiments with 1M KF solution. As in the experiments with 1 M concentration of KCl, clinopyroxenes of diopside-hedenbergite series (Table 2) and alkaline amphiboles of the riherite-cataphorite series were diagnosed in the products of these experiments. However, amphiboles of such composition were encountered by us in the ijolit-urtites of the Tikshozero massif. It is possible that subsequent post-magmatic carbonatization of the massif influenced the differences in the compositions of amphiboles.

Experiments with 2M KF solution. In the products of these experiments, the formation of a noticeable amount of fluorite was observed, which, apparently, is due to the high concentration of F- ions in the fluid, as well as the acicular release of fluorine-containing phlogopite. The conducted series of experiments showed the following results: The process proceeded at the high-

temperature post-magmatic stage at a temperature of the order of 850 ° C. The salt concentration (KCl or KF) in the fluid with high-temperature postmagmatic changes in gabbroids of the Tiksheozero massif fluctuated within 1 M. At lower concentrations, the formation of amphiboles did not occur, at large concentrations phlogopite and fluorite were formed. One of the possible mechanisms for amphibolization of the Tiksheozersky gabbroids was the separation of volatiles upon subsequent introduction of alkaline rocks, namely, ijolite-urtites, which is indicated by the similarity of late-generation amphibole compositions in gabbroids, iyolite-urtites, and in samples obtained in the course of the conducted experiments. Thus, our data characterize the temperature and fluid formation of amphibole rims around the clinopyroxenes in the Tiksheozero gabbroids, and also shows that a complex of differentiated rocks of the massif could be formed as a result of a complex evolution of the heterogeneous fluid-magmatic system.

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Limanov E.V.¹, Butvina V.G.¹, Safonov O.G.¹, Van K.V.¹ Experimental study of the grossular-pyrope-enstatite+ H₂O-KCl system at 3 and 5 GPa.

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Abstract. The paper presents the experimental results of phlogopite formation in the grossularpyrope–enstatite + H₂O–KCl system at 3 GPa and 850°C, also at 5 GPa and 1000°C. It was established that an increase of the salt component in the fluid leads to the decomposition of aluminum-containing minerals, such as enstatite and garnet, as well as the formation of phlogopite and diopside. The amount of aluminum in enstatite decreases, and the amount of chlorine in phlogopite increases with increasing X_{KCI} in the fluid. In experiments at $X_{KCI} = 0.05$, 0.1 T = 1000 ° C, and also in experiments at $X_{KCI} = 0.1 T =$ 850 ° C, X_{Grs} in garnet increases, which can explained by the two different reactions: 1/2Prp + $3/2En + [1/2K_2O + H_2O] = PhI and Di + 0.8CaTs +$ 0.3KCl + 0.2H₂O = 0.6Grs + 0.2Phl + 0.2Cl-Phl. At $X_{KCI} = 0.2 X_{Grs}$ in garnet decreases, which is explained by the reaction 1/2Prp + 1/2Grs + 6En + $[2KCI + H_2O] = 1/2PhI + 1/2CI-PhI + 3/2Di$. The established effects are good indicators of KCl activity in the fluid during the process of modal mantle metasomatism.

Keywords: mantle metasomatism, experiment, fluid, phlogopite, chloride, KCl.

Mantle xenoliths undergo plural changes in the course of their interaction with fluids and melts of different composition and origin. In addition to late kimberlite metasomatism, xenoliths are affected by early, mantle metasomatism, which results in the formation of minerals untypical for primary peridotitic paragenesis (for example, phlogopite, amphibole, titanite, ilmenite, apatite, carbonates, etc.). Various stages of sulfides. mantle metasomatism leads to a heterogeneous mantle formation, as evidenced by numerous studies of xenoliths, brought to the surface by melts of kimberlites and alkaline basalts on all continents (Sobolev, 1977; Dawson 1980).

The activities of perfectly mobile components play the role of intensive parameters that control the reactions occurring during metasomatism. In addition to H_2O and CO_2 , K and Na can play the role of perfectly mobile components in the modal mantle metasomatism. Numerous mineralogical and geochemical data indicate the active participation of these components (Kamenetsky et al., 2013). Alkaline components dissolve in fluids in the various salts form, among which chlorides play a particularly important role (Safonov and Butvina, 2016). The interaction of mantle rocks with alkaline fluids leads to a change in the composition of primary minerals, as well as to the formation of K and Na-containing minerals, such as phlogopite, a typical mineral indicator of modal mantle metasomatism. The phlogopite formation in mantle rocks during their interaction with K-containing fluids can be explained by the following reaction (Safonov and Butvina, 2013; 2016):

$$5MgSiO_{3} + CaMg_{2}Al_{2}Si_{3}O_{12} + [K_{2}O + 2H_{2}O] = K_{2}Mg_{6}Al_{2}Si_{6}O_{20}(OH)_{4} + CaMgSi_{2}O_{6}$$
(1)

or $5En + Grt + [K_2O + 2H_2O] = Phl + Di$, which is a combination of two boundary reactions

$$1/2Prp + 3/2En + [1/2K_2O + H_2O] = Phl$$
 (2)
 $1/2Grs + 9/2En + [1/2K_2O + H_2O] = Phl + 3/2Di$ (3)

In these model reactions, the alkaline component is represented as K_2O oxide. In natural fluids, potassium is present in the form of various salts (chlorides, carbonates, etc.). These reactions reproduce the process of gradual transformation of upper mantle garnet lherzolites and harzburgites through lead-free phlogopite-containing peridotites to phlogopite verlites. Such xenoliths are well known in kimberlites (eg van Achterbergh et al., 2001).

The study of the reactions responsible for the phlogopite formation in the mantle rocks during the modal mantle metasomatism is the key to understanding the mechanism of this process. Experimentally established patterns of changes in mineral associations and the composition of minerals from K and Na activities in fluids may be applicable to the assessment of K and Na activities, as well as the compositions of the fluids themselves.

The experiments were carried out in the system grossular-pyrope-enstatite + H_2O -KCl. The purpose of the study is to establish patterns of the mineral and chemical composition changes of the system, depending on the content of the salt component in the fluid. As a starting material, there was used a mixture of pyrope's and grossular's gels, brucite's and quartz's powders. KCl was added to produce the required starting $X_{KCl} = KCl/(KCl + H_2O)$ (0, 0.05, 0.1, 0.2, 0.4). The experiments were performed using highpressure apparatuses "anvil-with-hole" NL-40, also toroidal "anvil-with-hole" NL-13T to simulate the P-T conditions of the upper mantle. Two series of experiments were carried out under the following conditions: 1) P = 3 GPa and T = 850°C (exposure of 6 hours), 2) P = 5 GPa and T = 1000 °C (exposure of 48 hours). Analytical studies of the experimental products were carried out using a were analyzed using CamScan MV2300 (VEGA TS 5130MM) electron microscope equipped with EDS INCA

Energy 350 and Tescan VEGA-II XMU microscope equipped with EDS INCA Energy 450 and WDS Oxford INCA Wave 700. The study was done at the D.S. Korzhinskii Institute of Experimental Mineralogy Russian Academy of Sciences (IEM RAS).



Fig.1. Plots of a) X_{Grs} in garnet and b) Al apfu in clinopyroxene from X_{KCl} in the fluid. Legend: black triangles – the results of experiments at 3 GPa, white dots – the results of experiments at 5 GPa.

At a pressure of 3 GPa and $X_{KCl} = 0$, the system contains garnet with $X_{Grs} = 0.25$ (hereafter, mean values), aluminum-bearing enstatite and diopside. At $X_{KCl} = 0.05$, X_{Grs} of the garnet slightly decreases to a value of 0.23 (Fig. 1, a), and potassium-containing quenching phases appear in the experiment products. Phlogopite begins to form in the system at $X_{KCI} = 0.1$, which leads to a decrease of garnet and enstatite amounts according to reactions 2 and 3, as well as X_{Grs} in garnet increases to 0.31. The amount of garnet and enstatite decreases again at $X_{KCI} = 0.2$, accompanied by an increase in the amount of phlogopite and diopside. X_{Grs} of the garnet drops to 0.2. At $X_{KCl} = 0.4$, garnet is absent in the system, enstatite is rare, phlogopite and diopside dominate. Similar to the experiments at 3 GPa, at a pressure of 5 GPa and $X_{KCl} = 0$, the system contains garnet with $X_{Grs} = 0.03 - 0.04$, aluminum-bearing enstatite and diopside. Diopside disappears from the experimental products at $X_{KCl} = 0.05$, which is reflected in the composition of the garnet, increasing $X_{\mbox{\scriptsize Grs}}$ to 0.24 – 0.26 (Fig. 1, a). Diopside reappears among the experimental products at $X_{KCl} = 0.1$, as well as newly formed phlogopite. The amount of enstatite and garnet in the system decreases with increasing X_{KCI} in the fluid (according to reactions 2 and 3), so that at $X_{KCl} = 0.4$ enstatite and garnet are absent, and phlogopite and diopside dominate in the system. Changes of the mineral composition of the experimental products, depending on X_{KCI} in the fluid, are presented in Table 1. All experiments contained quenching phases, indicating the presence of a small amount of aluminosilicate melt.

The calcium content in the garnet is regulated by several reactions simultaneously or competing in the system. When the amount of salt component in the fluid is small ($X_{KCl} = 0.05 - 0.1$) X_{Grs} in garnet increases (Fig. 1, a), which can be explained by reaction 2. Pyropic component decomposes with

formation of phlogopite, which leads to an increase in the grossular component in garnet. The increase of X_{Grs} in garnet also can be explained by another reaction:

$$Di + 0.8CaTs + 0.3KCl + 0.2H_2O = 0.6Grs + + 0.2Phl + 0.2Cl-Phl$$
(4)

which at 5 GPa and $X_{KCl} = 0.05$ may be responsible for the disappearance of clinopyroxene from the experimental products, as well as for the decrease in the amount of aluminum in clinopyroxene at $X_{KCl} =$ 0.05 - 0.1 in both series of experiments (Fig. 1, b). Reaction 3 begins to dominate when X_{KCl} increases in the fluid, which leads to a decrease in the amount of garnet in the system and X_{Grs} in the garnet, also an increase in the amount of aluminum in clinopyroxene at $X_{KCl} = 0.2$. The amount of aluminum in clinopyroxene tends to decrease, which may be due to an increase in the amount of phlogopite in the system at $X_{KCl} = 0.4$, in experiments conducted at 3 GPa.

Table 1. Products of experiments.

X _{KC1}	850°C, 3 GPa,	1000°C, 5 GPa,			
	6 hours	48 hours			
0	$Grt + En + Di + Q^*$	Grt + Di + Q			
0.05	Grt + En + Di + Q	Grt + En + Q			
0.1	Grt + En + Di + Phl + Q	Grt + En + Di + Phl + Q			
0.2	Grt + En + Di + Phl + Q	Grt + En + Di + Phl + Q			
0.4	En + Di + Phl + Q	Phl + Q			
*Q – quenching phases					

The increase of X_{KCl} in the fluid is accompanied by the sequential decomposition of aluminum-rich phases, such as garnet and enstatite. The resulting relationships indicate the sequential implementation of the following reactions:

$$En + \frac{1}{3}Prp + \frac{2}{3}KCl + \frac{1}{3}H_2O] = \frac{1}{3}Phl + \frac{1}{3}Cl-Phl$$
(5)

Mineral equilibria at high PT-parameters

$$En + 1/5MgTs + [2/5KCl + 1/5H_2O] = 1/5Phl + +1/5Cl-Phl.$$
(6)

Reaction 6 is demonstrated in a decrease of aluminum in enstatite with an increase of X_{KCI} in the starting fluid (Fig. 2, a).

with an increase of the salt component in the fluid,

reaching in some cases values of 3.6 wt. % at X_{KCI} = 0.4 in experiments at 5 GPa and 1000°C (Fig. 2, b). Such high chlorine values in phlogopite can be explained by the fact that at a given salt concentration, phlogopite is not in equilibrium with a water-salt fluid, but with a water-containing salt The amount of phlogopite in the system increases melt.



Fig.2. Plots of a) content of Al apfu in En and b) Cl wt. % in Phl from X_{KCl} in the fluid. Legend: black triangles – the results of experiments at 3 GPa, white dots - the results of experiments at 5 GPa.

It can be seen from the experimental results that aluminum-rich enstatite and garnet become unstable in the presence of alkaline fluid H₂O-KCl. X_{Grs} in garnet increases and aluminum in clinopyroxene decreases at $X_{KCl} = 0.5 - 0.1$, but at $X_{KCl} = 0.2 X_{Grs}$ in garnet decreases, and Al in clinopyroxene increases due to several competing reactions in the system. The amount of aluminum in clinopyroxene tends to decrease at $X_{KCI} = 0.4$, P = 3GPa and T = 850 ° C, which may be due to an increase in the amount of phlogopite in the system. The amount of aluminum in enstatite decreases and the chlorine content in phlogopite increases with an increase in the salt component in the fluid. These effects can then be used to quantify the activity and concentration of KCl in the fluid in the processes of modal mantle metasomatism.

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Spivak A.V., Litvin Yu.A., Zakharchenko E.S. Experimental study of melting relations of multicomponent diamond-forming oxidesilicate-carbonate system at 15 GPa,

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Abstract. A preliminary experimental study of phase relationships of MgO - FeO - SiO₂ - Na₂O - CaO - K₂O -CO₂ system has been carried out at 15 GPa. It was determined that eutectic reaction of wadsleyite is crucial for processes of melting-crystallization of substance of the transition zone (at depths of \sim 400-450 km). The eutectic mechanism saves wadsleyite in magmatic and diamond-forming systems of the transition zone until the completion of the crystallization of ultrabasic melts.

Keywords: transition zone of the Earth's mantle, diamondforming systems, melting relations, physico-chemical experiment, high pressure

The study of melting relations of multicomponent magmatic and diamond-forming systems makes it possible to prove the physicochemical mechanisms of deep magmatism processes and regularity of mantle rocks and minerals genesis. In assessing of the overall chemical and phase composition of diamond-forming media in the mantle transition zone the mineralogical data of syngenetic inclusions in diamonds, whose genesis is associated with the corresponding depths of the Earth's mantle, are of particular importance. There are wadsleyite and ringwoodite (high pressure polymorphs of olivine composition (Mg,Fe)₂SiO₄)) and majoritic garnet as the main minerals within inclusions of natural diamonds (formed at the depths of the transition zone). Oxide minerals - magnesiowustite (Fe,Mg)O and stishovite SiO₂, and Na-, Mg-, Fe-, Ca-, and Kcarbonates are also found (Kaminsky, 2012). According to the mineralogical data, ultrabasic and oxide-silicate, as well as carbonatite basic associations were classified as the original material of the lower mantle.

The participation of components of the original silicate-oxide rocks of the transition and other mantle zones in the formation of diamond-forming silicateoxide-carbonate melts at all depths of the mantle was substantiated earlier (Litvin et al., 2016). Both ultrabasic and basic partially melted oxide-silicatecarbonate systems has been experimentally confirmed as diamond-forming media (Litvin, 2016; Spivak, Litvin, 2019). As a result of experimental researches of the reactionary interaction of ringwoodite in the silicate-carbonate system at 20 GPa, the peritectic reaction of ringwoodite with the formation of basic association of magnesiowustite and stishovite was justified both in the Mg₂SiO₄-Fe₂SiO₄ boundary system, and in the diamondforming one at presence of silicate-carbonate melt (Spivak et al., 2019).

The purpose of experimental investigations at 15 GPa is studying of melting phase relations of a pseudo-triple multicomponent oxide-silicatecarbonate system (MgO + Carb*) - (FeO + Carb*) - (SiO₂ + Carb*) to determine physicochemical mechanisms of a formation of corresponding subsolidus mineral associations.

Experimental studies of the melting phase relations of the MgO - FeO - SiO₂ - CaO - Na₂O - $K_2O - CO_2$ system were carried out at 15 GPa and 1000-1500 °C. The experiments were carried out using a multi-anvil cubic apparatus of high pressures and temperatures at the Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI) University of Bayreuth, Germany. Four starting compositions were used: (I) Mg₂SiO₄ -66.50, $Fe_2SiO_4 - 3.50$, $CaCO_3 - 10.20$, $Na_2CO_3 -$ 9.90, K₂CO₃ - 9.90; (II) Mg₂SiO₄ - 56.00, Fe₂SiO₄ -14.00, CaCO₃ - 10.20, Na₂CO₃ - 9.90, K₂CO₃ - 9.90; (III) Mg₂SiO₄ - 49.00, Fe₂SiO₄ - 21.00, CaCO₃ -10.20, Na₂CO₃-9.90, K₂CO₃-9.90; (IV) Mg₂SiO₄-28.00, Fe₂SiO₄ - 42.00, CaCO₃ - 10.20, Na₂CO₃ -9.90, K₂CO₃-9.90 (wt%).

Experimental samples were investigated by the scanning electron microscope CamScanM2300 (VEGA TS 5130MM) with spectral analyzer Link INCA at the Institute of Experimental Mineralogy RAS (operators – D.A. Varlamov, A.A. Viryus).

Raman–spectra of the experimental samples were measured in geometry of backscattering using the apparatus consisting of spectrograph Acton SpectraPro-2500i with detector cooling up to -70 °C CCD Pixis2K and the microscope Olympus with continuous solid-state monomeric laser with radiation wave length 532 nm and diode pumping at the Institute of Experimental Mineralogy RAS too.

An experimental study of melting phase relations of $Mg_2SiO_4 - Fe_2SiO_4 - CaCO_3 - Na_2CO_3 - K_2CO_3$ system was carried out at 15 GPa. It should be note that Mg₂SiO₄ - Fe₂SiO₄ system is a polythermal section of the key value for the rocks-forming periclase Per - stishovite Sti - wustite Wus system of the substance of the transition zone of the Earth's mantle. Olivine, wadsleyite, ringwoodite, enstatite, clinopyroxenes (augite, pizhonit), magnesite. carbonates (magnesite, Ca-magnesite, Ca, Na, Kcarbonates), melt were detected in experimental samples at 15 GPa and temperatures of 1500-1000 °C (Fig. 1).

The crystals of $(Mg,Fe)_2SiO_4$ compositions are solid solutions of the components Mg_2SiO_4 and Fe_2SiO_4 and are represented by three polymorphic modifications: olivine, wadsleyite and ringwoodite. Phase identification was carry out using microbrobe and Raman spectroscopy. #mg of olivine is within 0.74-0.98, wadsleyite - 0.57-0.65, ringwoodite -0.49-0.42. The components Ca, Na and K for olivine, wadsleyite and ringwoodite are impurity and are determined at the limit of detection.



Fig. 1. SEM images of the experimental samples of polythermal section $(Mg_2SiO_4)_{70}Carb^*_{30} - (Fe_2SiO_2)_{70}Carb^*_{30}$ at 15 ГПа after quenching: (a) $(Mg_2SiO_4)_{49.0}(Fe_2SiO_4)_{21.0}(Carb^*)_{30.0}$ at 1500°C; (b) $(Mg_2SiO_4)_{28.0}(Fe_2SiO_4)_{42.0}(Carb^*)_{30.0}$ at 1300°C; (c) $(Mg_2SiO_4)_{56.0}(Fe_2SiO_4)_{14.0}(Carb^*)_{30.0}$ at 1300°C; (d) $(Mg_2SiO_4)_{28.0}(Fe_2SiO_4)_{42.0}(Carb^*)_{30.0}$ at 1300°C; (c) $(Mg_2SiO_4)_{56.0}(Fe_2SiO_4)_{14.0}(Carb^*)_{30.0}$ at 1300°C; (d) $(Mg_2SiO_4)_{28.0}(Fe_2SiO_4)_{42.0}(Carb^*)_{30.0}$ at 1300°C. Symbols: L – melt, Ol - olivine, Wds – wadsleyite, FRwd – ringwoodite, Cpx – clinopyroxene, Mag –magnesite, Ca, Na, K-Carb – carbonate, MWus – magnesiowustite.

Enstatite En crystals present in experimental samples at all starting compositions. Clinopyroxenes are represented by two varieties - augite Aug and pigeonite Pgt. Phases differ in composition as well as Raman spectra. Alkaline components were included in the composition as impurities: pigeonite - Na₂O -3.80, K₂O - 0.21, augite - Na₂O - 4.99, K₂O - 0.22 Magnesiwustite MWus is present in wt%. experimental samples of IV starting composition and is a solid solution of periclase and wustite. At the same time, the value of #fe of magnesiowustites reaches an average of 0.95. Magnesite Mag and Ca magnesite Ca-Mag are first formed among the carbonate phases Carb*, then Ca,K-carbonate Ca,K-Carb and Ca,K,Na-carbonates Ca,K,Na-Carb join them with decrease of temperature.

A preliminary experimental study of reactions of polymorphic phases of the transition zone with the composition (Mg,Fe)₂SiO₄ at 15 GPa showed that coexistence of the three polymorphic phases olivine, wadsleyite and ringwoodite is revealed at partially melting of the $Mg_2SiO_4 - Fe_2SiO_4 - CaCO_3$ - Na₂CO₃ - K₂CO₃ system. Iron-containing olivine $(Mg,Fe)_2SiO_4$ is a metastable phase at these PT parameters. It was previously shown that presence of olivine is possible only in a case of the boundary composition Mg₂SiO₄ of the Mg₂SiO₄ - Fe₂SiO₄ system at a pressure of 15 GPa (Fei et al., 1991; Fabrichnaya et al, 2004). It should be noted that the mineral phase with the composition of olivine (Mg,Fe)₂SiO₄ was found among micro inclusions in superdeep diamonds in association with bridgmanite and Ca-perovskite. #mg of the phase varies over a

wide range, including its ferrous compositions 0.79-0.89 unusual for mantle olivine (Kaminsky, 2012). The formation of these "olivines" was connected with the retrograde transformation of higher pressure phase or with the retrograde reaction of ferropericlase *FPer* + ferrobridgmanite *FBrd* = olivine *Ol*.

The association of magnesiowustite and stishovite as a result of the peritectic decomposition of ringwoodite (Mg,Fe)₂SiO₄ (Litvin et al., 2017) was not found. For the section $Mg_2SiO_4 - Fe_2SiO_4$ at 15 GPa, the eutectic reaction of the wadslevite and ringwoodite (Mg,Fe)₂SiO₄ has a decisive role in the melting-crystallization processes. The eutectic mechanism saves wadslevite and ringwoodite in magmatic and diamond-forming systems until the completion of crystallization of ultrabasic melts. Thus, the ultrabasic-basic mantle evolution cannot occur even at the fractional crystallization. This mechanism is not limited by the participation of carbonate minerals and metasomatic clinopyroxene in the system. Carbonates and clinopyroxenes are as accompanying components in this case, suplementing the phase composition of the diamond-forming system.

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