

Mineral equilibria in silicate and ore systems

#Litvin V.Yu., Litvin Yu.A. Basic reactions of mantle forsterite and fayalite in the forsterite - fayalite - jadeite - acmite system at 6.5 GP (lithosphere garnetization effects)

key words [mantle olivine basic reactions garnetization Fe-NMS-phase]

Introduction. The modern convective model of the Earth's mantle has been created on the base of the recent empiric and theoretic data on the Earth's structure. One of the two main forms of convection is subduction of the oceanic crust. The second form is ascending plumes that transfer anomalously hot material from the Earth's depths. Mantle plumes are identified by geophysical methods, they are in conformity with komatiite magmatism of hot spots calling for a magmatic source with temperatures in excess of an upper mantle temperature by at least 200°C.

The basaltic oceanic crust, as it descends in subduction zones, undergoes phase transformations, the principal of which in the volume of the involved material is garnetization (beginning with basalt eclogitization). From the data of [1] garnetization of the descending oceanic basalts can reach 90% at a depth of 500-600 km and is of the order of 70% at a depth of 400 km. In a 4-22 GPa run an investigation of the forsterite (Fo) - jadeite (Jd) system [2], confined to the basalt tetrahedron base [3], revealed the effects of forsterite garnetization. Garnet formation is a result of chemical (subsolvus) reaction between forsterite Mg_2SiO_4 and jadeite $NaAlSi_2O_6$ (1, see below). In this case along with pyrope garnet $Mg_3Al_2Si_3O_{12}$ there also forms the NMS-phase of the composition $Na_2Mg_2Si_2O_7$ which is a most readily melting phase of all the known mantle minerals and is capable of causing a drastic decrease in the mantle solidus temperature.

The possibilities of formation of the NMS-phase of a more complicated componental composition were studied in runs with iron-bearing composition at 13.5 GPa [4]. As a result, a new iron-bearing phase having the formula $Na_2Mg_{4+x}Fe^{3+}_{2-2x}Si_{6+x}O_{20}$ isostructural with minerals of the aenigmatite group was found to form. The aenigmatite phase formation reaction(2), similar to the stated above for the NMS-phase was used to describe possible mantle processes. In doing so, the aenigmatic phase was relegated to a role of the NMS-phase under the iron-bearing mantle conditions.

Experimental results. In this work we study the forsterite - fayalite - jadeite - acmite system compositionally close to the starting material used in [4]. One has to mention the important methodical differences between the runs in [4], where a LaCrO₃

(oxidative) heater and a rhenium tube were employed, and our work where along with a graphite (reductive) heater we used a tungsten lining for platinum capsules leading in the course of the run to the formation of a reductive buffer pair W/WO₂ (possessing the properties close to Fe/FeO). One may assume that in the run performed in [4] the redox conditions favoured the stability of Fe³⁺. It has also been found that in the runs involving tungsten lining the redox conditions favour the stability of the Fe²⁺ which meets the actual redox conditions existing in the mantle to a greater extent [5]. We have focused our attention in this work on the Fo-Jd-Acm system; the runs in the Fa-Jd, Fa-Acm, and Fo-Acm systems were performed to find out the behaviour of individual components.

The Fa-Jd system. A large number of almandine garnets (Na-bearing), ferrosilite and the new phase $Na_2Fe^{2+}_{4.5}Si_{6.5}O_{18}$ subsequently termed as the NFS-phase (Na-Fe-silicate) were found. For this system reaction (3) can be written.

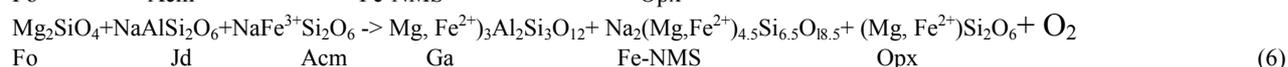
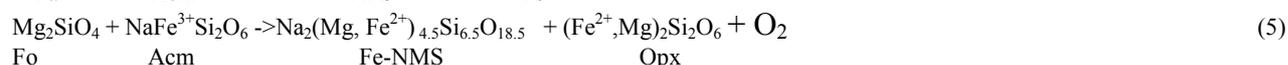
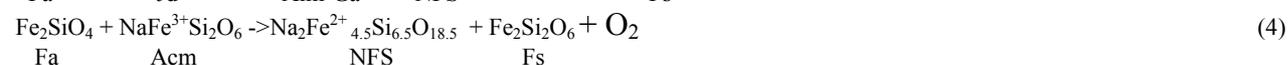
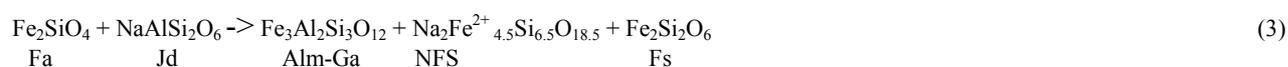
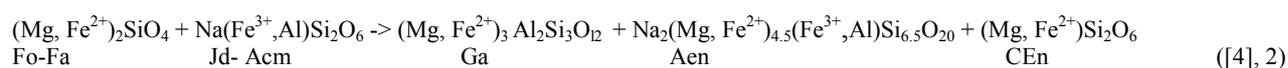
The Fa-Acm system, The run products were: the NFS-phase $Na_2Fe^{2+}_{4.7}Si_{6.4}O_{18.5}$ and ferrosilite $Fe^{2+}_2Si_2O_6$. It was assumed that in the presence of Fe³⁺ the formation of garnet could take place with the Al→Fe³⁺ substitution but garnet was not, however, identified. All the iron transited to the divalent state in the course of the run. That was indicated by indirect signs, e.g. the formation of ferrosilite $Fe^{2+}_2Si_2O_6$. We shall term the new phase of the composition $Na_2(MgFe^{2+})_{4.5}Si_{6.5}O_{18.5}$ as the iron-bearing Fe-NMS phase. It can be assumed that the new phase also possesses a lower melting temperature compared to the order mantle minerals. As for its pressure stability field, than it is likely to be broader compared with the field of $Na_2Mg_2Si_2O_7$ which would have reflected the general tendency of the Fe/Mg substitution in minerals with the increasing pressure. For this system one can write the reaction (4).

The Fo-Acm system. The run products were $Na_2(MgFe^{2+})_{4.7}Si_{6.4}O_{18.5}$, orthopyroxene and olivine, no garnet phase was found. The valence behaviour of iron was analogous to that in the previous system. The stability of divalent form alone is supported by the presence of orthopyroxene $(Mg,Fe^{2+})_2Si_2O_6$ and solid solutions of Mg-Fe olivines. The composition of the Fe-NMS phase $Na_2(MgFe^{2+})_{4.7}Si_{6.4}O_{18.5}$ is likely to reflect the stability of continuous solid solutions with the NFS phase $Na_2Fe^{2+}_{4.7}Si_{6.4}O_{18.5}$ the chemical behaviour of the system is subject to reaction (5).

The Fo-Jd-Acm system. The run products were: Mg-Fe garnets, orthopyroxene and $Na_2(MgFe^{2+})_{4.7}Si_{6.4}O_{18.5}$. This suggests reaction (6). Interestingly, that the phases of reaction (6) replicate nearly completely compositions of the phases obtained in [4]. In our version there are no Al and Fe³⁺ in the $Na_2(MgFe^{2+})_{4.7}Si_{6.4}O_{18.5}$ phase which is due to full binding of aluminium by garnet and instability of Fe³⁺.

The following reactions were considered above:

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Discussion and conclusion. Mantle convection does not contradict the model of homogeneous ultrabasite composition of the mantle enriched in olivine as suggested by the composition of its upper 200 km zone, "sampled" by means of the mantle xenoliths.

The experimental data obtained for the forsterite-fayalite-jadeite-acmite system indicate an important role of the reactions (3) and (6) played in the evolution of the upper mantle substance and, possibly, more deep seated zones. These are the mantle olivine garnetization reactions accompanied by the formation of comparatively readily melting NFS and Fe-NMS-phases. The proceeding of these reactions necessitates rather high concentration of Na-alkaline components, higher than in the generally accepted models of the upper mantle compositions [1]. The occurrence under the upper mantle conditions of regions having an increased concentration of alkali components is attributed in the present-day mantle dynamics models to boundary (contact) regions between the descending oceanic platforms and the surrounding mantle in the subduction zones [6] and the ascending high temperature mantle plumes and the surrounding mantle in hot spots [7]. The possibility of formation of high-alkaline melts at low degrees of partial melting of the mantle substance itself (hosting subducted platforms "slabs") and ascending plumes was mentioned, for example, in [8]. Low degrees of ultrabasite mantle melting can be realized in thermal halos of mantle plumes. The global abundance of high-alkaline alumina melts of the mantle origin in the regions of intraplate magmatism was attested by a lot of evidence generalized in [9]. These melts are exclusively enriched in Na₂O (to 6.5 wt%), K₂O (more than 6.5 wt%), Al₂O₃ (to 23.5 wt%), SiO₂ (more than 62.5 wt%). The new experimental results obtained for the forsterite-fayalite-jadeite-acmite system under a high "mantle" pressure suggest that under the mantle conditions along with metamorphic garnetization of crust oceanic basalts in subduction zones there can manifest themselves other garnetization mechanisms with the mantle substance proper being involved. Garnetization of the mantle olivine can herewith be accomplished both in subsolidus reactions and garnetization reactions of the magmatic substitution type.

The idea of stability of the aenigmatite phase containing Fe³⁺ in association with garnet, having a strong affinity to ferric iron and buffering appreciably oxygen fugacity, under the deep-seated mantle conditions [4]

necessitates, for real mantle, high values of the redox potential providing the stability of the Fe³⁺ form. In principle, under the dynamic mantle conditions local sites of increased oxygen fugacity values can possibly, arise and provide for the realization of iron in the form of Fe³⁺. For example, Fe³⁺ in relatively high concentrations occurs in lower mantle minerals from inclusions in diamonds from Sao Luiz, Brazil (as derived from the Mossbauer spectroscopy data) [10]. Nevertheless, this question is ambiguous, and the possibility of the reaction (2) in deep-seated mantle is problematic. An alternative is the process of iron-bearing Na-Mg-silicate of tentative composition Na₂(Mg, Fe²⁺)_{4.5}Si_{6.5}O_{18.5} first identified in this work.

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#Chudinovskikh L.T., Jones A.P., Litvin Yu.A., Matveev Yu.A., Beard A. Ultra-high-potassic clinopyroxenes: experimental study at 7 GPa and 1000-1700°C

key words [high pressure high temperature]

The discoveries of potassium-bearing clinopyroxenes both in nature and in high-pressure experiments show that clinopyroxene can be a fundamental concentrator of potassium in the Earth's interior. Under experimental modelling the origin of carbonate-silicate rocks of the Kokchetav diamond-bearing complex, the system K_2CO_3 -diopside – grossular has been studied at 7 GPa and 1000-1700°C using an “anvil - with - hole” thoroidal type apparatus. The results of experiments and electron-microprobe analyses are presented in [1]. At 7 GPa and 1500-1600°C we obtained clinopyroxenes with ultra-high potassium content (up to 5.7 wt%); this value exceeds all the known from literature up to now, even when obtained in experiments at much higher pressures (up to 17 GPa) [2,3]. It is shown that these clinopyroxenes are complicated solid solutions of the end-member components: $KAlSi_2O_6$, $CaAl_2SiO_6$, $Ca_{0.5}K_{0.5}AlSi_2O_6$, $CaMgSi_2O_6$, and $MgSiO_3$ or $CaSiO_3$. Cation deficiency (the existence of vacancies) in M2 site of the structure due to the end member $Ca_{0.5}K_{0.5}AlSi_2O_6$, which we named Ca-Eskola's molecule [4,5], may facilitate substitution of such high potassium amount into the pyroxene structure even at 7 GPa. The following crystallochemical formulae for clinopyroxenes with the highest potassium content can be written according to microprobe analyses:

- 1110°C: $(Ca_{0.80}K_{0.14}Mg_{0.03}K_{0.03})(Mg_{0.78}Al_{0.22})(Al_{0.04}Si_{1.96})O_6$
- 1200°C: $(Ca_{0.78}K_{0.17}Mg_{0.01}K_{0.04})(Mg_{0.76}Al_{0.24})(Al_{0.03}Si_{1.97})O_6$;
- 1300°C: $(Ca_{0.81}K_{0.15}Mg_{0.00}K_{0.04})(Mg_{0.79}Al_{0.21})(Al_{0.04}Si_{1.96})O_6$;
- 1400°C: $(Ca_{0.78}K_{0.18}Mg_{0.00}K_{0.04})(Mg_{0.73}Al_{0.27})(Al_{0.01}Si_{1.99})O_6$;
- 1500°C: $(Ca_{0.78}K_{0.24})(Mg_{0.70}Al_{0.28})(Al_{0.03}Si_{1.97})O_6$;
- 1600°C: $(Ca_{0.77}K_{0.27})(Mg_{0.67}Al_{0.27})(Al_{0.01}Si_{1.99})O_6$;
- 1710°C: $(Ca_{0.75}K_{0.22}Mg_{0.02}K_{0.01})(Mg_{0.74}Al_{0.26})Si_2O_6$.

Noticeable discontinuity in the trend of K-Ca and K-(Mg+vacancies) relationships for M2 site (Fig.1) gives indirect evidence of some structural transformation [6], here – presumably from pure clinopyroxene to clinopyroxene, partially inverted to wollastonite (the excess of Ca in M2 site), when potassium content exceeds a certain limit under certain experimental parameters. Future studies should be done to confirm this assumption.

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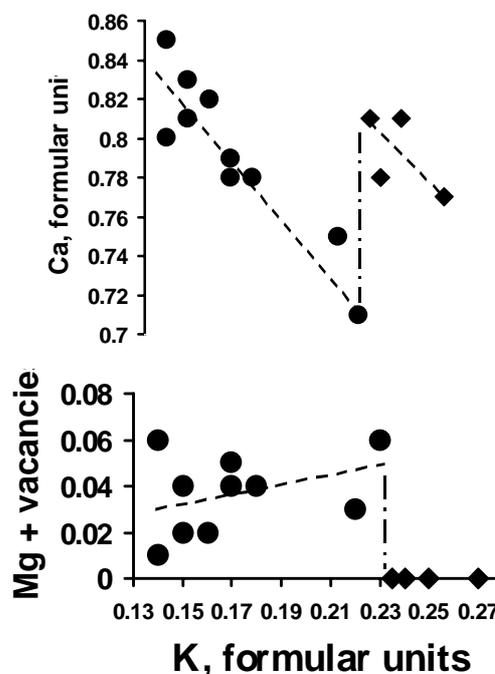


Fig.1. K-Ca and K-(Mg+vacancies) relationships in M2 site of clinopyroxenes with the highest potassium content at 7 GPa and 1110-1710°C.

#Litvin Yu.A., Zharikov V.A. Genesis of diamond: progress in experimental modeling.

key words [*diamond genesis carbonatite inclusions experiment pressure*]

The problem of diamond genesis is coming to a close due to combination of high pressure runs [1-3] and

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information on primary fluid inclusions in cubic and octahedral diamonds with a fibrous texture from kimberlites of Zaire [4] and Botswana [5] and on cloud-like fluid inclusions of the analogous composition in diamond single crystals of both peridotite and eclogite parageneses from deposits of South Africa, Siberia, and China [6]. The inclusions were found to "keep the memory" of their trapping by diamonds under the conditions close to the diamond-graphite equilibrium curve (4.5-7.5 GPa, 930-1350°C) [6-7]. Those and other features of the "in situ" trapping of inclusions at growth of diamond crystals provided reason enough to identify the inclusion substance as solutions wherefrom diamonds crystallized under the mantle conditions [5,6]. So, the information on the chemical composition of primary fluid inclusions in natural diamonds turned out decisive in devising high pressure runs.

The idea of the chemical composition of primary fluid inclusions in mantle diamonds is illustrated in table 1 compiled on the base of micro-X-ray spectral determinations with the use of marrow electron beam. (0.1 µm in dia) [5]. The results of the analyses are normalized under the assumption that the "nonvolatile" fraction is composed of 95 wt% of Si, Al, Ti, Fe, Ca, Mg, K, and Na oxides and 5 wt% of Cl, P and other rare elements. The table gives the compositions of inclusions for the samples demonstrating highest concentrations of K₂O, Na₂O, CaO, MgO, FeO, SiO₂, CO₂ and H₂O separately. The component concentrations range appreciably. In order to approximate the

true compositions of fluid inclusions in diamonds it was proposed to regard them as mixtures of two model boundary compositions defined as carbonatite and water-siliceous ones [5,6]. In recalculating chemical compositions of fluid inclusions and model boundary compositions to molecular pct for the 100-pct sum (table 2), a relative contribution of individual components to the composition of the inclusions becomes more apparent (we recalculated 8 above mentioned components of the "nonvolatile" fraction, given in table 1 within the 95-pct sum). It is clear that important parts are played by the alkali group of oxides K₂O+Na₂O, group of alkali-earth elements and iron CaO+MgO+FeO, and silica SiO₂. The K₂O-Na₂O-CaO-MgO-FeO-CO₂ system was taken as the basic one for experiment, the model composition being the boundary carbonatite composition on the base of which the starting material composition was calculated for the runs. The starting material for high pressure runs was prepared from a mixture of K, Na, Ca, Mg, and Fe carbonates, and the iron-rich carbonate was natural mineral siderite composed of FeCO₃-94.8, MnCO₃- 4.5, MgCO₃ - 0.7 wt%. In the end the composition of the starting carbonate mixture was as follows: K₂CO₃ - 27.21, Na₂CO₃ - 2.89, CaCO₃ - 26.91, MgCO₃ - 17.35, siderite (Fe,Mn,Mg)CO₂ - 25.63 wt% was mixed with graphite powder (1:1) in weight. A cuboctahedral seed crystal was employed in order to qualitatively estimate the degree of supersaturation in carbon of the crystallizing carbonate melt-solution and to test the morphologic features of seed single crystal growth on the unlike octahedral {111} faces or cubic {100} faces. A high pressure anvil-with-hole apparatus was used in the runs [8].

Table 1. Mean compositions of fluid inclusions in some diamonds from Botswana approximating their model boundary compositions and variations of fluid componental contents, based on the data [5]

Samples	JWN108	JWN90	JWN87	JWN91	JWN92	JWN93	Boundary comp		Variations of contents
Number of analyses	(70)	(50)	(92)	(34)	(42)	(36)	Hydrous carbonate		(601)
SiO ₂	23.9	25.1	25.6	45.1	47.8	52.3	58.4	13.6	23.9-52.3
TiO ₂	4.6	4.7	5.1	4.9	4.2	4.2	4.3	4.6	4.2-5.1
Al ₂ O ₃	2.5	2.5	2.0	5.4	5.5	5.6	6.8	0.8	2.0-6.2
FeO*	15.2	16.1	17.5	10.7	9.9	8.8	7.6	19.5	8.8-17.5
MgO	10.9	10.1	10.8	5.7	4.8	5.1	3.3	13.2	4.4-10.9
CaO	13.3	15.6	16.3	5.8	4.7	5.5	0.0	20.5	3.2-16.3
Na ₂ O	2.2	2.6	2.2	1.6	3.0	2.0	2.2	2.2	0.3-3.0
K ₂ O	22.2	18.3	15.4	16.4	15.3	11.5	12.3	20.7	11.5-22.2
P ₂ O ₅	2.3	2.4	1.4	0.8	1.2	0.7	0.7	2.4	0.5-2.6
Cl	1.5	1.3	1.0	0.8	0.8	0.7	0.9	1.3	0.7-1.7
Mg (Mg+Fe)	0.56	0.53	0.52	0.49	0.46	0.51	0.44	0.52	0.39-0.56
H ₂ O(ppm)	192	320	506	192	115	-	-	-	19-506
CO ₂ (ppm)	910	940	540	285	70	-	-	-	15-940
H ₂ O (H ₂ O+CO ₂) (mole fract.)	-	0.3	0.5	0.7	0.6	0.8	0.9	0.1	0.3-0.9

Note: *all Fe as FeO

Table 2. Molecular contents (in mole%) of oxides of "nonvolatile" fraction of the inclusion substance in diamonds (for the sum total of 100%) as a result of table 1 data recalculation.

Samples	JWN108	JWN90	JWN87	JWN91	JWN92	JWN93	Boundary comp	
							Hydrous	carbonatite
SiO ₂	30.6	31.0	31.5	55.2	57.5	61.8	69.3	17.4
TiO ₂	4.4	4.2	4.9	4.2	4.1	4.0	4.1	4.3
Al ₂ O ₃	2.2	2.8	1.4	3.5	4.1	4.0	4.8	0.7
FeO*	16.1	16.9	18.2	11.2	9.6	8.7	7.5	20.3
MgO	14.6	13.4	14.0	7.7	6.2	6.7	4.1	18.1
CaO	14.6	16.2	18.2	4.9	4.8	5.4	-	21.8

Na ₂ O	2.9	2.8	2.8	2.1	3.4	2.0	2.7	2.9
K ₂ O	15.3	12.7	10.5	11.2	10.3	7.4	7.5	14.5

The diamond formation in the model carbonatite solvent of the K₂O-Na₂O-CaO-MgO-FeO-CO₂ system at 7.5-9.5 GPa and 1850°C had the character of overall spontaneous nucleation, in the course of crystallization there formed numerous octahedral crystals, spinel twins and oriented intergrowths. Despite high crystallization rates, plane-faced crystals, devoid of any features of skeletal crystallization formed. The crystals measured, mainly, less than 50 microns. At decompression down to 7 GPa, 1700°C, the nucleation density decreased noticeably, and the crystals gained more favourable growth conditions as a results of which the crystal size increased to 150 microns and more.

So the crystallization of carbon was accomplished for the first time in a multicomponental carbonatite system "extracted" from fluid inclusions in natural diamonds, i.e., inclusions the substance of which, to all appearances, is the parental medium wherefrom natural diamonds crystallized under the mantle conditions. It may become therefore possible to experimentally model the process of natural "synthesis" of diamond in multicomponental carbonatite system which maximally approximates to the natural one, i.e. the key problem of diamond genesis is likely to be solved. In physicochemical respect the principal features of formation and growth of diamond crystals under the mantle conditions can be stated as follows: 1) pressure and temperature of the diamond formation process comply with its thermodynamic stability field; 2) the basic system responsible for the diamond formation is the natural multicomponental K₂O-Na₂O-CaO-MgO-FeO-CO₂-C system the composition of which can be complicated by the presence of some other components, such as SiO₂, TiO₂, Al₂O₃, P₂O₅, Cl, H₂O, and others, but they are of secondary importance in the diamond formation processes - they play the part of impurities of variable concentrations, 3) the carbon source for the diamond crystallization process is "mantle carbon" or "asthenospheric carbon" [6], 4) the processes of spontaneous nucleation and crystal growth of diamond under natural mantle conditions proceed in multicomponental carbonatite melts forming the base of "fluidized" carbonatite - hydrosiliceous material medium of diamond formation; 5) the time-period of diamond crystallization under natural conditions is geologically short, the kinetic parameters of the natural diamond formation processes are comparable with those mastered in the present-day high pressure laboratories - hours, days, weeks.

The problem of genesis of fluidized carbonatite-hydrosiliceous substance trapped by diamonds in the process of their growth and preserved in a strongly compressed state in inclusions (that is why chemical analytic studies of this substance as being maternal medium for natural diamonds growth are so valuable) is very important for developing further programs for cardinal solution of the problem of diamond genesis under the mantle conditions. In our opinion, one of the ways leading to success in this domain is to study the version of alkali carbonate-silicate liquid immiscibility under the mantle conditions as a possible mechanism of formation of

the maternal substance for the diamond formation. The facts of alkali carbonate-silicate liquid immiscibility were identified by us in high-pressure runs in the forsterite (Mg₂SiO₄)-K₂CO₃-Na₂CO₃-K₂SiO₃ system that models the interaction of active agents of high temperature plumes with hosting lithosphere material in hot mantle sites (preliminary results were reported in work [11]). two equilibrium liquid phases form herewith, namely, alkali-silicate melt and alkali-carbonatite melt. The alkali-carbonatite melt forming in the process in question is undoubtedly a melt capable of providing diamond formation processes.

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#Bulbak T.A., Shvedenkova S.V., Savinov A.V., and Water content in synthetic Mg- and Fe⁺²-cordierites

key words: [hydrothermal synthesis, Mg,Fe-cordierite, water content, volatile components]

The study of dependence of the water content in cordierites on their iron content has a long history. In the experimental works [1-9], it is claimed that H₂O concentration in cordierites depends on P_{H₂O} and T of cordierite synthesis. The role of iron content in cordierite ($F = Fe^{2+} / (Fe^{2+} + Mg)$) in the process is still unclear. The available data are not systematized and sometimes are discrepant (Fig.1). This problem has a principal significance because with its solution many questions

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become well-defined. It concerns such questions as a degree of H₂O influence on the position of monovariant reactions and angle of lines of the displaced equilibrium with participation of cordierite of variable composition, in particular, in paragenesis q+crd+gr+sill, which is used as geobarometer, and many others. The purpose of the proposed work is an inspection and analysis of preliminary results on experimental determining the dependence of water content in cordierites on their iron content.

The runs were conducted on an apparatus UVD-1000. Tuttle tube equipped by cooled seal was used as a reactor. Water was used as a medium for pressure transfer. The accuracy of the maintained run parameters was: P = ± 2.0 MPa, T = ± 5°C. To prevent the water drop from the mineral, the cooling of reactor up to 400°C was provided along the water isochore V = 36.241 cm³/mole. At lower to room temperatures, it was cooled down along a constant-pressure line at the level 80-100 MPa during 40 minutes.

The starting Mg-cordierite was synthesized by sintering the dried gel with the composition 2MgO-2Al₂O₃-5SiO₂ in atmosphere at T=1400°C during an hour. The cordierites of variable iron content (step F = 0.1) were obtained by hydrothermal synthesis from the gels of corresponding composition. All initial gels were prepared by nitrate technique. The water saturation of ferrous minerals in the field of their stability (Table 1) was performed following the synthesis scheme while magnesian cordierites were saturated both by synthesis and diffusion scheme.

Table 1. The parameters of synthesis saturation of the synthetic cordierites.

Run series	T, °C	P, MPa	t, h
B	710	250	62
C	710	210	66
D	650	255	88
E1	730	190	66
E3	730	190	48
K	650	200	118

The run schemes were arranged both on the base of a conventional double-capsule technique (a single sealed Pt-capsule with cordierite gel and water charge into Au-capsule with water-buffer mixture) and with some variations. A specific feature in the B and C series was that not single but eleven Pt-capsules (12×4×0.1), charged with starting material, were placed into the outer aurum capsule (100×10×0.3 mm). The height and position in stainless steel reactor of 'many-storied' pyramid from Pt-capsules were not out of gradient-free zone in the external heating furnace. Thus, the cordierites of all compositions from pure Mg (F=0) to F=1 grew and saturated under the same conditions. All capsules were sealed by an arc welding at cooling by liquid nitrogen. Their airtightness was checked by weighting before and after the run. Mica gaskets were inserted amongst capsules for their comfortable separation from each other after experiment. The cordierite synthesis was performed without seed crystals in all runs except E3 run (F=1), in which inoculations from E1 run (F=0.5) were used. The optimal value of oxygen buffer for stability of

Fe²⁺-bearing compositions was experimentally determined in our runs and maintained by wuestite/iron buffer.

A monomineral composition of cordierites with F=0 to F=0.4 was confirmed by the x-ray analysis, while in more ferrous cordierites (up to F=0.8) the mullite impurity was determined (not above 5 wt%). In cordierite compositional range depleted in Mg (F=0.9-1), Fe-spinel and mullite crystallized alongside the main phase. Their total mass was also not above 5 wt%. An estimation of impurity quantities was performed with standard mixtures.

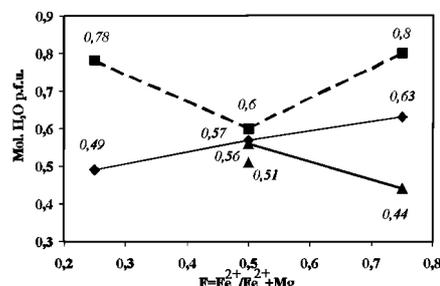


Fig.1. The dependence of water content in cordierites on their iron content based on experimental data (Boberski & Schrayner, 1990). The dashed line is refers to the results of the runs at 700°C and 700 MPa, the thin line is for 700°C and 500 MPa but thick line and triangles stand for 550°C and 200 MPa.

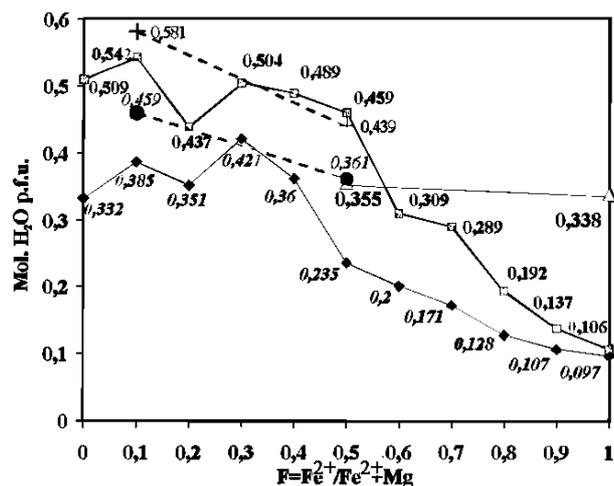


Fig.2. The dependence of water content in the synthesized cordierites on their iron content. The results of mass-spectroscopy analyses are presented by dashed lines; circles are for K run series (650°C, 200 MPa, 118 h); crosses are for D series (650°C, 255 MPa, 88 h). The gas-chromatographic analyses of water are marked as follows: rhombs – B series (710°C, 250 MPa, 62 h); squares – C series (710°C, 210 MPa, 66 h); triangles – E series (E3 with F=1, 730°C, 190 MPa, 48 h; E1 with F=0.5, 730°C, 190 MPa, 66 h).

Water content in cordierites was identified by mass-spectroscopy and gas-chromatography methods. The results of experiments are illustrated in Fig.2. Their analysis suggests that water content in cordierites decreases with increasing iron content other factors being equal. The curves, corresponding to this dependence (for B and C series), have maxima in the compositional range F=0.3-0.5. The wide variations in H₂O concentration for these series might be perhaps due to considerable water lost by more ferrous phases at the stage of P and T drop. It corresponds to intersection of the lines with lower

equilibrium water content on the cordierite-H₂O diagram. This is due to the fact that crystal sizes of grown ferrous phases are an order of magnitude lower than those of essentially magnesian phases. Nevertheless, the negative slope of dependence lines is inherent in the phases of different composition but with similar distribution of crystal sizes by fractions (D, E, K series).

Thus, the results of experimental investigations apparently testify that water concentration in cordierites is controlled not only by P_{H₂O} and T of the synthesis but also by the iron content in cordierites. This must be also taken into account while solving a reverse problem of reconstruction of water pressure regime in cordierite-bearing metamorphic complexes.

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Bulbak T.A., Shvedenkova S.V., Savinov A.V. Experimental study of the muscovite + phlogopite + quartz = cordierite + K-feldspar + H₂O reaction in a water-carbon dioxide fluid.

key words [*cordierite fluid experiment*]

Mineral association K-feldspar + cordierite + micas + quartz is abundant in contact metamorphic metapelite rocks. The reaction that governs this association is also of

interest, because cordierite, participating in it is capable of containing in its structure channels variable amounts of H₂O and CO₂ fluid components which influences the shift of the dehydration reaction at variable P_{H₂O}. The reactions, involving these minerals, were not studied earlier in the presence of a complex fluid.

This work is concerned with an experimental determination of the position of one of these transformations, namely, muscovite (mu) + phlogopite(phl) + quartz(q)=cordierite(crd) + K-feldspar (ksp)+H₂O, in the T-X_{CO₂} co-ordinates. A method of monovariant reaction and starting crystalline material was used. The runs were carried out in a high-pressure apparatus HPA-100[1]. The temperature and pressure maintenance accuracy was ±5°C and 2MPa, respectively. The run durations were selected experimentally to be from 10 to 44 days. Water was the medium, transmitting the pressure onto gold capsules, containing the material. It took 15-20 min for the reactor with the capsules to cool down to room temperature. The run preparation procedure was as follows. The annealed gold capsule (50x0.3x5 mm) was filled with the starting mixture of minerals and silver oxalate that generates CO₂ upon thermal decomposition. The latter was loaded into a thinner annealed gold capsule (30x0.2x2 mm) with squeezed ends preventing the mineral mixture from intermixing with the forming silver. Thus loaded capsules were electric-spark welded under liquid nitrogen cooling. The air tightness was controlled by the weight constancy before and after the runs. The concentration of CO₂ in the capsule after the run was determined gravimetrically on a Mettler AE240 balance (the weighing accuracy 10⁻⁵ g) from its weight loss after it was opened at cooling in liquid nitrogen, and the concentration of water was derived from the mass difference between the opened (after degassing) and dry capsule.

The starting mineral powders were synthesized from predried gels of the corresponding composition in noble-metal capsules: Mg-cordierite - at T=1400°C, P=0.1 MPa for 1h in air with subsequent annealing at T=850°C (8h) in order to obtain rhombohedral modification, muscovite and phlogopite at T=600°C, P_{H₂O}=0.1 MPa, t=20h, K-feldspar (sanidine) - 700°C, P_{H₂O}=200 MPa, t=80h. Fine-ground optical quartz from the Aldan deposit was added to the monovariant mixtures. The monomineral nature of the synthesized powders was confirmed by an X-ray phase analysis. In order to obtain more contrast results, the initial mixture of the reacting minerals 6KAl₃Si₃O₁₀(OH)₂(mu) + 2KMg₃AlSi₃O₁₀(OH)₂(phl) + 15SiO₂(q) = 3Mg₂Al₄Si₅O₁₈(crd) + 8KAlSi₃O₈(ksp) + 8H₂O was taken in the ration of the starting materials to the reaction products 7:3. The equilibrium shift was defined by means of quantitative X-ray phase analysis, carried out under identical conditions, from a change in the mu/cr, mu/ksp, q/crd, q/ksp intensities ratios. Non-superimposing reflections with Müller's indices (110, 020) for cordierite, (-111) for muscovite, (002 and 040) for K-feldspar, and (100 and 100) for quartz were selected. The reaction reversibility was most clearly manifested in the observable growth or disappearance of micas in the associations. We, therefore, took special measures to avoid micas texturing in the samples. To prevent the minerals from hydrolysis when investigating the reaction under the close-to-purely-water

conditions, we loaded water into the capsule in amounts not exceeding 15% of the initial mineral charge weight.

The main experimental results are shown in fig.1. With the aim of determining the monovariant reaction position and further correlating it with the experimental data, we performed the thermodynamic calculation of the multisystem pertinent to the nonvariant point (μ , phl , q , crd , ksp , and and) (see in the same fig.). The self-consistent thermochemical values for each reaction were borrowed from the same source [2]. The line complying with the experimental data (fig.1., discontinuous curve) was plotted by the least squares method using the data of the runs where no equilibrium shift was observed.

As follows from the derived calculated data, the calculated reactions on the T- X_{CO_2} diagram are, on average, by 50-60°C higher than the corresponding experimental ones. When calculating, we did not allow for a change in water concentration in cordierite as a function of variable temperature pressure, and fluid composition. In all the calculations the thermodynamic data were taken for a water-free mineral. The effect of water incorporation into cordierite is shown on curve 7, corresponding to the reaction $\mu+phl+q=crd+ksp+H_2O$. It was calculated for cordierite containing one water molecule per f.u. which is wittingly higher than an equilibrium concentration of H_2O at run parameters. As seen, with allowance for water in cordierite the dehydration reaction temperature decreases but the inconsistency cannot be attributed to this effect alone. Besides, the phase transition sanidine-microcline at the decreasing temperature stage was not taken into account in the calculation.

Conclusion: the position of the transformation $\mu+phl+q=crd+ksp+H_2O$ is defined by the monovariant reaction method. Its reversibility in the temperature range of 525-410°C at $P_{H_2O+CO_2}=100MPa$ is shown. The reaction is stable at a change of X_{CO_2} from 0 to ≈ 0.7 .

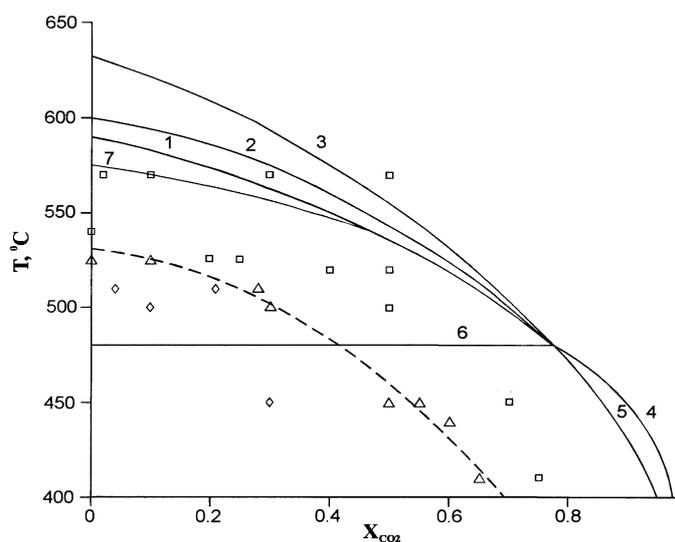


Fig.1. Numbers and continuous lines designate the calculated reactions (to the right is the high temperature part) - 1. $\mu+phl+q=crd+ksp+H_2O$ (and), 2. $q + \mu = ksp + and + H_2O$ (phl), 3. $crd + \mu = phl + ksp + and + H_2O(q)$, 4. $q + phl+and = crd+ksp+H_2O$ (μ), 5. $q + \mu = ksp+and+H_2O(crd)$, 6. $q + phl+and = crd+\mu(ksp)$; curve 7 corresponds to the reaction $\mu+phl+q = ksp + and + H_2O$ with the use of thermochemical constants for hydrous cordierite. The symbols stand for: \square -shift of the equilibrium being studied towards the reaction products

($crd+K$ -feldspar); \diamond - shift towards the initial materials; Δ -intensity ratio in mineral mixture did not change after the run compared to the starting one. The discontinuous line is plotted from the experimental data and corresponds to reaction 1.

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Ostapenko G.T., Gorogotskaya L.I., Timoshkova L.P., and Kuts V.A. On decomposition of kyanite and andalusite at temperatures above 800°C and elevated water pressures

key words: [*andalusite, kyanite, sillimanite, mullite, metastable reaction.*]

Al_2SiO_5 polymorphs – andalusite, kyanite, and sillimanite – are stable at heating in air up to temperature (T) $\sim 1200^\circ C$ above which they decompose to mullite and quartz [1].

At water pressures 7-8 kbars and temperatures 700-800°C (stability field of sillimanite), kyanite and andalusite can disintegrate to corundum and quartz (metastable reactions) [2].

It is also interesting to elucidate the behavior of kyanite and andalusite (at temperatures up to 800°C and above) in the presence of quartz and at not very high water pressures (P_{H_2O}).

We have conducted a series of experiments where ground grains (10-100 mkm) of one or other modification (kyanite, andalusite, and sillimanite) with quartz additions (10-15%) were held in the presence of water at $P_{H_2O} = 2$ kbars and temperatures 800, 900, 950, 1000, and 1100°C. The sample, together with water, was kept in a platinum ampoule.

Experiments were run in the gas pressure vessel under argon pressure. The duration of runs was 1-2 days. After experiments, samples were studied by x-ray analysis and under the microscope.

It was revealed that kyanite decomposed to mullite and quartz at temperatures 900°C and above. Andalusite decomposed by the similar reaction starting from 1000°C. Sillimanite was still unaltered up to 1100°C under experimental conditions.

The obtained results are in agreement with the position of calculated equilibrium PT-curves of the following reactions: $3Kyanite = Mullite + Quartz$ and $3Andalusite = Mullite + Quartz$ (Fig.) (thermodynamic data from [3] were used for calculations). These equilibria, located in the stability field of sillimanite, are metastable. The corresponding reactions of kyanite and andalusite decomposition take place apparently due to relative easiness of mullite nucleus formation and extreme stagnation of sillimanite formation. In the presence of

sillimanite grains, kyanite→sillimanite and andalusite→sillimanite reactions proceed with significant rate that was also confirmed in our experiments [6].

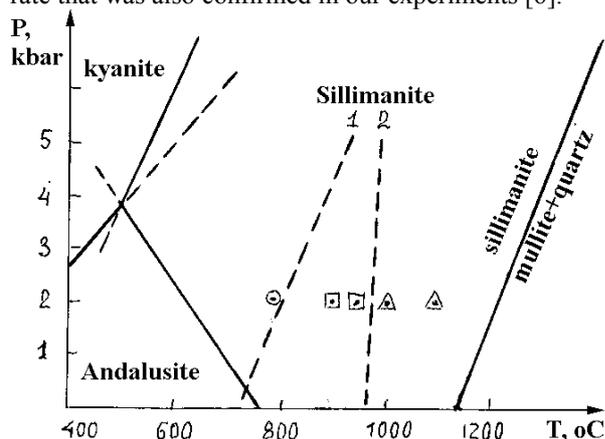


Fig. Experimental data on kyanite and andalusite decomposition. The positions of calculated metastable equilibrium curves: $3\text{Kyanite} = \text{Mullite} + \text{Quartz}$ (dashed line 1) and $3\text{Andalusite} = \text{Mullite} + \text{Quartz}$ (dashed line 2) on the ternary Al_2SiO_5 -diagram [4]. The location of calculated (based on data from [3]) equilibrium curve $3\text{Sillimanite} = \text{Mullite} + \text{Quartz}$ is in agreement with data from [5].

Experimental results:

- kyanite, andalusite, and sillimanite do not decompose;
- kyanite disintegrates to mullite + quartz; andalusite and sillimanite do not decompose; kyanite (more intensively) and andalusite (less intensively) disintegrate to mullite and quartz; sillimanite does not decompose.

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#Krigman L.D., Ishbulatov R.A., Veksler I.V., Nielsen T.D.F. Phase analysis of the silica-undersaturated part of normative kalsilite-forsterite-larnite H_2O tetrahedron at a pressure 2 kb.

key words [*phlogopite kalcilite forsterite experiment*]

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Petrologic and geochemical studies of the Gardiner complex which revealed a close association between melilite and phlogopite led Nielsen (1994) to propose a mechanism of the melilite formation based on the fact that crystallization of phlogopite brings about a rapid decrease in the concentration of magnesium and a corresponding growth of CaO/MgO , favouring the crystallization of melilite in a silica-undersaturated melt. Investigations of microinclusions (Veksler et al., 1998) showed that phlogopite is a daughter mineral of melt inclusions of a larger number of minerals from the Gardiner complex. The reality of this mechanism was experimentally proved in a number of joins of fluorine-modified kalsilite basalt tetrahedron (Veksler et al., 1998). The fluorine-modified system is an extremal case of the phlogopite stability. Inasmuch as the system kalsilite-forsterite-larnite-quartz is basic for the understanding of mineral parageneses of K-rich rocks (Yoder, 1986) we first attempted to carry out a systematic experimental study of key joins (diopside-phlogopite and kalsilite - diopside - water) of that system under a pressure 0.2 GPa which ensures the stability of phlogopite under the temperatures conditions of true magmatic process.

Synthetic diopside produced by sintering of the appropriate oxides and carbonates, a charge having a stoichiometric composition of phlogopite, and a charge of the composition $\text{KAlSiO}_4\text{-H}_2\text{O}$ were used as starting materials. The two latter charges were produced by mixing aluminium hydroxide $\text{Al}(\text{OH})_3$ and glasses of the composition $\text{KMg}_3\text{Al}_{0.33}\text{Si}_3\text{O}_{10}$ and $\text{KAl}_{0.33}\text{SiO}_3$, respectively, prefounded from oxides of silicon, magnesium, potassium carbonate and aluminium hydroxide at 1350°C .

The quenching runs were carried out in a piston-cylinder-with-gas-media apparatus (CPG) where the pressure is produced with an inert gas (argon). This original apparatus works at the P-T parameters of a bomb with internal heating, providing quenching at a rate $300^\circ/\text{min}$ and is simple in operation.

The runs were performed in welded platinum capsules with 15-20 mg charges. The measurement accuracy of the temperature was 5° , that of the pressure - 50 bar. The obtained products were studied optically with an immersion method, and with an X-ray diffractometer. Phase analyses were performed using an electron microprobe Jeol 7 Superprobe of the Copenhagen University.

Crystal phases. Olivine is represented by practically pure forsterite. The concentration of calcium in olivine varies from 0 to 1.3%. Diopside has the composition close to stoichiometric, a small excess of magnesium against calcium (2-8 mol%) and substitution of aluminium for silicon to 3 mol% being normally observed. Magnesium substitutes for calcium in small amounts also in wollastonite (to 1.5 wt%). Akermanite, on the contrary, is magnesium-depleted ($\text{Ca/Mg}=2.05\text{-}2.10$) and contains 3 wt% Al_2O_3 . Lucite and kalcilite form pure mineral phase within the analytic accuracy. Phlogopite ($\text{KMg}_3\text{Al}(\text{OH})_2\text{Si}_3\text{O}_{10}$) crystallizes in the form of solid solutions with eastonite ($\text{K}_2\text{Mg}_5\text{Al}(\text{OH})_4\text{Si}_5\text{Al}_2\text{O}_{20}$) the concentration of which can reach 20%. Two inordinary phases were found in the diopside-kalsilite-water join. One of the phases represents a complicated aluminosilicate of

potassium, calcium, and magnesium crystallizing in association with diopside and kalsilite. The phase stoichiometry can be expressed most adequately as the 71%Di + 20.5%Ks + 6% Tsch (Tsch being Tschermak's molecule $\text{CaAl}_2\text{SiO}_6$).

The second phase was revealed in the form of flat transparent hexagonal mica-like flakes measuring to 1 mm that consisted of 86.7% Al_2O_3 , the rest being water, which is very close to the stoichiometry of boehmite (AlOOH) (Tetenhorst R. and Hofman D.K., 1980). Possibly, the crystals grow from a fluid phase. The parameters at which this phase was found are inordinary. It is believed that above 600°C at pressures 200-10000 bar the corundum + water association is stable (Kennedy, 1959).

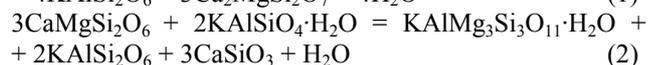
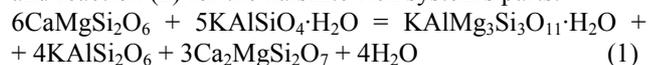
Pseudobinary join diopside-phlogopite, fig.1.

In the presence of diopside the thermal stability of phlogopite decreases appreciably. The crystallization of the mixtures proceeds via a series of intermediate phase associations of forsterite, diopside, and leucite combined with a water-bearing melt. The solubility of water in equilibrium melts is 3-7 wt%. In the phlogopite stability field the earlier precipitated leucite and forsterite react with the melt and the fluid, yielding phlogopite by the scheme: $lc+fo+l+v=phl$. In the subsolidus region diopside and phlogopite form a stable mineral association throughout the whole range of compositions.

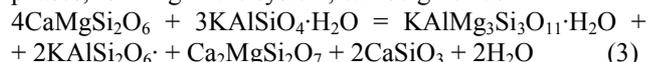
Pseudobinary join diopside kalsilite - water, fig.2.

The introduction of water changes radically the topology of the undersaturated part of the potassium normative tetrahedron. All the compositions of the diopside - kalsilite - water join are beyond the crystallization field of forsterite. High silica activity in the presence of water is responsible for the fact that diopside and akermanite are crystalline magnesian phases, with phlogopite joining them in its stability field. In the diopside-rich part of the join along with diopside there crystallizes one more silica-saturated K-phase-

wollastonite. K-bearing crystalline phases are represented by kalsilite and leucite. The vapour phase, at least for the compositions containing less than 50% Di is always present, and as the capsules are opened, it evolves as water droplets. Potassium and aluminium behave as independent components in the vapour phase. It follows from the fact that in the melt $\text{K/Al} \neq 1$, and moreover, Al_2O_3 forms the phase of its own. In the subliquidus region the diagram topology is dictated by the reaction (1) for diopside-rich and reaction (2) for the kalsilite-rich system's parts.



The total reaction reflecting the principal mineral phases, forming in the system, can be given as



The crystallization of phlogopite was experimentally found for the composition 50%Di+50%Ks in approaching an equilibrium from below (sample 25) and from above (sample 32). In accordance with the reactions (1) and (2) crystallization on phlogopite in the extremes of the join will, possibly, take place at lower (<1000°C) temperatures, i.e. the stability of phlogopite decreases both in more acidic and more basic systems.

The phase associations of subsolidus were not studied experimentally, but on the base of the obtained data the associations $\text{Phl} + \text{Lc} + \text{Wo} + \text{Di}$, $\text{Phl} + \text{Lc} + \text{Ak} + \text{Ks}$, $\text{Phl} + \text{Lc} + \text{Wo} + \text{Ak}$ seem to be most possible.

With allowance for the data on Ca-free system Ks-Fo-Q-H₂O (W.C. Luth, 1967) one will hardly expect the appearance of forsterite- (or enstatite) bearing parageneses instead of phlogopite-bearing ones in the low-temperature region of the system.

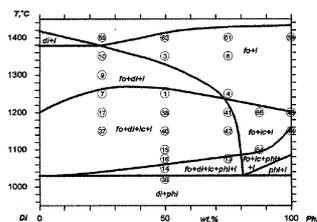


Fig.1. T-x phase diagram of the diopside-phlogopite pseudobinary join. In the circle is the number of the run.

Table 1. Experimental conditions at 6.5 GPa and the phase compositions in the pyrope(Prp)-almandine(Alm) system.

No run	Alm-Prp compos. mol%	T°C	duration, min	phases	mol%		sum	equil. assoc.
					Alm	Prp		
244	100-0	1500	10	Aim	100	0	100	Grt
245	50-50	1500	40	Grt	41.1 63.5 30.3	58.9 36.5 69.7	100	Grt
246	50-50	1600	30	Grt Grt Grt Grt	52.3 62.7 65.2 33.5	47.7 37.3 34.8 66.5	100	L
247	50-50	1700	15	Grt Grt L	58.2 64.9 75.1	41.8 35.1 24.9	100	Grt+L
250	50-50	1750	0	Grt Grt Grt L L	48.1 50.3 50.4 73.2 72.9	51.9 49.7 49.4 26.7 27.1	100	Grt+L
251	0-100	1700	5	L	100	0	100	L
252	75-25	1650	30	Grt Grt Grt Grt Grt Grt Grt	79.8 80.1 75.9 77.6 77.7 75.3 75.7	20.2 19.9 24.1 22.4 23.0 24.7 24.3	100	Grt
253	0-100	1600	2	Aim	100	0	100	Grt+L
333	75-25	1850	20	Grt Grt Grt Grt	69.5 74.8 93.2 92.2	30.5 25.2 6.8 7.8	100	Grt
332 (fig.1)	75-25	1800	20	Grt Grt Grt Grt	82.3 73.7 57.3 54.3	17.7 26.3 42.7 45.7	100	Grt
322	60-40	1800	10	Grt Grt Grt Grt	58.8 65.8 65.0 58.5	41.2 34.2 35.0 41.5	100	Grt
372	75-25	1900	10	Grt Grt Grt Grt Grt	72.6 74.0 72.2 81.6 66.7	27.4 26.0 27.8 18.4 33.3	100	Grt

The runs were conducted in a high-pressure anvil-with-hole apparatus at the Institute of Experimental Mineralogy, RAS. Two run series were performed at different P-T parameters using different starting materials. Phase ratios of the pyrope-almandine system were studied at a pressure of 6.5 GPa, at temperatures 1500-1900°C. The starting materials were synthesized from the end members of the system taken in different proportions (table 1). Some experimental results are presented on figs.1 and 2. The aim of the second part of experiment was to determine the melting temperature of almandine at a

pressure 6.5 GPa. At T=1700°C a homogeneous glass of almandine composition was produced. At T=1600°C almandine crystals measuring 20 µm were found in the quenched glass.

Based on the obtained data, a fusibility diagram with Rosenbom's type 1 solid solutions was plotted for the pyrope-almandine system (fig.3). A substantial data spread was observed in some runs due to incomplete diffusion of pyrope and almandine: the temperature was rather low and duration insufficient.

From the stand point of this diagram one can explain some natural observations. The zoning with increasing magnesianity towards grain edges can be attributed to a pressure decrease at garnet crystallization: the diagram "shifts" downwards.

The following results were obtained:

1) the runs were performed for the pyrope-almandine system at a pressure of 6.5 GPa, the diagram was plotted for the compositional region enriched in almandine component;

2) the runs were performed to find the melting temperature of almandine, the melting temperature of almandine was first obtained for a pressure of 6.5 GPa,

almandine was found to melt congruently at high pressures;

3) the natural data on the anomalous Fe/Mg zoning of garnets from eclogite associations were explained on the basis of the derived fusibility diagram of the pyrope-almandine system in terms of the ideas of natural garnets crystallization mated with synchronous pressure decrease.

The results suggest the following principal conclusions:

1) pyrope and almandine form a series of Rosenbom's type 1 continuous solid solutions;

2) the experimental data can be used to explain natural phenomena, namely, crystallization of garnet in eclogite parageneses of supposedly mantle origin.

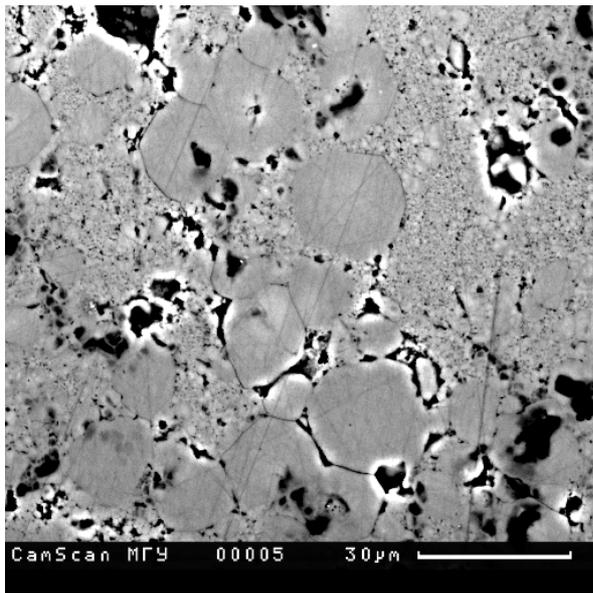


Fig.1. Garnet grains (75 mol% Alm - 25 mol% Prp) in a fine-grained mass of garnet with higher iron content. (samp. 332a, 1800°C)

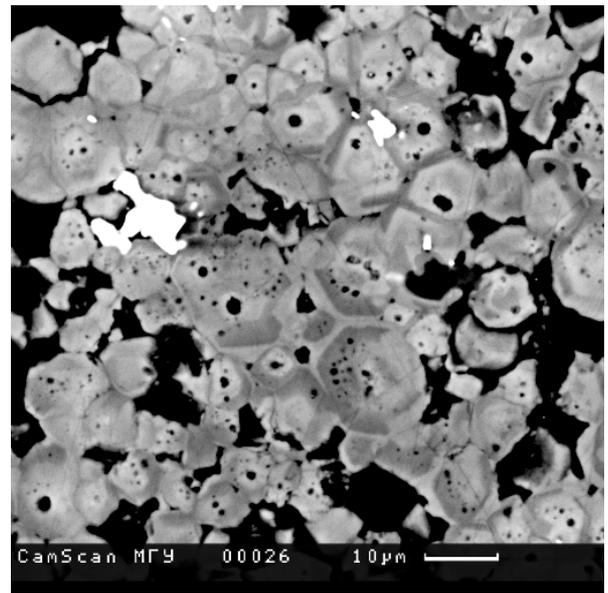


Fig.2. Zoned garnet grains (75 mol% Alm - 25 mol% Prp) (samp. 252a, 1650°C)

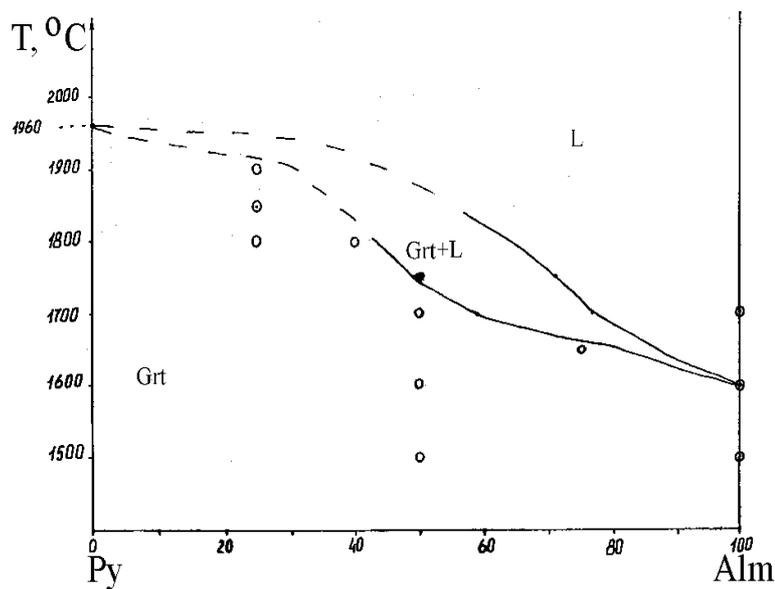


Fig.3. Preliminary fusibility diagram of the pyrope-almandine system at a pressure 6.5 GPa.

