# **Selected papers of the year report of IEM**

# <sup>#</sup>Litvin Yu.A. Experimental study of magmatic and metasomatic processes in hot spots at the mantle-plum boundary at pressures up to 10 GPa.

Transformations in a strongly compressed substance of the deep mantle, which are conditioned by global dynamic factors of the Earth evolution, are in a focus of an experiment at high pressures. Earlier [1, 2], an experimental study on interaction of active agents of plumes with lithospheric rocks at their boundaries in hot spots of the mantle began. The purpose of this study is to reconstruct conditions of genesis of intraplate alkaline rocks, including diamond-bearing ones. The study in the model system Mg<sub>2</sub>SiO<sub>4</sub>-K<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>SiO<sub>4</sub> at 3.7 GPa allowed to find subsolidus metasomatic reactions between forsterite (mantle component) and K<sub>2</sub>CO<sub>3</sub> (active agent of These reactions showed a possibility of plumes). carbonation mantle olivine (and. of possibly, orthopyroxene) with formation of carbonate minerals, i.e. magnesite MgCO<sub>3</sub> and bicarbonate  $K_2Mg(CO_3)_2$ . A the polythermal melting diagram for join  $(Mg_2SiO_4)_{50}(K_2SiO_3)_{50}-K_2CO_3$  was constructed [2]. Three four-phase assemblages, i.e. forsterite-magnesite, magnesite-K-Mg-carbonate, and K-Mg-carbonate (the assemblages also include MgO, K<sub>2</sub>SiO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>), exist in the subsolidus of the system. Three five-phase eutectics corresponding to the assemblages are found in the solidus. The only liquidus phase is periclase. Along with it, preliminary data show, that two types of melt, i.e. carbonate and silicate, isolated from each other, exist in the experimental samples. This fact is extremely important for understanding the differentiation mechanism of primary alkaline mantle magmas. Carbonate minerals forming on the mantle-plume boundary show congruent melting at high pressures. The carbonate melt of  $K_2Mg(CO_3)_2$  at pressures above 7 GPa is found to be able to form highly concentrated melt-solutions of carbon, from which diamonds crystallize [3, 4]. It is interesting, that a composition of this bicarbonate is a simplified model for primary fluid inclusions, which represent a maternal media captured by growing diamonds in the mantle conditions [5]. Another model system, forsterite Mg<sub>2</sub>SiO<sub>4</sub>-nepheline NaAlSiO<sub>4</sub>-silica SiO<sub>2</sub> in its pseudobinary join enstatite MgSiO<sub>3</sub>-nepheline NaAlSiO<sub>4</sub> was studied at pressure 6.5 GPa. It is found, that solid-state reaction of forsterite with jadeite is characteristic of the subsolidus. This reaction gives rise to pyrope garnet, enstatite, and Na<sub>2</sub>Mg<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

This reaction was first found in the system forsterite  $Mg_2SiO_4$ -jadeite  $NaAlSi_2O_6$  at a pressure above 4.5 GPa [8]. A possible appearance of the reaction at the mantleplume boundary is the process of garnetization of mantle peridotite [7, 9].

The further study on the problem of evolution of the substance of hot spots in the mantle was aimed at approaching experimental conditions to natural ones. It called for the widening of compositional range of the systems studied at high pressures. The following systems were considered:

1) alkali carbonate-silicate system forsterite  $Mg_2SiO_4$ - $Na_2CO_3$ - $K_2CO_3$  at 3.7 GPa (in order to investigate carbonate-silicate liquid immiscibility as a mechanism of magmatic differentiation at the mantle-plume boundary);

2) alkali-ferrous silicate-alumosilicate system forsterite  $Mg_2SiO_4$ -fayalite  $Fe_2SiO_4$ -jadeite  $NaAlSi_2O_6$ acmite  $NaFeSi_2O_6$  at 6.5 GPa (in order to study the conditions of garnetization of mantle peridotite at the mantle-plume boundary);

3) multicomponent carbonate-silicate melts, analogous in composition to primary (maternal for diamonds) fluid inclusions in natural diamonds, at 5-9 GPa (in order to reconstruct the physico-chemical conditions of diamond formation).

As a result, new experimental data were obtained from the studies at high pressures. The present paper considers the most significant results.

The experimental study in the pseudobinary system Mg<sub>2</sub>SiO<sub>4</sub>-Na<sub>2</sub>CO<sub>3</sub> and the internal join (Mg<sub>2</sub>SiO<sub>4</sub>)<sub>50</sub>(K<sub>2</sub>SiO<sub>3</sub>)<sub>50</sub>-Na<sub>2</sub>CO<sub>3</sub> was carried out at 3.7 Gpa and 1200-1600°C in the system Mg<sub>2</sub>SiO<sub>4</sub>-Na<sub>2</sub>CO<sub>3</sub>- K<sub>2</sub>CO<sub>3</sub>. This system is a model for the interaction of ultrabasic mantle with active agents of plumes in high-temperature aureoles of hot spots. The experiments showed new reactions, which can provide the processes of carbonation of mantle peridotite, such as substitution of olivine for magnesite MgCO<sub>3</sub> and Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> under metasomatic influence of Na<sub>2</sub>CO<sub>3</sub> melt (the component of plums). Reaction of forsterite and Na<sub>2</sub>CO<sub>3</sub> melt at 3.7 GPa also yields Na-Mg-silicate Na<sub>2</sub>MgSiO<sub>4</sub>, which was previously found at 13.6-16.0 GPa in the experiments in the silicate system enstatite MgSiO3-jadeite NaAlSi<sub>2</sub>O<sub>6</sub> [10]. Fig.1 demonstrates a displacement of metasomatic front of Na<sub>2</sub>CO<sub>3</sub> melt (it forms finely acicular textures after quenching) in forsterite grain. Magnesite MgCO<sub>3</sub>, binary carbonate Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>, and alkali silicate Na<sub>2</sub>MgSiO<sub>4</sub>, which forms strongly porous grains with numerous inclusions of quenched Na<sub>2</sub>CO<sub>3</sub> (Figs.2 and 3), appear at the front of the metasomatic reaction.

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**Fig1.** Metasomatic front of Na<sub>2</sub>CO<sub>3</sub> melt on forsterite Mg<sub>2</sub>SiO<sub>4</sub> (Fo) grain. Sample 287, composition (Mg<sub>2</sub>SiO<sub>4</sub>)<sub>30</sub>(Na<sub>2</sub>CO<sub>3</sub>)<sub>70</sub>, mol. %, pressure 3.7 GPa, temperature 1400°C.



**Fig.2.** Na-Mg-silicate Na<sub>2</sub>MgSiO<sub>4</sub> (N2MS) with inclusions of the metasomatic Na<sub>2</sub>CO<sub>3</sub> melt (gray inclusions in light grain). Sample 360, composition (Mg<sub>2</sub>SiO<sub>4</sub>)40(Na<sub>2</sub>CO<sub>3</sub>)<sub>60</sub>, mol. %, pressure 3.7 GPa, temperature 1300°C.



Fig.3. Grains of forsterite (Fo) and  $Na_2MgSiO_4$  ( $N_2MS)$  with inclusions of the metasomatic melts. Sample 355, composition

 $[(Mg_2SiO_4)_{50}(K_2SiO_3)_{50}]_{40}[Na_2CO_3]_{60},$  mol. %, pressure 3.7 GPa, temperature 1400°C.



**Fig.4.** Effect of alkali carbonate-silicate liquid immiscibility: spherolites of silicate melts in the quenched carbonate melt ground mass (with finely acicular textures). Sample 297, composition  $[(Mg_2SiO_4)_{50}(K_2SiO_3)_{50}]_{70}[Na_2CO_3]_{30}$ , mol. %, pressure 3.7 GPa, temperature 1500°C. Composition of silicate melt (wt. %): SiO<sub>2</sub> 47.9, MgO 36.1, K<sub>2</sub>O 10.3, Na<sub>2</sub>O 5.7 (carbon content was not analyzed).



Fig.5. Spherolitic and columnar texture of quenched silicate melts, immiscible with carbonate melts (finely acicular texture). Sample 301, composition  $[(Mg_2SiO_4)_{50}(K_2SiO_3)_{50}]_{50}[Na_2CO_3]_{50}$ , mol. %, pressure 3.7 GPa, temperature 1300°C. Composition of silicate melt (wt. %): SiO<sub>2</sub> 51.3, MgO 33.6, K<sub>2</sub>O 10.6, Na<sub>2</sub>O 4.5 (carbon content was not analyzed).

Effects of alkali carbonate-silicate liquid immiscibility (Figs. 4-6) were observed at 3.7 GPa in the system Mg<sub>2</sub>SiO<sub>4</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> in the join (Mg<sub>2</sub>SiO<sub>4</sub>)<sub>50</sub>(K<sub>2</sub>SiO<sub>3</sub>)<sub>50</sub>-Na<sub>2</sub>CO<sub>3</sub>. It should be noted, that shape of silicate glasses in the experiment is not always regular spherical. The possibility of differentiation of magmatic melts, formed during complicated and joint processes of high-temperature metasomatism and magmatism on the mantle-plume boundary by the mechanism of carbonate-silicate liquid immiscibility, can be significant in petrology of mantle magmatism, for formation of primary magmas for carbonatites, kimberlites, and alkali basalts of intraplate series, in particular. It can be assumed, that the mechanism plays an important role in the formation of diamond forming carbonatite melts, captured during diamond growth as strongly compressed fluid inclusions [5].

The study of the alkali-ferric system forsterite Mg<sub>2</sub>SiO<sub>4</sub>-fayalite Fe<sub>2</sub>SiO<sub>4</sub>-jadeite NaAlSi<sub>2</sub>O<sub>6</sub>-acmite NaFeSi<sub>2</sub>O<sub>6</sub> is carried out at 6.5 GPa. Concerning the mantle dynamics, this system models an interaction of mantle peridotite with active alkalic components of the boundary zones mantle-ascending plume, mantle-buried plate, and lithosphere-astenosphere. Appearance of Mg-Fe garnet in reaction of forsterite and favalite with alkalic components in the binary and ternary joins of the above system (Figs. 7 and 8) buffered by the W/WO<sub>2</sub> pair (bivalent iron is stable) is found experimentally. It corresponds to reality of the process of lithosphere garnetization on the mantle-plume boundary during metasomatic and magmatic interaction of active alkalialumosilicate components of plums with minerals of lherzolite mantle, first of all, with olivine. Possible new mantle minerals, Na<sub>2</sub>(Mg,Fe<sup>2+</sup>)<sub>4.5</sub>Si<sub>6.5</sub> (NMFS-phase) and  $Na_2Fe^{2+}_{4.5}Si_{6.5}$  (NFS-phase) in the absence of Mg, form in these reactions. Melting of the system in the ternary join forsterite-jadeite-acmite at 6.5 GPa and 1450°C is peritectic and controlled by the reaction forsterite + L (melt) = NMFS-phase at the solidus. The obtained experimental data show the new "chemical" mechanisms of garnetization of mantle peridotite in the conditions of the dynamic mantle. These mechanisms are attended by formation of fusible aluminum-free silicates, such as NMFS-phase, which can participate in the formation of primary alkaline magmas in the boundary zones of the mantle.

The experiments on diamond crystallization in multicomponent systems, which are close in composition to primary fluid inclusions in natural diamonds [5], were conducted at pressures 5-8 GPa and temperatures 1200-1600°C, which corresponds to the PT conditions of diamond stability according to the carbon phase diagram. Diamonds were synthesized from the mixtures of graphite with model multicomponent carbonate compound [11], as well as with carbonate-silicate compound, which is analogous to fluid inclusions (up to 41 wt. % of SiO2) in sample JWN91 from the Jwaneng kimberlite pipe (Botswana) (Figs. 9 and 10). The experimental modeling of diamond crystallization in natural media gives a possibility to find out a physico-chemical mechanism of diamond nucleation and growth in the mantle conditions. The results of high-pressure experiments on diamond crystallization from multicomponent carbonate-silicate system allow to clarify the problem of formation of natural diamonds and substantiate the carbonatitic model of diamond genesis from kimberlites and lamproites. This idea is supported by the recent discovery of diamondbearing magmatic carbonatites of mantle genesis in the Chaganai Complex, Uzbek Republic [12].

Thus, the experimental studies at high pressures show the new results, which imply the following physicochemical processes at the mantle-plum boundary in the mantle hot spots.

1) Carbonation of mantle peridotite as a consequence of reactions of olivine (and orthopyroxene) with alkalicarbonate and alkali-silicate metasomatic agents, such as  $Na_2CO_3$ ,  $K_2CO_3$ ,  $K_2SiO_3$ . Magnesite MgCO<sub>3</sub>, as well  $Na_2Mg(CO_3)_2$ ,  $K_2Mg(CO_3)_2$  and  $Na_2MgSiO_4$  form during the reactions.



**Fig.6.** Shapeless glasses, formed during quenching of silicate melts, immiscible with carbonate melts (finely acicular texture). Sample 298, composition  $[(Mg_2SiO_4)_{50}(K_2SiO_3)_{50}]_{50}[Na_2CO_3]_{50}$ , mol. %, pressure 3.7 GPa, temperature 1500°C. Composition of silicate melt (wt. %): SiO<sub>2</sub> 50.3, MgO 36.8, K<sub>2</sub>O 9.6, Na<sub>2</sub>O 3.3 (carbon content was not analyzed).



**Fig.7**. Crystallization of almandine gamet in the system fayalite  $Fe_2SiO_4$ -jadeite NaAlSi<sub>2</sub>O<sub>6</sub>. Sample 311, composition ( $Fe_2SiO_4$ )<sub>50</sub>(NaAlSi<sub>2</sub>O<sub>6</sub>)<sub>30</sub>, mol. %, pressure 6.5 GPa, temperature 1400°C.



**Fig.8.** Crystallization of Mg-Fe garnet in the system forsteritejadeite-acmite in the presence of W/WO2 buffer. Sample 389, composition  $(Mg_2SiO_4)_{20}(NaAlSi_2O_6)_{40}(NaFeSi_2O_6)_{40}$ , mol.%, pressure 6.5 GPa, temperature 1450°C. Garnet composition:  $Na_{0.1}Mg_{1.7}Fe_{1.3}Al_{1.9}Si_3O_{12}$ .



Fig.9. Diamond crystallization from the carbon solution in multicomponent carbonate melt. Sample 363. Composition of the carbonate dissolvent:  $K_2CO_3$  27.21,  $Na_2CO_3$  2.89,  $CaCO_3$  26.91,  $MgCO_3$  17.35, FeCO\_3 25.63, wt. %. Pressure 7.0 GPa, temperature 1650°C.



**Fig.10.** Diamond crystallization from the carbon solution in multicomponent carbonate-silicate melt, compositionally analogous to inclusions in natural diamond JWN91 [5]. Sample 455. Composition of the carbonate-silicate dissolvent: SiO<sub>2</sub> 45.1, TiO<sub>2</sub> 4.9, Al<sub>2</sub>O<sub>3</sub> 5.4, FeO 10.7 (as FeCO<sub>3</sub>), MgO 5.7 (as MgCO<sub>3</sub>), CaO 5.1 (as CaCO<sub>3</sub>), Na<sub>2</sub>O 5.7 (as Na<sub>2</sub>CO<sub>3</sub>), K<sub>2</sub>O 16.4 (as K<sub>2</sub>CO<sub>3</sub>), P<sub>2</sub>O<sub>5</sub> 1.0 (as K<sub>4</sub>P<sub>2</sub>O<sub>7</sub>), Cl 0.8 (as NaCl), wt. %. Pressure 6.0 GPa, temperature 1340°C.

2) Magmatic differentiation as a result of alkali carbonate-silicate liquid immiscibility, which is observed in the system forsterite-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>SiO<sub>3</sub> at pressure 3.7 GPa. Carbonate-silicate liquid immiscibility can provide the effective physico-chemical mechanism for magmatic differentiation of primary alkaline magmas with the formation of initial magmas for carbonaties, kimberlites, and alkali basalts of intraplate series, as well as maternal carbonate melt for diamond crystallization.

3) Chemical garnetization of mantle peridotite as a consequence of olivine (and orthopyroxene) reactions with alkali-alumosilicate and alkali-ferric agents of active plums, such as jadeite, acmite, and nepheline component. Mg-Fe garnets, as well as aluminum-free alkalimagnesium compounds, i.e.  $Na_2Mg_2Si_2O_7$ ,  $Na_2(Mg,Fe^{2+})_{4.5}Si_{18.5}$  and  $Na_2Fe^{2+}_{4.5}Si_{18.5}$  (possible new mantle minerals) form during the reaction.

4) Diamond formation in multicomponent carbonatesilicate (carbonatitic) melts, which are able to form highly concentrated carbon solutions at high pressures. It is an adequate variant for diamond genesis, supported by experiments on diamond crystallization in multicomponent systems, reproducing the composition of primary fluid inclusions (inclusions of maternal substance) in natural diamonds.

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# <sup>#</sup>Dadze T.P., Kashirtseva G.A., Akhmedzhanova G.M. Gold complexation in sulfidebearing aqueous solutions at 300°C.

Gold solubility in sulfide-bearing aqueouse solutions has been studied experimentally with further processing of the results obtained. Thioacetamide  $(CH_3CSNH_2)$  was used as an H<sub>2</sub>S sourse [1]. We also carried out the experiments with the addition to the system of sodium sulfate to provide an increase in pH of solutions and redox potential of the system (sulfide-sulfate buffer).

An analysis of the literature and experimental data suggests that gold dissolution in sulfide solutions proceeds by the following reactions:

$Au + H_2S = Au(HS)o + S H_2(aq)$	(1)
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$Au + 2H_2S = Hau(HS)o_2 + 1/2H_2(aq)$ (2)	2)	)
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 $Au + H_2S + HS = Au(HS)_{2+} + S H_2(aq)$  (3)

The neutral form  $HAu(HS)^{\circ}_{2}$  may prevail in acid and neutral solutions at high H<sub>2</sub>S fugacity, the form AuHSo is predominant at low H<sub>2</sub>S fugacity, Au(HS)<sub>2</sub> prevails in alkaline medium.

In order to analyze the dependence of experimental Au solubility on solution composition and to identify the reaction governing the solubility value, one should know the concentrations (activities) of  $H_2S$ , HS, and  $H_{20}(aq)$  under the experimental conditions in each run. For this purpose we performed the computer modelling of the equilibrium composition of the system Au-H<sub>2</sub>O-CH<sub>3</sub>CSNH<sub>2</sub> using the Shvarov's "GIBBS" program (version 3.1) [2].

An analysis of changes in experimental values of gold solubility in the solutions studied and  $H_2S$  and HS concentrations in them shows that the value of gold solubility is a result of the combined effect of some of the mentioned reactions (1-3). So, it is impossible to evaluate the reaction governing the solubility within the whole concentrations interval by the slope of gold solubility curve (fig.1). By comparing  $H_2S$  and HS concentrations in various run series and calculating the dependence of the forms of gold hydrosulfide complexes on pH [3] we came

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to the conclusion that the highly possible fraction of the form Au(HS)<sub>2</sub> should exist in the solutions with the starting pH=7.4 and addition of 0.0469 m Na<sub>2</sub>SO<sub>4</sub> (table 1). So, we calculated the reaction (3) constant assigning in the first approximation all the dissolved gold to the form  $Au(HS)_2$ . In the sulfide sulfur concentrations range of 0.2-0.5m the average value  $K_3 = 0.00102$ . Using the obtained value  $K_3$  we calculated the Au(HS)<sub>2</sub> concentration in the experiments with starting pH=7.4 without addition of Na<sub>2</sub>SO<sub>4</sub> at 300oC and 300bar (table 2). We subtracted the value of the calculated form Au(HS)<sub>2</sub> from the experimental Au solubility value and assigning the remainder to the form AuHS° calculated the reaction (1) constant. The avarage value K<sub>1</sub>=0.000012 was obtained as an arithmetic mean for the CH<sub>3</sub>CSNH<sub>2</sub> concentration interval 0.2-0.5m. The Gibbs energies of AuHS° and  $Au(HS)_2$  complexes (table 3) and their complete dissociation constants (pK AuHS° =15.57 and pK Au(HS)<sub>2</sub>=17.50) have been determined at 300°C and 300bar from the values K1 and K2 and Gibbs energies of the substances participating in the reactions (1) and (3).



Fig.1. Au solubility in sulfide solutions at  $300^{\circ}$ C, pH<sub>st.</sub>=7.4; 1-at P<sub>sat</sub>, without Na<sub>2</sub>SO<sub>4</sub>; at 2-300 bar with Na<sub>2</sub>SO<sub>4</sub>; at 3- 300 bar without Na<sub>2</sub>SO<sub>4</sub>.

М	$m_{Au} \bullet 10^4$	acti	vities in solution	K <sub>3</sub>	
CH <sub>3</sub> CSNH <sub>2</sub>	exp.	$H_2S(aq)$	HS	$H_{2}(aq)$	$m_{Au} a^{1/2}_{H2} / a_{H2S} a_{HS}$ -
0.05	0.88	0.0146	0.0821	0.00117	0.00251
0.1	4.77	0.0573	0.0891	0.00150	0.00362
0.2	3.72	0.1540	0.0911	0.00170	0.00109
0.3	3.99	0.2510	0.0919	0.00188	0.00075
0.4	7.98	0.3480	0.0924	0.00206	0.00113
0.5	9.57	0.4430	0.0928	0.00224	0.00110

**Table 1.** Calculation of the reaction (3) constant from the experimental gold solubility in the  $CH_3CSNH_2+Na_2SO_4$  solution at 300 °C and 300 bar.

**Table 2.** Calculation of the reaction (1) constant from the experimental gold solubility in the  $CH_3CSNH_2$  soluon at 300°C and 300 bar.

М	$m_{Au} \bullet 10^4$	activities in solution (m)			$*m \bullet 10^4$	m •10 <sup>4</sup>	K <sub>1</sub>
CH <sub>3</sub> CSNH <sub>2</sub>	exp.	$H_2S(aq)$	HS	$H_{2}(aq)$	$Au(HS)^{-}_{2}$	AuHS <sup>o</sup>	$m_{Au} a^{1/2}{}_{H2}/a_{H2S}$
0.05	0.069	0.0492	0.000818	0.00187	0.01	0.06	0.052
0.1	0.210	0.0982	0.001730	0.00188	0.04	0.17	0.074
0.2	0.830	0.1960	0.003420	0.00191	0.16	0.67	0.150
0.3	0.790	0.2930	0.005360	0.00209	0.36	0.43	0.066

	. 1/2						
0.5	2.200	0.483	0.009640	0.00246	0.99	1.21	0.120
0.4	1.860	0.3880	0.007440	0.00228	0.64	1.22	0.145

 $*m_{Au(HS)-2} = K_3 \bullet a_{H2S} \bullet a_{HS} - /a_{H2}^{1/2}$ 

Then from the values of dissociation constants at 25°C, 1bar and 300°C, 300 bar, the coefficients of the BR model [5] and Gibbs energies of AuHS° and Au(HS)<sub>2</sub> have been determined at 300°C and a pressure of saturated water vapor (table3).

Table 3. Gibbs energies of the substances [4] used in the experimental data processing.

	Gibbs energy (J/mol)					
Substance	25°С, н.п.	300°С, н.п.	300°C, 300 bar			
H <sub>2(</sub> aq)	17723	-12654	-11736			
$H_2S(aq)$	-27920	-77780	-76836			
HS	11966	5102	3844			
Au (s)	0	-17270	-17051			
AuHS <sup>o</sup>	35606	(-35612)**	(-34023)*			
$Au(HS)_2$	10163	(-50259)**	(-51352)*			
$Au^+$	163176	132033	132979			
$H_2(g)$		-38837	-38837			

calculated from the experimental determinations of K1 and K3.

\*\* calculated by the BR model [4].

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# <sup>#</sup>Ivanov I.P., Kanazirsky M., Karadjiv M. Paragenesises of sulfides and oxides of iron and copper in the system Fe-Cu-S-H<sub>2</sub>O open for sulfur and oxygen at 400°C and 1 kbar.

A quantitative analysis of phase equilibria in the open system Fe-Cu-S-H<sub>2</sub>O vs sulfur (S  $_{2(gas)}$ ) and oxygen (O<sub>2(gas)</sub>) fugacity has been performed at 400°C and P= 1kbar. The system contains pyrite (Py), pyrrhotite (Po), magnetite (Mag), hematite (Hem), chalcopyrite (Ccp), bornite (Bn), covellite (Cv), chalcocite (Cc), cuprite (Cup), native copper (Cop). The quantitave diagram with lgfS2-lgfO<sub>2</sub> axes has been plotted. Presented on the diagram are the stability fields of binary parageneses in a binary system and monomineral fields in the end systems Fe-S-H<sub>2</sub>O and Cu-S-H<sub>2</sub>O. The Yu.V. Svarov's program and "Unitherm" database (1992) were used for calculations.

Bivariant fields of the binary mineral parageneses are confined on the diagram by the monovariant lines (reactions):

$2 Py + 1.5O_2 = Hem + 2S_2$	(1)
$3Py + 2O_2 = Mag + 3S_2$	(2)
Py = Po + 0.5S	(3)
$3Po + 2O_2 = Mag + 1.5 S_2$	(4)

<sup>&</sup>lt;sup>#</sup> The work has been supported by RFBR (project 99-05-64908)

$Mag + O_2 = 1.5 Hem$	(5)
$Py + 5Cv = Bn + 3.5S_2$	(6)
$0.5 \text{ Hem} + 5\text{Cv} = \text{Bn} + 0.75\text{O}_2 + 0.5\text{S}_2$	(7)
$0.5 \text{ Hem} + 2.5 \text{ Cc} + 0.75 \text{S}_2 = \text{Bn} + 0.75 \text{ O}_2$	(8)
$0.33 \text{ Mag} + 2.5 \text{ Cc} + 0.75\text{S}_2 = \text{Bn} + 0.65\text{O}_2$	(9)
$4 Py + Bn = 5Ccp + S_2$	(10)
$2 \operatorname{Hem} + \operatorname{Bn} + 3\operatorname{S}_2 = 5 \operatorname{Ccp} + 3\operatorname{O}_2$	(11)
$1.33 \text{ Mag} + \text{Bn} + 3\text{S}_2 = 5\text{Ccp} + 2.66\text{O}_2$	(12)
$4Po + Bn + 2.5S_2 = 5Ccp$	(13)
$Cc + 0.5S_2 = 2Cv$	(14)
$Cc + 0.5O_2 = Cup + 0.5S_2$	(15)
$Cc = 2Cop + 0.5S_2$	(16)
$2Cop + 0.5 O_2 = Cup$	(17)

The diagram shows the disposition of the stability fields of sulfides and oxides od iron and copper. The bornite (FeCu<sub>5</sub>S<sub>4</sub>) field overlaps the fields of pyrite and pyrrhotite and gets in touch with the fields of hematite and magnetite. It is confined by reactions 6-9 and is shown by vertical hatching. The chalcopyrite (Cu FeS<sub>2</sub>) field shown by skewed hatching is "incorporated" into the bornite field and confined by reactions 10-13. The latter involves the cubanite field which is not shown on the diagram.

The parageneses Py+Bn, Bn+Cv, Bn+Hem, Bn+Cc, Mag+Ccp, Hem+Ccp, Mag+Ccp, Po+Ccp are within the bornite field. The chalcopyrite field besides the extensive Ccp-Bn region involves the parageneses Py+Ccp, Hem+Ccp, Mag+Ccp, Po+Ccp. Parageneses involved in other fields are presented on the diagrams "compositionparagenesis" Based on the diagram lgfS<sub>2</sub>-lgfO<sub>2</sub> the Shvarov's program allows to calculate the solubility of minerals and mutual (eutonic) solubility of mineral parageneses, bulk concentrations of S, Fe, Cu in equilibrium solutions, concentrations of major particles in them and acidity of solutions. The presented diagram may be well used to estimate physical-chemical parameters governing ore parageneses of copper-porphyry deposits.



Fig.  $lgf(S_2)$ - $lgf(O_2)$  diagram of the system Fe-Cu-S-H<sub>2</sub>O at 400°C and 1 kbar. 1-17 – monovariant reactions. The bornite field is shown by vertical hatching., chalcopyrite field – by skewed hatching.

# <sup>#</sup>Ivanov I.P., Tkachenko N.A. Parageneses of aluminosilicates in the system Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-HCl open for Na at T=200-450°C and P=1kbar.

Phase equilibria have been calculated in the system  $Na_2O-K_2O-Al_2O_3-SiO_2-H_2O-HCl$  open for the  $N_2O$  component at T=200-450°C and P= 1 kbar. The parameters of equilibrium solid phase assemblages (mineral parageneses) with excessive quartz have been calculated. The system involvs quartz (Qtz), kaolinite (Kln), pyrophillite (Prf), andalusite (And), muscovite (sericite) (Ms), microcline (Kfs), paragonite (Prg), and albite (Ab).

 $^{\#}$  The work has been supported by RFBR, project N 99-05-64-908

Table1. Compositions of the solutions equilibrium with mineral parageneses(Qtz-in excess), in the system Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-HCl, open for sodium, P=1 kbar,  $m_{HCl}$ =0,1 mole/kg H<sub>2</sub>O.

Parameters	Qtz+Kln+	Qtz+Prl+	Qtz+And+	Qtz+Pg+	Qtz+Ab+	Qtz+Ab+
of edges	+Ms	+Ms	+Ms	+Ms	+Ms	+Kfs
			T=200°C			
Lgf <sub>Na2O</sub>	-35.3	-	-	от -35.2	от -34.8	-34.1
	and lower			до -34.9	до -34.2	and hower
Solution:Na	9.905 E-02	-	-	9.912 E-02	9.909 E-02	9.612 E-02
	and lower			9.916 E-02	9.624 E-02	and hower
K	1.024 E-03	-	-	9.583 E-04	1.041 E-03	4.183 E-03
	and lower			9.586 E-04	4.025 E-03	and hower
Al	4.295 E-06	-	-	4.802 E-06	6.267 E-06	E-06
	and lower			5.931 E-06	6.319 E-06	and hower
Si	4.793 E-03	-	-	4.858 E-03	4.913 E-03	5.093 E-03
	and lower			4.875 E-03	4.983 E-03	and hower
pH	6.110	-	-	6.164	6.366	6.736
	and lower			6.314	6.679	and hower
			T=300°C			
Lgf <sub>Na2O</sub>	-	-30.4	-	от -30.3	от -29.6	-29.0
		and lower		до -29.7	до -29.1	and hower
Solution:Na	-	9.73 E-02	-	E-02	9.686 E-02	8.983 E-02
		and lower		9.742E-02	9.055 E-02	and hower
K	-	2.72 E-03	-	2.699E-03	3.283 E-03	1.047 E-02
		and lower		2.700 E-03	9.703 E-03	and hower
Al	-	1.36 E-05	-	1.437 E-05	2.048 E-05	2.137 E-05
		and lower		2.026 E-05	2.074 E-05	and hower
Si	-	1.31 E-02	-	1.312 E-02	1.323 E-02	1.354 E-02
		and lower		1.316 E-02	1.329 E-02	and hower
pH	-	5.466	-	от 5.517	от 5.872	6.210
		and lower		до 5.817	до 6.151	and hower

		T=395°C			
Lgf <sub>Na2O</sub>		-26.26	от -26.25	от -26.20	-25.60
		and lower	до -26.21	до -25.70	and hower
Solution:Na		9.52 E-02	9.519 E-02	9.476 E-02	8.240 E-02
		and lower	9.521 E-02	8.507 E-02	and hower
К		4.92 E-03	4.878 E-03	5.321 E-03	1.779 E-02
		and lower	4.871 E-03	1.509 E-02	and hower
Al		4.13 E-05	4.025 E-05	4.039 E-05	4.017 E-05
		and lower	4.268 E-05	3.880 E-05	and hower
Si		2.69 E-02	2.629 E-02	2.646 E-02	2.697 E-02
		and lower	2.654 E-02	2.649 E-02	and hower
pH		5.613	от 5.610	от 5.639	6.003
		and lower	до 5.637	до 5.935	and hower

The Yu.B. Shvarov's program has been used (Shvarov, 1979) which offeres the database "Unitherm" for minerals and particles in an aqueous solution. The results are presented on the diagram T-lg( $\Sigma Na/\Sigma H$ ) at P=1kbar and 0.1mHCl, where  $\Sigma Na = m_{Na^+}+m_{NaCl}(aq)$  and  $\Sigma H=m_H+m_{HCl}(aq)$ .

The diagram is divided into four fields (facies) I, II, III, IV by the monovariant hydrolysis reactions (1-5):

$0.5 \text{ Ms} + 3\text{Qtz} + \text{Na}^{+} = 0.5\text{Kfs} + \text{Ab} + \text{H}^{+}$	(1
$0.5Prg + 3Qtz + Na^{+} = 1.5Ab + H^{+}$	(2
1.5Kln + Na <sup>+</sup> = Prg + H <sup>+</sup> + $2.5$ H <sub>2</sub> O	(3
$1.5Prl + Na^{+} = Prg + 3Qtz + H^{+}$	(4
1.5And $+1.5$ Otz $+$ Na <sup>+</sup> $+1.5$ H <sub>2</sub> O $=$ Prg $+$ H <sup>+</sup>	(5

Field I is represented by the parageneses Qtz + Kfs + Aband Kfs + Ms + Ab, field II – by the parageneses Qtz + Kfs + Ms and Qtz + Ms + Ab, field III – by the parageneses Qtz + Kfs + Ms and Qtz + Ms + Prg, and field IV – by the parageneses a) Qtz + Kfs + Ms and Qtz + Ms + Kln, b) Qtz + Kfs + Ms and Qtz + Ms + Prl; c) Qtz + Kfs + Ms and Qtz + Ms + And.

As it is shown on the diagram, with decreasing sodium concentration and increasing acidity of the solution, paragenetic mineral assemblages change in the following sequence: bifeldspar parageneses (fields I, II), mica (paragonitic) assemblage (field III), and assemblages of alkali-free aluminosilicates (field IV). Field IV is devided by reactions of hydration-dehydration 6, 7:

$Kln + 2Qtz = Prl + H_2O$	(6)
$Prl = And + 3Qtz + H_2O$	(7)
$\mathbf{U}_{\mathbf{U}} = \mathbf{U}_{\mathbf{U}} + \mathbf{U}_{\mathbf{U}} + \mathbf{U}_{\mathbf{U}} + \mathbf{U}_{\mathbf{U}} + \mathbf{U}_{\mathbf{U}} + \mathbf{U}_{\mathbf{U}}$	

into temperature sufacies IVa, IVb, IVc.

The chemical potential of the Na<sub>2</sub>O component at the calculations was preset by the ratio  $\mu_{Na2O}$ +RTlgf<sub>Na2O</sub>, where  $\mu$  is a chemical potential , f – fugacity of the Na<sub>2</sub>O component. The compositions of the solutions ( and their acidity) equilibrium with mineral parageneses within the fields shown in fig.1 are presented in table 1 for T=200, 300, and 395°C and P=1 kbar. The table also presents the lgf<sub>Na2O</sub> values at the interfaces of fields I-IV (reactions 1-5).

As it is seen in the table, sodium has the highest concentration in the solutions, an order of magnitude higher than potassium concentrations. Aluminium is the lowest concentrated component. Silicon concentrations are about the same as in pure water. The solutions are weakly acid.



**Fig.** Parageneses of aluminosilicates in the system Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-HCl open for sodium depending on temperature, sodium concentration in the solution and solution acidity at P=1 kbar and 0.1m HCl; (1-5) – monovariant hydrolysis reactions; (6,7) reactions of hydration-dehydration; I-IV – divariant fields (facies) of mineral parageneses; a, b, c – sufaces of field IV; trianglular diagrams – parageneses of aliminosilicates with excessive quartz.

Phase associations within fields I-IV (fig.1) model mineral parageneses of the first zone in the columns of quartz-feldspar, quartz-sericite, quartz-paraganite metasomatites and secondary quartzites ( additionary zoning). The results obtained are in a satisfactory agreement with experimental data (Ivanov, 1980, 1984).

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# Fedkin A.<sup>1</sup>, Melzer S.<sup>2</sup>, Seltmann R.<sup>3</sup>, Zaraisky G.<sup>1</sup> Experimental studies of the Ab-Or binary system under H<sub>2</sub>O-HF fluid pressure.

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**Abstract.** The liquidus position for the system Ab-Or-F with water in excess has been investigated experimentally at P = 1 kbar. Compared to previous studies on this system without fluorine (Tuttle and Bowen 1958), the liquidus temperature decreases by 50-70°C in the system studied here.

Introduction. Most highly evolved mineralized granites are characterized by development of layered textures common for the apical parts of granitoid intrusions. Such rocks are considered to be the late differentiates of baren two-mica granite magma evolution. An example for orebearing granites are the Orlovka and Etyka Ta deposits, Eastern Transbaikalia. These Li-F granites are famous due to their rhythmically layered textures consisting of albiteamazonite-layers. These so-called "line rocks" occur preferentially in F-enriched granite cupolas showing high concentrations of Ta, Nb, Pb, Sn and other rare metals. Formation of such granitic textures is still under question. The knowledge of melting relations of coexisting albite (Ab) and orthoclase (Or) under certain fluid regimes is a prerequisite to understanding the formation of the mineralized line rocks. Therefore, the major goal of this study is to determine the liquidus and solidus curves in the F-bearing binary system albite-K-feldspar (NaAlSi<sub>3</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub>) under water-saturated conditions at 1 kbar. Temperatures range between 500°C and 900°C.

**Current knowledge.** The haplogranite system and the binary system Ab-Or have been studied at water pressures from 0.5 to 4 kbar (Tuttle and Bowen 1958). The minimum crystallization temperature is  $T=857^{\circ}C$  at  $P_{H2O}=1$  kbar,  $T=950^{\circ}C$  at  $P_{H2O}=0.5$  kbar and  $T=1070^{\circ}C$  under "dry" conditions. Manning (1981) describes the influence of fluorine on the liquidus phase relationships in the haplogranite system with excess water at 1 kbar. The addition of fluorine shifts the system composition in the Qtz-Ab-Or system during crystallization of a granitic melt toward the albite apex and strongly decreases the liquidus and solidus temperature. The eutectic composition  $Qtz_{37}Ab_{34}Or_{29}$  at  $730^{\circ}C$  for the fluorine free system strongly differs from that ( $Qtz_{15}Ab_{58}Or_{27}$  at  $630^{\circ}C$ ) for the system with 4 wt % F added .

Many other experimental studies on granitic systems have concentrated on a better understanding of granite melting relations. Luth et al. (1964) experimentally investigated the granite system at pressures ranging between 4 and 10 kbar. In this study liquidus phase relationships, thermal minima and minimum melt compositions were defined. On the other hand, the system Ab-Or-H<sub>2</sub>O was studied in detail at low temperatures (700-550°C) in order to constrain the position of the feldspar-solvus (Orville 1963; Luth and Tuttle 1966; Seck 1972; Smith and Parsons 1974; Parsons 1978). At H<sub>2</sub>Osaturated conditions the temperature at the peak of the solvus slightly increases with increasing pressure, whereas the solidus temperature strongly decreases. Consequently, at pressures of about 4 kbar solidus and solvus curves intersect and phase relationships change from minimum at lower pressures to eutectic type at higher pressures (Luth et al. 1964; Morse 1970; Tuttle and Bowen 1958). At H<sub>2</sub>Osaturated conditions the eutectic composition does not significantly vary as a function of pressure (Or<sub>30</sub> at 1, 2, 5, 10 kbar; Tuttle and Bowen 1958; Luth et al. 1964; Morse 1970). Holtz et al. (1992) studied experimentally the influence of water on the haplogranitic system at 2 and 5 kbar. At both pressures a decreasing H<sub>2</sub>O-content of the melt results in an increasing liquidus temperature and a progressive shift of minimum and eutectic compositions towards the Qtz-Or join. This effect is much stronger for albite than for orthoclase-rich melt compositions, because water is more soluble in Ab-rich than in Or-rich melt. Melting relationships in the more complicated granite Qtz-Or-Ab-An-H<sub>2</sub>O model system (An=anorthite;  $CaAl_2Si_2O_8$ ) have been studied by Johannes (1984) to derive the P-T diagram (T=500-750°C, P=1-10 kbar). Minimum melting temperatures are positively correlated with An-content. Up to 40 mol% An-component (Ab<sub>60</sub>An<sub>40</sub>) in plagioclase, the increase of solidus temperatures relative to the system Ab-Or-Qtz-H2O is rather small ( $\approx 10^{\circ}$ C), whereas the solidus temperatures differ by about 40°C in this system between Ab<sub>60</sub>An<sub>40</sub> and  $An_{100}$ . These differences are quite small in comparison to shifts in solidus temperatures of several hundred degrees due to the addition of other volatile components such as B or F to granitic melts

**Experimental and analytical methods.** The temperature interval investigated was 700-900°C at P=1 kbar. In a few runs the run temperature was overstepped by either 150°C or 200°C for 3 days (Table 1). Duration was 7-10 days. Synthetic feldspar gels prepared by the Hamilton method (1968)were used as starting powders. Fluorine was added as 0.1 m HF solution. The calculated approximate value of fluorine content in the starting mixture was 0.2 wt%. Four different feldspar compositions were prepared as starting materials:  $Ab_{90}Or_{10}$ ,  $Ab_{30}Or_{70}$ ,  $Ab_{75}Or_{25}$ ,  $Ab_{65}Or_{35}$ . In addition, in a few experiments homogeneous glasses composed of  $Ab_{89}Or_{11}$  and  $Ab_{44}Or_{56}$  were used as starting materials (Table 1).

Table 1	<ol> <li>Composition</li> </ol>	ns of starting	mixtures (	1-4	columns - sy	nthetic, 5-6 –	natural).

	Ab <sub>90</sub> Or <sub>10</sub>	Ab <sub>75</sub> Or <sub>25</sub>	Ab <sub>65</sub> Or <sub>35</sub>	Ab <sub>30</sub> Or <sub>70</sub>	AbOr1(n)	$AbOr_2(n)$
$P_2O_5$	-	-	-	-	0.08	0.27
SiO <sub>2</sub>	68.32	67.70	67.30	65.91	72.15	65.71
$Al_2O_3$	19.32	19.15	19.03	18.64	21.02	18.83
FeO	-	-	-	-	0.09	0.07
CaO	-	-	-	-	0.11	0.05
Na <sub>2</sub> O	10.57	8.73	7.52	3.40	7.98	4.74
K <sub>2</sub> O	1.79	4.42	6.15	12.05	1.42	9.29
Rb <sub>2</sub> O	-	-	-	-	0.12	0.43
Total	100	100	100	100	102.98	99.39
Ab	90	75	65	30	89.0	43.6
Or	10	25	35	70	10.4	56.2

	_					
An	-	-	-	-	0.7	0.3

Table 2. Experimental results (D – run duration in days).

Run no.	Ab	Or	T°C	P, kbar	D	Resulting phases
37	90	10	900	1	7	G
36	65	35	900	1	7	G
30	30	70	870	1	7	G
31	75	25	870	1	7	G+Qtz
32	65	35	870	1	7	G+Qtz
9	90	10	850	1	7	G
21 (natural)	89	11	850	1	7	G+AF
10	30	70	850	1	7	G+AF
27	75	25	850	1	7	G
28	65	35	850	1	7	G
25 (natural)	89	11	830	1	7	G+AF
26 (natural)	44	56	830	1	7	G+AF
5	90	10	800	1	7	AF
33	90	10	800	1	7	G+AF
34	30	70	800	1	7	G+AF
11	75	25	900-700	1	3+7	AF

The glasses were produced by melting natural albitemicrocline mixtures at 1300 °C.

Compositions of products, both glasses and feldspars, were determined by Cameca SX100 electron microprobe. Run products were also examined using a Zeiss DSM962 scanning electron microscope.

**Experimental results.** The most representative results of the experimental runs are listed in Table 2. Depending on the temperature the run products consist of either glass (G) or glass plus crystals or only crystals (Fig. 1). In the diagram the glass and crystal compositions of the same run are connected by thin arc-shaped lines. Besides alkali feldspars (AF), quartz was found as an additional crystalline phase in products of a few runs. Quartz is interpreted as quench phase, because it appears as extremely small rounded grains within the melt matrix (Fig. 2). However, even massive quench crystallization of Qtz would only slightly change the melt composition with respect to the relative amounts of Ab and Or.

Compositions of product feldspars and glasses (quenched melts) are plotted in the binary diagram Ab-Or (Fig. 1). Our experimental results indicate, that the liquidus phase relations are of minimum type. The liquidus and solidus curves are plotted lower than those of Tuttle and Bowen by approximately 50°C at marginal compositions and by 70°C or even higher near the eutectic area, which is poorly defined. All runs below 800°C yielded only crystalline phases as run products.



**Fig. 1.** Measured glass and feldspar compositions projected on the binary Ab-Or F-free system at  $P_{H2O}=1$  kbar by Tuttle & Bowen (1958). Dashed bold curves are the estimated liquidus and solidus in the system Ab-Or-H<sub>2</sub>O-HF at P=1 kbar on data of this study.

Discussion. The approximate liquidus curve for the Fbearing system Ab-Or-H<sub>2</sub>O (dashed line in Fig. 1) based on our experimental results, plots 50-70°C lower than that for the same system without F reported by Tuttle & Bowen (1958). The difference between the liquidus position resulting from our study and that one achieved by Tuttle and Bowen (1958) may be explained by the influence of fluorine on the melting temperature. Although the concentration of F in the melt is too low to be detected by electron microprobe, the melting temperatures are substantially decreased. A difference in the same order of magnitude exists between the liquidus temperatures of the F-bearing (Manning 1981) and the F-free (Tuttle and Bowen 1958) system Ab-Or-Qtz-H<sub>2</sub>O. However, crystallization kinetics could effect the melting temperature, and, thus, the projected curve should be verified by the reversal experiments.

The experimental results demonstrate that even tiny amounts of fluorine significantly effect the melting conditions in magmatic systems. It was difficult to determine precisely the beginning of melting, however, the approximate intervals corresponding to liquidus, subliquidus, and subsolidus were derived. Compositions of melt and coexisting feldspars provide the basis to define the solidus and liquidus curves.

Inconsistencies of the resulting and initial compositions may easily be explained by quench crystallization of quartz due to enrichment of the system by  $SiO_2$  after dissolution of alkalis to the coexisting fluid. However, this has no significance for the major conclusions of this study.





b)

**Fig.2.** a) feldspar crystals in  $T=700^{\circ}$ C, P=1 kbar run series; b): feldspar and glass with quartz inclusions (dark spots in the light background).

**Conclusions.** At a water pressure of 1 kbar, the addition of fluorine depresses the melting temperature in the binary Ab-Or system under H<sub>2</sub>O-saturated conditions by 50-70°C. In the whole range of studied feldspar compositions the minimum temperature for the superliquidus field is estimated to be 830°C. The subliquidus field embraces the temperature interval 800-850°C.

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# Karasyova O.N., Lakshtanov L.Z., Ivanova L.I. Effect of temperature and atmospheric $CO_2$ on the strontium adsorption on hematite

Adsorption by mineral surfaces strongly controls the mobility of many trace metals in sediments and soils. Hematite is a mineral with the well-described stable surface whose structure is close to that of iron hydroxides forming by weathering of base and ultra-base rocks. Among the most dangerous radioactive substances <sup>90</sup>Sr is formed in nuclear reactions of the uranium fission. Because <sup>90</sup>Sr is much more mobile than other hazardous radioactive elements, it is important to determine and understand the chemical conditions that control strontium interaction with soil and rock-forming minerals.

The adsorption of strontium on hematite at the background of 0.1 NaCl solution was studied by the method representing a combination of acid-base potentiometric titrations with metal adsorption data. We have investigated Sr sorption dependence on pH and sorbate/sorbent (Sr<sup>2+</sup>/ $\equiv$ FeOH) ratio at atmospheric pressure of carbon dioxide at 25<sup>0</sup>, 50<sup>0</sup>, and 75<sup>o</sup>C.

The experimental data were evaluated according to the Extended Constant Capacitance Model (Nilsson, 1995).

The calculation of the hematite( $\equiv$ FeOH) – H<sup>+</sup> – Sr<sup>2+</sup> – CO<sub>2</sub> model consisted of testing the possible combinations of surface complexes of strontium via the computer program FITEQL 3.1 (Herbelin and Westall, 1994).



Fig.1. Effect of atmospheric carbon dioxide on sorption of strontium on hematite. Conditions:  $T=25^{0}$ C,  $[\equiv$ FeOH] = 1.1 mM,  $[Sr^{2+}/ \equiv$ FeOH] =0.1, Specific area 4.5 m<sup>2</sup>/g, ionic strength 0.1 M NaCl.

The experimental data fit best in the model including the formation of inner-sphere monodentate complexes:  $\equiv FeOH + H_2CO_3 + Sr^{2+} \Leftrightarrow \equiv FeOHSrHCO_3^{+} + H^{+},$  $\equiv FeOH + H_2CO_3 + Sr^{2+} \Leftrightarrow \equiv FeOHSrCO_3^{0} + 2H^{+}.$ 

The corresponding intrinsic constants of formation of these complexes were calculated for  $25^{\circ}$ ,  $50^{\circ}$ , and  $75^{\circ}$ C.

The presence of atmospheric  $CO_2$  has a similar effect on strontium adsorption as the temperature increase: the Sr adsorption edge shifts to the lower pH values (fig.1). The temperature effect is more pronounced in the absence of  $CO_2$ . On the other hand, the Sr adsorption edge in the presence of  $CO_2$  covers a much more narrow pH range that is testified to by a stronger interaction with the surface.

The combined effect of the  $pH_{pzc}$  decrease and the positive enthalpies of surface complexes formation is in favor of Sr adsorption on hematite at enhanced T as well as under atmospheric conditions. Adsorption and retardation in the natural aquatic environment is unlikely at ambient T and pH but may be significant in the radioactive waste disposals at elevated temperatures.

# <sup>#</sup>Ivanov I.P., Shapovalov Yu.B., Kashirtseva G.A., Tkachenko N.A. Stability fields and solubility of sulfides and oxides of iron in the system Fe-S-H<sub>2</sub>O-O<sub>2</sub> open for sulfur and oxygen at 400°C and 1 kbar.

The boundaries of stability fields and solubility of pyrite (Py), pyrrhotite (Po), hematite (Hem) and magnetite (Mag) have been calculated in the system Fe-S-H<sub>2</sub>O-O<sub>2</sub> open for sulfur and oxygen under oxidation conditions at T=400°C and P=1kbar. The calculations were performed

by the Shvarov's program [1999] which includes the database on the properties of minerals and particles in the aqueous solution "Uniterm". The phase diagram of the system has been plotted as related to the  $lgf_{o2}$ - $lgm_{stot}$  coordinates (fig.1). The values of sulfur and oxygen chemical potentials in the system were preset by S<sub>2</sub> and O<sub>2</sub> fugacities. Shown on the diagram are the stability fields of minerals, the field boundaries are shown by solid lines. The dashed lines are isolines of the pH value of equilibrium solution (long dashes), isolines of bulk concentration of iron in the solution – Fe<sub>tot</sub>mole/kg H<sub>2</sub>O (short dashes), and the line of pH of water neutral point at T=400°C and P=1 kbar (medium dashes).

The pyrite field on the diagram falls into the region of sulfur concentrations in the equilibrium solution above n  $*10^{-2}$ mole/kg H<sub>2</sub>O. At the oxygen fugacity to  $lgf_{O2}=23.63$  it borders the hematite field, at oxygen fugacity from 23.63 to 25.75 –the magnetite field, at lower oxygen fugacity – the pyrrhotite field.

At the pyrite/oxides interface the extremum with minimun by sulfur is observed (1.25  $10^{-2}$  mole/ kg H<sub>2</sub>O) which is related to sulfur oxidation from S<sup>-2</sup> to S<sup>+6</sup>.

In the ragion of oxygen fugacity below -25, H<sub>2</sub>S (aq) prevails in the solution, in the region of oxygen fugacity above  $-23.63 - SO_2$  (aq), HSO<sup>-</sup><sub>4</sub> are predominant.

The pH line for neutral water point shows that stability fields of Hem, Py, and Mag are in the region of acid solutions. The magnetite stability field is in the region of both acid and week-alkaline solutions. The pH values of the solution in the left part of the diagram are governed by  $H_2S$  (aq). When approaching the extremum, pH isolines bend sharply towards low sulfur concentrations in the solution. Here the curve inflexion with increasing fO2 is determined by the complexes  $H_2S$  (aq),  $SO_2$  (aq), and  $HSO_4$ . A reverse inflection of the curve is observed in the hematite field where  $SO_2$  (aq) and  $HSO_4$  are predominant in the solution. The solution acidity increases sharply along the interface of Py/Hem fields with increasing fO<sub>2</sub>.

The character of the isolines of iron bulk concentrations in the equilibrium solution suggests the complicated topology of sulfide and oxide solubilities within the interval of their stability. The highest solubility of iron was fixed at the interface of the iron sulfides stability fields and their oxides. Since the mineral solubilities differ, so sharp inflexions of the isolines of iron bulk concentrations are observed in the equilibrium solution.

Maximum iron concentration in the solution  $(n*10^{-1} \text{ mole/kg H}_2\text{O})$  was fixed at the Py/Hem interface at the highest values of  $f_{O2}$  and  $m_{Stot}$  in the solution. It is by 4-5 orders of logarithm scale higher than iron concentration at the Py/Mag interface in the inflexion zone of the isoline of pH solution.

Iron concentration in the solution decreases essentially leftwards along the Py-Hem interface line up to the non-variant point. This tendency remains as the Py-Hem line goes over into the Py-Mag line . With decreasing  $f_{02}$ , iron concentration in the solution is slowly growing along the Po-Mag interface begining from the non-variant point Py-Po-Mag . Extremum points on the isolines of iron solubility in equilibrium solutions within the Py and Mag stability fields lie on the inflection points of the isolines of pH solutions.

<sup>&</sup>lt;sup>#</sup> The work has been supported by the RFBR (project N 99-05-64908).

The presented calculations are of great importance for the physical-chemical estimation of the formation conditions of sulfide and oxide iron-bearing ore deposits.



**Fig.** Phase diagram of the system  $\text{Fe-S-H}_2\text{O-O}_2$  depending on oxygen fugacity and sulfur concentration in the equilibrium solution at T=400°C and P=1 kbar.

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# <sup>#</sup>Khodorevskaya L.I. Experimental study on the granite-amphibolite interaction at 800°C and 7 kbar.

According to D.S. Korzhinsky's granitization hypothesis [1] granite formation occurs under the action of transmagmatic solutions with the high content of silica and alkalis. As a result of such action host rocks undergo changing (feldspathization). The components excessive with respect to granite eutectics are being trapped out of the granitization zones and granite components dissolved by magma. Leucocratic melts first form in the rear column zones and substitute the transformed host rocks. Such a consecutive transformation of rocks gives rise to formation of different type zonings.

Korzhinsky's ideas were supported by the field studies of the rocks of granulite and amphibolite metamorphic facies. Different types of granitization columns have been described, substances balance has been considered, the distinctions assigned to the composition of active granitoides and peculiarities of minerals of variable composition have been indicated.

The direct experimental modeling of the granitization processes seems problematic because the components transfer by a fluid phase in an open system at high parameters is difficult to realize. That is why we decided to reproduce diffusional magma-rock interaction when the difference in chemical potentials of components in two media provides components diffusion both in the crystalline medium and in the melt. Unfortunately, such an approch to the experemental modelling has a disadvantage: the rock transformation is followed beginning from the second stage- melt generation, missing the first stage- rock feldspathization under the action of hydrothermal fluid.

This paper presents the results of the experimental study on the granite-amphibolite interaction at 800°C and 7 kbar with the description of one of the zoning types.

Experiments were carried out at 800°C and 7 kbar in a high gas pressure apparatus with the inner heating by the quenching method. The starting materials were finely-ground (5-20mkm) amphibolite 13/2-St-88 and preliminary synthesized haplogranite. The compositions of the starting phases are presented in the table . The amphibolite is mainly composed of hornblende, biotite, and plagioclase, sphene, magnetite being also present.

The amphibolite sample 200-300 mg in weight was ground and tightly filled into the capsule, 0.04-0.05 ml of water and 200-300mg of granite were added and the mixture was tightly packed. A thin ring of copper wire was placed round the capsule so that the starting contact can be fixed. The capsule was sealed and held under experimental conditions for 4 days. In order to prevent iron loss due to diffution into the capsule walls, the experiments were carried out in gold capsules. The oxygen fugacity fO2 was not controlled, admitting that in the runs without a fluid phase fO2 is close to the Ni-NiO buffer [2]. After the run the capsule was cut along the sample, all the sample was treated with ciacrine (C6H7NP2) and dried. Then the sample was placed into epoxy resin and cut lengthwise by a thin diamond saw. One half of the sample was polished to take the microprobe analysis, another one served as a duplicate. The analysis of mineral chemical compositions was performed on the electron microprobe "Camscan" with EDS Link AN10/85S in the microanalytical Lab of the petrological department of th Moscow state University.

The sample after the run was a sintered inhomogeneously colored fragment. The bottom part containing amphibolite was dark gray, the top one with the starting granite in it formed transparent colorless glass colored slightly gray in the near contact area. The general view of the sample is given in Fig 1. Three zones of the rock transformation along the sample have been distinguished with account of quenched glass amount, mineral composition, morphological properties of crystals, and their sizes. The right part of the sample is formed by dark-gray glass, the left one - by amphibolite with darkgray inclusions of glass and plagioclase. The dashed line separates the area of variable width (zone 2a). 77% of this area is formed by the quenched glass with individual crystals appearing. Presented in the table is the chemical composition of phases, quenched glass, and average bulk composition in each zone. All the compositions are recalculated to 100%. The bulk composition has been determined from the 0.25 mm<sup>2</sup> area of each zone along the section A-A. Phase compositions are given in the table as the coefficients of the crystallochemical formulas, composition of starting rock, quenched glass and bulk composition - in wt%.

<sup>&</sup>lt;sup>#</sup>The work has been supported by the RFBR (project 00-05-64036).

№ zone,	Nº									
Ratio	spectrum	phase	$SiO_2$	TiO <sub>2</sub>	$Al_2O_3$	MgO	FeO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
Gl/crystal										
(vol%)										
0,		starting	74.65		12.16				6.32	6.86
		granite								
1,	26	Gl	71.14	0.27	16.16	0.14	0.73	1.47	5.96	3.86
2,	31	Gl	70.31	0.16	17.62	0.07	0.86	1.78	5.02	3.62
77 /23										
	29	Am	6.77	0.12	2.13	2.37	2.25	1.95	0.58	0.22
	28	Bt	3.02	0.20	1.52	1.47	1.24		0.02	0.98
	30	Bt fine-ground	2.94	0.18	1.69	1.73	0.96		0.14	0.90
	27	bulk	63.36	0.76	16.49	2.80	4.87	2.25	3.98	4.51
		composition	60.66	0.70	16.06	2.78	4.51	2.10	3.96	4.22
2a,	33	Gl	68.46	0.22	18.02	0.16	0.94	2.20	5.89	3.66
33 / 67										
	34	$Am_1$	6.79	0.15	2.07	2.37	2.28	1.92	0.41	0.24
	38	$Am_2$	6.84	0.12	2.04	2.44	2.18	1.90	0.43	0.21
	35	$Bt_1$	3.01	0.22	1.54	1.50	1.16		0.09	0.98
	37	$Bt_2$	3.04	0.19	1.53	1.66	1.06		0.11	0.94
	32	bulk	56.65	0.81	16.16	3.04	6.05	6.87	4.69	3.03
		composition								
3,	43	Gl	68.55	0.18	19.89	0.19	0.68	2.46	4.07	3.76
33 / 67										
	40	$Am_1$	6.71	0.09	2.23	2.36	2.29	1.91	0.56	0.19
	41	$Bt_1$	3.04	0.21	1.53	1.47	1.20		0.08	0.95
	42	Pl	2.65		1.34			0.34	0.63	
	39	bulk	54.28	1.14	19.61	3.06	6.50	7.14	4.68	2.68
		composition								
3a	45	Gl -24 wt%	67.46	0.27	19.50		0.61	2.34	5.49	4.07
24 / 76										
	46	Am <sub>1</sub>	6.76	0.12	2.13	2.43	2.27	1.94	0.31	0.24
	47	$Bt_1$	3.08	0.16	1.53	1.58	1.10		0.08	0.94
	48	Pl 48	2.49		1.50			0.47	0.51	
	49	bulk	54.09	1.10	19.88	3.18	6.60	6.84	5.16	2.43
		composition								
sample edge	51	Gl	71.49	0.33	19.52		0.89	2.26	2.09	2.97
1 0	50	Am,	6.69	0.11	2.17	2.35	2.42	1.93	0.46	0.21
		Pl, Bt								
stating amphibolite		Bt	38.17	2.84	15.36	13.66	18.48			9.87
0 1		Am	42.88	1.11	10.09	10.76	16.72	11.03	1.55	1.06
		Pl	62.39		24.14		0.06	5.60	8.67	0.12
		bulk	51.76	1.03	18.83	4.20	8.68	8.11	5.63	1.64
		composition								

Gl II (1) contaminated Gl II (2) Am+Bt+Gl II(3) Am+Bt+Pl+GlII



Fig 1. General view of the sample 1 D.

Quenched glass was found in all the sample zones. The diffusion of elements from amphibolite to starting granite was observed. Ca, Mg Fe are present in the composition of the quenched glass from the side of starting granite at the edge zones of the sample at the distance of 3.6 mm (pattern N 26 in the table). Herewith, the drop of alkali concentrations has been noted. Amphibole and biotite are the major minerals in the contact zone, biotite being predominant in zone 2a. By its chemical composition biotite is divided into two

generations: the coarse crystals and small crystals. The coarse crystals contain somewhat more Al (Bt N28 in the table) than starting biotite, the iron content being close.

The small (20mkm) crystals have a higher Mg and Al content compared to the starting biotite (Bt N30 in the table). The regular increase in iron content is observed in large biotite crystals in the direction from amphibolite to its contact with granite. Small biotite crystals (N30, 37 in table 2) have a lower iron content compared to the large ones, alumina content being close. This is likely the newly formed biotite. The starting amphiboles and amphibolites at the sample edge in zone 3 belong to the magnesial hornblend [3], but in all the amphiboles the silicon content after experiment is higher than in starting ones. The content of CaO+Na2O+K2O in amphiboles increases with approaching the contact zone. No essential distinctions were noted in chemical compositions of small and large amphiboles.In zone 3 plagioclase appeared alongside with amphibole and biotite. Its basicity increased from Pl35to Pl48 (table 2 N 42, 48) with the distance from the contact. The zone is 7000 mkm wide.

So, the run products allow to trace two processes: 1partial melting of amphibolite, 2- diffusional magmasubstrate interaction.

Partial melting of amphibolite is most clearly manifested in the third zone. In this process plageoclase

gets enriched in anorthite component (from  $Pl_{30}$  to  $Pl_{48}$ ), the melt of acid composition of the quartz monzonite ? type forms (pattern 51 in the table) with remaining biotite and amphibole.

Diffusional interaction of the granite melt with amphibolite is observed in the first and second zones. In this process amphibolite intensively losses Si and K and gains Ca, Mg, Fe, Al. No essential changes in Na content are observed along the sample. This is likely related to close Na contents in the starting granite and amphibolite. Al content sharply decreases compared to starting amphibolite, which is a possible reason of plagioclase disappearing in zones 1, 2. Quenched glass in the contact zones is trondiemite? [3]. The granite-amphibolite reaction zone where major changes in component contents take place is about 1500 mkm. The changes in mineral composition along the sample related to magmatic substitution of amphibolite may be presented as the following zoning:



Fig 2. Variation diagram of the rock-forming oxides in the sample along the A-A section.

Fig. 2 presents the variation of the bulk composition of the system in each zone of the column in mg/cm relative to starting amphibolite. This may be a characterization of the gain-loss of elements and related changes in mineral composition in the zones. The data on the densities of major phases with account of crystals quantity and melt amount in each zone [4] have been used for calculations.

So, on an example of one sample one can follow the changes characterizing two processes: the transformations related to the magmatic substitution of a metamorphic rock in zones 1-2, and its partial melting in zone 3. The amount of acid melt in zone 2 reaches 70 vol%, and in zone 3 - 24vol%. Otherwise, the amount of melt obtained as a result of magmatic substitution of amphibolite in the course of experiment was three time as much as that obtained by its partial melting.

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# <sup>1,2</sup>Perchuk L.L., <sup>2,1</sup>Gerya T.V., <sup>3</sup>van Reenen D.D., <sup>1</sup>Krotov A.V., Smit C.A.<sup>3</sup> Equilibria in the sheared zones separated cratons from granulite facies terrains as an indicator of dynamics of the Lower Precambrian crust.

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*P*-*T* evolution of mica schists from two regional scale tectonic (shear) zones that separate high grade terrains ("mobile belts") from cratons are described. These are the 2.4 -1.9 Ga Tanaelv belt (TB), a suture zone that separates the Lapland granulite complex (LGC) from the Karelian craton (Kola Peninsula-Fennoscandia), and the 2.69 Ga Hout River Shear Zone (Belt) that separates the > 2.9 Ga Kaapvaal craton from the 2.69 Ga South Marginal Zone of the Limpopo high-grade terrain (South Africa).

The 1.9 Ga Korva Tundra Group of the TB is composed of Chl+St schists overlaying gneisses of the Karelian craton and Ky-Bt rocks underlying garnet amphibolites of the TB, which are in tectonic contact with the LGC. The rotated garnet porphyroblasts in these rocks contain numerous inclusions (Otz, Chl, Ms), and show clear Mg/Fe chemical zoning that records both the prograde and retrograde history. A peak of metamorphism at  $T = 650^{\circ}$ C and P = 7.5 kbar is recorded in the Ky-Bt zone and characterized by snowball garnet. A minimum of metamorphic conditions along the retrograde PT-path are  $T = 530^{\circ}$ C and of P = 5 kbar.

The Hout River Shear Zone (South Africa) shows metamorphic zoning from greenschists through epidote amphibolites to garnet amphibolites. Rare strongly deformed mica schists (Chl+Grt+Pl+Ms+Bt +Qtz)record a prograde *P*-*T* path with a peak of T = 600 °C and  $P \sim 5.5$  kbar. The retrograde stage is documented by the reaction Prp+2Ms+Phl => 6Qtz+3Eastrecording a minimum  $T = 520^{\circ}$ C and  $P \sim 3.3$  kbar.

Narrow clock-wise P-T loops recorded in mica schists from both studied shear zones are very similar to each other suggesting similarity in geodynamic history of both shear zones under consideration.

<sup># 1,2</sup>Perchuk L.L., <sup>2,1</sup>Gerya T.V., <sup>3</sup>van Reenen D.D., <sup>1</sup>Krotov A.V., <sup>3</sup>Smit C.A., <sup>2</sup>Safonov O.G., <sup>1</sup>Shur M.Yu. Petrology of some granulite facies terrains: examples from Fennoscandia and South Africa

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Detailed studies of rocks from the Limpopo (South Africa) and Lapland (Kola-Fennoscandia) high-grade terrains were conducted in order to reveal similar

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geological and thermodynamic conditions of their formation. Both complexes (1) are situated between the Archean greenstone belts, (2) are younger then the greenstone belts, (3) are bounded by crustal-scale shear zones, (4) have a similar intrusive-like (harpolith) geometry, and (5) show similar reaction textures that reflect both breakdown and growth of garnet in each highgrade terrains. Local mineral equilibria within the textures indicate their successive formation with cooling of the high-grade terrains. Some of the textures in the metapelites must have resulted from reversible reactions Grt+Qtz $\langle = \rangle Opx+Crd$  and/or  $Grt+Sil+Qtz \langle = \rangle Crd$ . Based on these data, both the decompression cooling and the nearisobaric cooling P-T paths were deduced for both highgrade terrains. The near-isobaric cooling PT-path are characteristic of the marginal zones of both terrains. All above features suggest similar exhumation mechanisms for both granulitic complexes. The geodynamic consideration of detailed petrologycal data lead to a conclusion that both complexes were exhumed as giant diapirs (Ramberg, 1981) whose ascent was initiated by the Mantle derived fluid-heat flow (Perchuk et al., 1993).

# Perchuk L.L., Yapaskurt V.O., Safonov O.G. Potassium-bearing pyroxenes crystallized from ultra-high potassium liquids under Earth 's mantle conditions

The potassium-bearing very coarse-grained (megacrystal) diamond-free garnet-pyroxene rock occurs in the Kumdy-Kol microdiamond *deposit* that is situated in the Kokchetav massif, northern Kazakhstan. The deposit is composed of a variety of metasedimentary and magmatic rocks *metamorphosed* under amphibolite facies conditions at ~530 Ma. The quartz free rock studied forms interbeds and lenses in biotite-garnet gneisses near their contacts with calc-silicate rocks. Garnet of this rock contains micro-inclusions (from 50 to 185 µm in size) of relict clinopyroxenes (*Cpx*<sub>1</sub>) with a high potassium content. No potassium-bearing minerals occur around *Cpx*<sub>1</sub> inclusions.

Analytical data suggest that potassium enters clinopyroxene as K jadeite (KAlSi<sub>2</sub>O<sub>6</sub>) resulting from the ultra-high-pressure isomorphic substitution KAlSi<sub>2</sub>O<sub>6</sub> -Ca(Mg,Fe)Si<sub>2</sub>O<sub>6</sub>. A major constituent of the rock is potassium-free clinopyroxene  $(Cpx_2)$ . Cores and central portions of large (up to 90 mm in size) idiomorphic crystals of  $Cpx_2$  contain microcrystals of Kfs, while the  $Cpx_2$  rims are free of such inclusions. The Kfs microcrystals in  $Cpx_2$  form a lamellae-like texture that allows using the defocused beam for measuring bulk composition of homogeneous clinopyroxene. The K<sub>2</sub>O content of both clinopyroxenes varies systematically from cores to rims (Perchuk et al., 1996; Perchuk & Yapaskurt, 1998).

Microprobe profiles across both clinopyroxenes show complex, but similar changes in potassium Mg/Fe ratio.  $K_2O$  of  $Cpx_1$  decreases toward a rim grain from 1.05 to 0.47 wt. % each (Fig. 1*a*), while that of  $Cpx_2$  is about 0.45 in core and centre of a megacryst reaching zero in the rim of the grain (Fig.1b). The chemical zoning of  $Cpx_1$ provides evidence for its crystallization before garnet under very deep mantle conditions from a liquid (1) that was very rich in potassium (Shimizu, 1974; Harlow, 1997). Since a decrease in T and P,  $Cpx_1$  sharply loosed potassium till 0.45-0.47 wt. % at the moment of crystallization of garnet from a liquid.  $Cpx_2$  has been reacting with liquid that was oversaturated with potassium after the peritectic reaction  $KAlSi_2O_6 + [SiO_2]_{m/fl}$ KAlSi<sub>3</sub>O<sub>8</sub>, i.e. Kid + (silica from liquid) = San (lamellae in  $Cpx_2$ ). The  $Cpx_1$  micro-inclusions were isolated from the ascending liquid by garnet crystals being unable to react with the liquid anymore. The Kfs+Grt+Cpx intergrowth around garnet presumably crystallized at the freezing point. At the final stage of evolution, the rock experienced regional eclogite and then amphibolite facies metamorphism recorded in the (i) formation of the Ep-Kfs

pseudomorphose after  $Cpx_1$ , and (*ii*) Possible Ca $\rightarrow$ Mg substitution in garnet: both resulted from the fluid-rock interaction. Ultrahigh-potassium liquids were found in diamonds from kimberlites (Table 1).

		-				
Table 1. Metal oxides,	water and caronate	e in microincl	lusion-bearing	diamonds (	Nevon et al.,	1988)

	СТР	СТР	СТР	СТР	СТР	СТР	GRR	GRR	GRR	GRR	GRR	GRR	GRR	GRR	GR
Sample	6268	L0	L6	LB	Z4	MM1	1503	1504	1508	861.2	1155	1515	1517	1518	R 151
Morpholog y				Oc	tahedro	ons		Cubes							
Province	Bots- Zair wana							Uncertain source (probably Zair)							
Points	4	5	2	2	3	2	7	8	10	5	10	7	3	2	2
Si0 <sub>2</sub>	31.9	41.2	43.3	34.6	67.7	40.4	35.6	42.3	42.4	51.1	53.6	45.1	30.3	42.4	45.9
TiO <sub>2</sub>	4.2	2.4	2.5	2.1	2	2.9	2.8	2.6	2.7	2.4	4	2.3	3.4	2.9	2.6
$Al_2O_3$	2.9	6.1	5.4	5.6	5.9	4.5	3.3	4.9	4.9	5.4	4.3	4.6	5.3	4.4	4.8
FeO	15.7	5	5.6	4.9	3.3	7.2	8.3	11.1	6.1	6.8	6.6	10.1	5	8	8.8
MgO	5.7	2.8	3.8	2.3	1.3	4.6	6.1	4.6	3.6	5.7	2.6	8	4.3	4.9	4.9
CaO	10.5	10.7	10.6	12.3	1.6	13.9	16.8	7.8	11.9	8.6	7.2	7.6	18.7	9.8	12.4
Na <sub>2</sub> O	2.6	3	2.9	3.5	1	3.8	2.9	2.3	2.4	2.1	1	4.8	2.7	3.4	3.4
K <sub>2</sub> O	21.4	23.7	20.8	29.7	12.3	17.7	18.6	19.4	21.1	11.6	15.5	12.4	25.2	19.3	12.1

O	xides,	1195	433	211	247	1412	107	559	1207	508	80	551	628	22	118	99
pp H <sub>2</sub>	om 2O ,ppm	407	191	118	140	294	165	282	619	269	98	168	241			148
C	O <sub>2</sub> , ppm	600	79	44	66	107	89	292	135	133	67	173	139			44
X	fl * H2O	0.5	0.8	0.8	0.8	0.7	0.6	0.9	0.8	0.7	0.6	0.7	0.8		0.8	0.9

 $* X_{H2O}^{fl} = H_2O/H_2O + CO_2$ , molar fraction.



**Fig.1.** Compositional profiles across  $Cpx_1$  (*a*) from inclusion in garnet and  $Cpx_2$  (*b*) from the matrix clinopyroxene containing *Kfs* lamella from studied *Cpx-Grt* rocks.



**Fig.2.** Schematic non-isobaric *T-X* melting diagram for the

pseudobinary system garnet-potassium-bearing *Cpx*. The diagram was deduced from the microprobe profiling data of Fig.1.

Profiling across  $Cpx_2+Kfs$  has been carried out with defocused beam if the CamScan and Camebax microbes. It is clearly seen that minimum of K in  $Cpx_2$  corresponds to maximum of potassium in  $Cpx_2$ . Points P1 in both diagrams indicate beginning of decrease in pressure and temperature, and appearance of the first grains of  $Cpx_2$ , while points P2 in the diagrams reflect peritectic reaction KAlSi<sub>2</sub>O<sub>6</sub> + [SiO<sub>2</sub>]<sub>m/fl</sub> = KAlSi<sub>3</sub>O<sub>8</sub>, i.e. Kjd + (silica from liquid) = San (lamellae in  $Cpx_2$ ).

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# <sup>#</sup>Fed'kin V.V. Peculiarities of metamorphic evolution in diverse geodynamic zones of the Earth crust

Methods of mineralogical geothermobarometry are widely used to study metamorphic complexes and allow to identify a character of temporal and spatial evolution of physico-chemical conditions of metamorphism. It is known, that rock-forming minerals in metamorphic rocks are able to preserve their composition in the conditions of varying metamorphic parameters. As large grains grow, their composition records the variations of physicochemical conditions of mineral formation on different stages of evolution of a complex, while P-T paths for separate complexes and samples reflect the character of a

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geothermal flow. The geothermal flow is a totality of factors, which are responsible for the grade of metamorphic processes, i.e. fluid flux intensity, availability of weak tectonic permeable zones, background geothermal gradient of a studied portion of the Earth crust, etc. Using this fact and solving the reverse problem, the whole sequence of temporal and spatial changes in metamorphic conditions can be established with data on compositions of coexisting phases. It allows, in turn, to create a geodynamic model for formation of the complex.

From these positions, with using of uniform methods of the physico-chemical analysis of mineral parageneses, detailed microprobe analyses of compositions of coexisting minerals, and mineralogical thermobarometry, three fragments of the Earth crust of different age and geologic position are studied:

1) the Batocina complex (Serbia), which is an ancient, relatively consolidated portion of the continental crust within the basement of the Serbo-Macedonian terrane;

2) the fragment of the oceanic crust of the Balkan peninsular within the ophiolite Dinaridic fold belt, presented by a block of ultramafic rocks of the Bistrica Block and contact aureoles around it; and

3) the eclogite-glaucophane-schist Atbashi complex (South Tien Shan), which is genetically related to an intercontinental trough zone. These complexes underwent different geologic history and have principally different features of metamorphic evolution of rocks.

The volcanogenic-sedimentary Batocina complex is composed of Precambrian and low-Paleozoic sedimentary and magmatic domains of intermediate and high metamorphic grade. They include diverse gneisses with subordinate mica schists, lenses of amphibolites, marbles, and quartzites. An age of the early metamorphism of the Batocina complex is Caledonian (450-550 Ma). However, the final period of the formation of the complex corresponds to middle-upper-Jurassic-lower-Cretacious subduction of the Vardar oceanic plate under the complex The prograde and retrograde character [7]. of metamorphism are recorded in mineral assemblages of the complex. Prograde paths of different depth levels (from t =  $430-530^{\circ}$ C and P = 5-8.2 kbar to t = 620-680°C and P = 9-10 kbar) are recorded in garnet amphibolites, while the later retrograde stage from epidote-amphibolite facies (t = 540-580°C, P = 8-9 kbar) to green-schist facies (t = 340- $420^{\circ}$ C at P = 0.4-1.5 kbar) is found in staurolite and mica schists [5]. The opposite direction of metamorphic processes in the rocks of the single complex is related to different ability of rock-forming minerals to preserve their compositions and record the conditions of mineral formation on the different metamorphic stages. Nevertheless, both paths finally result in the single P-T path of the maximal metamorphic grade, which, in our opinion, reflects the final thermal flow in the post-Mesozoic time.



**Fig. 1**. Relationships between evolution of the Batocina complex (BC) and the Bistrica contact aureole (BUB). 1 - initial metamorphism of the complexes; <math>2 - P-T path of metamorphic evolution of the Batocina complex; 3 - sub-isobaric retrograde paths of the Bistrica Block

The Vardar zone and the Dinaridic ophiolite belt are situated to the west of the Serbo-Macedonian massif and represent relics of an ancient ocean, which existed from the beginning of Paleozoic to upper-Jurassic and lower-Cretacious. Tectonically, the Dinaridic belt is assumed to be the zone of formation of an oceanic basin on the Paleozoic basement of the Balkan Peninsular. Its formation began in lower-Triassic from continuous deepening of the Paleozoic complexes. The subsequent spreading, accompanied by the formation of the ophiolite complexes, continued until the end of Jurassic, when collision of continental blocks resulted in closure of the Vardar basin, while the ophiolite lenses were dismembered and overthrusted on the Paleozoic complexes. The "hot" slabs of ultramafic rocks produced contact aureoles with reverse zoning (i.e. increase of metamorphic grade up the cross section, toward the ultramafic slabs) in the host Paleozoic rocks. As an example of the oceanic crust, the aureole around the ultramafic slab in the Bistrica region was studied. An age of metamorphism of this complex, similar to the whole Dinaridic belt, is Alpine (180 Ma).

In the contact aureoles around the ultramafic bodies in the Bistrica region, prograde metamorphism resulted in formation of Grt-Cpx-Hb-Pl crystalline schists and garnet amphibolites. The prograde zoning, which reflect the initial, the most strong metamorphic stage, was preserved in the central zones of grains of rock-forming minerals. Compositions of rims of coexisting phases (Grt, Cpx, Hb) recorded the retrograde stage with decrease of parameters from t = 740-830°C and P = 8-10 kbar to t = 570-680°C and P = 3.5-7.0 kbar. Finally, the retrograde stage reaches the same parameters (geothermal gradients) as the Batocina complex, but in opposite direction, i.e. from the higher P and T values.

Thus, the both tendencies of evolution of metamorphic parameters of the two terranes, different geologically, i.e. the continental Batocina complex and oceanic Bistrica Block, resulted in the single P-T path on the final (post-Mesozoic) stage. This path reflects the position of the geothermal gradient in the region at that time (Fig.1).

The Atbashi eclogite-glaucophane schist complex is included in the intracontinental Uralz-Tien Shan Hercinian fold belt and is attached to the important tectonic boundary between the Southern Tien Shan and the North Tien Shan. An age of metamorphism in the Atbashi complex is 320-360 Ma [1], although there are some older dates, 1100 and 520-550 Ma. The glaucophane belts are suggested to be ancient analogies of "Benioff zones", which confine the ancient oceanic crust. However, attempts to reconstruct the ancient ocean in this area are not persuasive, for they are related to large horizontal motions of huge platforms, Russian, Siberian, Sino-Korean, etc. The most probable hypothesis is that the system of relatively narrow troughs with oceanic crust (of Red Sea type) existed in the region, whereas glaucophane-schist belt marked the boundary of the troughs on the stage of their compression ("subduction") [2].



**Fig. 2.** Evolution of P-T parameters of metamorphism for the Atbashi complex (South Tien Shan), reconstructed with using of mineralogical geothermobarometry (generalized data) of eclogites and Grt-Cpx crystalline schists (1), Grt-Gl assemblages (2), and Grt-Chl diaphthorites (3).

Such geologic position of the complex conditioned the specifics of its metamorphism, whose high-pressure prograde paths coincided with the geothermal gradient of  $\sim 10^{\circ}/\text{km}.$ The Atbashi complex consists of diaphthoresized eclogites, diverse Grt-Gl, chloritecarbonate, and zoisite rocks, quartz schists, and greendiaphthorites [3]. Complex petrographic schist relationships in this mixed complex and reaction relations between minerals correspond to multi-stage nonisochemical metamorphism, complicated with processes of Mg-Ca metasomatism and quartzitization (on the stage of acidic leaching). The gradual transition from eclogites to Grt-Gl rocks, quartz schists, and chlorite diaphthorite is reflected in P-T paths of formation of corresponding mineral assemblages. The most high-pressure and hightemperature paths are recorded in Grt-Cpx rocks and eclogites, intermediate paths characterize Grt-Gl assemblages, whereas Grt-Chl-Mu assemblages and carbonate equilibria show the most low-pressure and relatively low-temperature parameters (down to t = 250- $300^{\circ}$ C at P = 0.3-1.8 kbar). The strongest Mgmetasomatism appreciably changed compositions of coexisting minerals. So, in the conditions of low temperatures of the retrograde stage and diaphthoresis, an equilibrium between coexisting phases, apparently, was not reached in some cases. As a result, compositions of silicates in most cases preserved just traces of the hightemperature prograde metamorphism. Only displacement

of P-T paths for mineral assemblages and rare retrograde paths allow to reconstruct the whole metamorphic evolution of the complex (Fig. 2).

These are "clock-wise" P-T paths with low (~ $10^{\circ}$ /km) geothermal gradient and maximal parameters of t = 650-700°C at P = 14-15 kbar for Grt-Cpx rocks and eclogites and t = 550-580°C at P = 9-11 kbar for glaucophane schists. Such a path is typical for intercontinental sutures. The minimal parameters for the Atbashi complex are within the low green-schist facies, i.e. from t = 550-570°C at P = 3.5-5.0 kbar to t = 350-400°C at P = 0.5-1.8 kbar. These parameters are recorded in chlorite-carbonate rocks, muscovite-quartz schists, Chl schists, and quartzites.

Comparing the physico-chemical conditions of metamorphism of the complexes formed in different geodynamic environments, i.e. in the fold basement of the continental crust, in the high-gradient conditions of its oceanic fragments, in the interactive continental zones of the troughs type, and in the Precambrian shields, we concluded, that metamorphism within the main geologic types of the crust is appreciably different not only in its grade (P-T parameters and fluid regime), but also in evolutionary direction of the parameters as well as in thermal flow of the ancient geologic periods (Fig. 3).



Fig.3. Evolution of physico-chemical conditions metamorphism of the complexes from different geodynamic fragments of the Earth crust: 1-2 - prograde-retrograde paths for fold fragments of the continental basement (2) and its trough zones (1), 3 - fragments of the oceanic crust, 4 - Precambrian shields, 5 - fragment of the final stages of metamorphism. Complexes: ALD – granulites of the Aldan shield [8], ATB – the Atbashi eclogite-glaucophane-schist complex, South Tien Shan, BC - the Batocina vulcanogenic-sedimentary complex, the Serbo-Macedonian massif (Serbia), BUB - the contact aureole around the ultramafic block in the Bistrica region, ophiolite Dinaridic belt (Serbia), NP - Bortshitskaya Series, North Pamirs [4], UKR - granulite complex of the Western portion of the Ukrainian shield [6].

### Bondarenko G.V. and Gorbaty Yu.E. A Raman study of hydrothermal electrolyte solutions.

Using a new high-pressure high-temperature Raman cell, experiments have been performed aimed at the understanding of the effect of various ions on the structure of supercritical aqueous solutions. Another goal was to test the performance of a new cell specially designed to study supercritical electrolyte water solutions. It was interesting at the initial stage of the experimental work to obtain Raman spectra of solutions with the multiatomic anion like

 $[NO_3]$  revealing strong lines in the Raman spectra. The spectra of ca. 5 mol. % NaNO<sub>3</sub> and Zn(NO<sub>3</sub>)<sub>2</sub> in water were obtained at a constant pressure of 1000 bar and temperatures, correspondingly, up to 300 and 400°C. At supercritical temperature of 400°C the spectrum of Zn(NO<sub>3</sub>)<sub>2</sub> became very weak and at the further temperature rise it disappeared completely. In the spectrum obtained at 400°C a new band near 1860 cm<sup>-1</sup> may be observed that can be attributed to NO molecule.

So, it may be guessed that  $[NO_3]$  anion becomes unstable at supercritical temperature. Fig.1 demonstrates the spectra of  $Zn(NO_3)_2$  solution.

The most intensive lines in spectra belong to  $NO_3^$ anion and H<sub>2</sub>O. At room temperature the spectra of NaNO<sub>3</sub> and Zn(NO<sub>3</sub>)<sub>2</sub> solutions are much alike. However, an essential difference is observed as temperature increases, especially in the region of the bending vibrational mode v<sub>4</sub> (1200–1600cm<sup>-1</sup>). In general, if the flat four-atomic molecule [NO<sub>3</sub>] is perfectly symmetric, only one spectral band should be observed in this region due to the degeneration of vibrational levels.



Fig.1. Raman spectra of the aqueous solution of  $Zn(NO_3)_2$ 

However, if the molecular configuration gets distorted the band splits into two bands. At room temperature weak distortion of symmetry is observed for both solutions. As temperature increases, the shape of  $v_4$  band spectra of the NaNO<sub>3</sub> solution remains unchanged at least up to 300°C, while in the spectra of  $Zn(NO_3)_2$  the separation between two components of the band grows rapidly. Moreover, it seems that in the case of  $Zn(NO_3)_2$  this spectral region contains two overlapping doublets. We can guess that the reason for such a strange behavior is the phenomenon of "ion pairing". At high temperatures the probability of  $Zn^{2+}[NO_3]^{-}$  pair increases resulting in strong deformation of the anion. As may be assumed, pairing of the anion with

the  $Na^+$  cation does not change the symmetry of the  $NO_3^-$  anion or the pairing phenomenon is more weak in this case.

These are just preliminary results. The study is in progress and we hope to obtain more interesting data in due course. In particular, the drastic changes in the shape of stretching band of  $H_2O$  are certainly very important and worth studying.

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## Okhulkov A.V. and Gorbaty Yu.E. An X-ray study of NaCl aqueous solution up to 500°C at a constant pressure of 1000 bar.

The structure factor and pair correlation functions have been obtained for the 1.1 M NaCl aqueous solution at temperatures up to 500°C and at a constant pressure of 1000 bar with the energy-dispersive x-ray diffraction technique. The same data have been also obtained for the 0, 0.55, 1.1, and 2.2 M solutions in water at ambient conditions.

Fig. 1 shows the pair correlation functions g(r) of liquid water and 0.55 M, 1,1 M, and 2.2 M solutions of NaCl in water. One can see that dissolving NaCl in water causes essential changes in the pair correlation functions. The dramatic decreasing of the peak at 2.8 Å at increasing concentration of  $Na^{T}$  and  $Cl^{T}$  ions evidences destroying of hydrogen bonds in water. At 2.2 M concentration of NaCl the peak turns into a shoulder of the next peak at  $\sim 3.3$  Å. It is not surprising inasmuch as nearly half of water molecules form hydration shells around the ions at such a high concentration. The increasing correlation at ~3.3 Å is also a result of the growing amount of non-bonded molecules. However, the Cl-O pairs should also reveal in this range of r (~3.15 Å [1,14]). Most likely, the growth of the shoulder that at maximal concentration of NaCl turns into the most prominent peak is a combined result of these two factors.



**Fig.1**. The pair correlation functions of NaCl aqueous solutions with different concentrations. **Fig.2**. The effect of temperature on the pair correlation function of 1.1 M NaCl solution

The pair correlation functions of 1.1 M NaCl water solution obtained at isobaric heating up to 500°C are shown in Fig. 2. The temperature effect on the structure of the solution resembles to some extent the effect of concentration. The peak at ~2.8 Å decreases, while the correlation at 3.3 Å grows with the temperature rise. However, an essential difference between the effects of concentration and temperature can be easily noticed. The peak at about 4.5 Å that is resulted from the tetrahedral nearest ordering decreases rapidly as temperature grows. So, redistribution of correlation between the peaks 2.8 Å and 3.2 Å is most likely a result of the reducing probability of hydrogen bonding.

It has been found that the peak at 4.5 Å in pure water practically disappears near the critical isotherm at isobaric heating. Surprisingly, at higher temperatures the peak begins to grow again despite the fact that the degree of hydrogen bonding at 500°C is very low (on the average 0.7 H-bond per molecule). This remarkable phenomenon gave rise to the concept of *preferential structure fluctuations* that predicts short-living clusters of hydrogenbonded molecules to arise in some parts of the system while in other parts no at all hydrogen bonds occur.

It is clearly seen in Fig. 2 that the peak at 4.5 Å in the pair correlation functions of the NaCl solution shows a similar behavior. It practically disappears at 300°C. However, it arises again at 400 and 500°C. This means that in the spaces between coordination shells of ions water molecules behave exactly in the same way as in pure water, that is to say, we can expect short living clusters of hydrogen bonded molecules along with non-bonded molecules alternatively and quickly replacing each other.

## <sup>#</sup>Suk N.I. Experimental study on silicatecarbonate systems with phosphorus and chlorine.

The paper presents the results of the experimental study of liquid layering in carbonate-silicate systems at  $T=1250^{\circ}C$  and P=2 kbar as well as of phosphorus-

carbonate-silicate and chlorine-carbonate-silicate systems. The character of partitioning of some ore elements (REE, Nb, Ta) between immiscibile phases was also the matter of discussion.

Experiments were carried out in sealed platinum capsules 3 mm in dia using a high gas pressure apparatus. The duration was 6 hrs with subsequent quenching. Starting charge was prepared from natural minerals (albite and diopside) with addition of alcaline carbonate (Na<sub>2</sub>CO<sub>3</sub>) or its mixture with kalcite (Na<sub>2</sub>CO<sub>3</sub>+CaCO<sub>3</sub>). In some experiments chloride (NaCl) or phosphorus-salt (NaPO<sub>3</sub>) were added.

Ore components were introduced into the system by adding the following oxides:  $La_2O_3$ ,  $Ce_2O_3$ ,  $Y_2O_3$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ . The samples obtained were analyzed on an X-ray microanalyzer "Camabax" with energy dispersion attachment "Link".

At the above parameters (T= $1250^{\circ}$ C and P=2 kbar) the starting silicate-carbonate melts has been observed to split into two liquids- silicate and carbonate throughout a wide interval.

The silicate phaase was a homogeneous glass, either carbonate drops in a silicate matrix and silicate drops in a carbonate matrix being observed. Phase boundaries between melts were clearly shown up.

The study on the partitioning of REE (La, Ge, Y), Nb, Ta between immiscible silicate and carbonate liquids showed them to preferentially concentrate in a silicate melt. The coefficients of the REE partitioning between layered phases ( $K=C^{REE}_{carb}/C^{REE}_{sil}$ ) are below 1.

The effect of phosphorus on the silicate-carbonate layering and REE partitioning between immiscible phases is well illustrated by the results of our experiments at 1250°C and 2 kbar with addition of phosphorus salt NaPO<sub>3</sub> to the studied silicate-carbonate system (8 and 15wt%) which corresponds to 5.6 and 10.4 wt%  $P_2O_5$ ). The salt phase in the studied systems is of phosphorus-carbonate composition. Herewith, the coefficient of REE partitioning between immiscible phases was found to increase with the addition to the system of phosphorus. In alkaline systems REE were even for the most part extracted by a salt melt (K > 1). With increasing phosphorus content in starting melts there appears inhomogeinety i.e. isolations of carbonate and phosphate composition within the salt phase. The phosphate phase is more effective in concentrating REE than carbonate one and gets enriched in these elements. Thus the experiments showed that the presence of phosphorus has a positive effect on the

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extration of REE by salt melts in the systems studied. The effect of chlorine on the silicate-carbonate partitioning has been studied at T=1100oC and P=2 kbar with addition to the system of chloride (NaCl). The isolation of carbonatechloride melt from the silicate ones was observed in the chloride-carbonate-silicate systems. The salt phase forms a layer in the upper part of the sample and drops in a silicate melt. The salt liquid is inhomogeneous in composition and dissociates into chloride (NaCl with admixture of Ca and Mg) and carbonate liquids. The salt phase is depleted in REE, Nb and Ta which concentrate in a silicate melt. However, some increase in REE concentration in carbonate phases as compared to chloride ones was noted. Thus, the presence of chlorine has no positive effect on the extration of ore elements by the salt melts. On the contrary, the addition of chlorine to the alkaline systems at 1100°C leads to the depletion of salt liquids in REE which remain in a silicate melt whereas in pure silicate-carbonate systems they were found to be extracted by carbonate liquids.

# Chichagov A.V., Varlamov D.A., Dokina T.N., Drozhzhina N.A., Samokhvalova O.L., Ushakovskaya T.V. Myncryst-universal information-calculating system on crystal structure data for minerals.

In 1999 the development of Mincryst has been continued in the following directions:

1. The Information Fund has been permanently supplemented and by January 2000 contains 4.7 thousand records in the Crystal Structure Database.

2. The work concerned with search and correction of Mincryst Database errors has been continued, the records of the local Mincryst version have been brought in complete conformity with those of the Internet version.

3. Mincryst WWW-version.

Mincryst Database format has been widen which allows to display crystal structure model and polycrystal xray diffraction patterns ( x-ray line diagrams) using Javaapplets. The Java-applets enable transmitting the crystal structure model image and the X-ray diffraction powder Line-Diagram image from the Server to the Client PC at a rate of the text information translation and provides the work in interactive regime. In particular, continuous and discrete rotation of the crystal structure model is possible as well as changing the vertical and horizontal scales of line diagram (O, 2O, and d(hkl)) and determination of hklindexes of reflexes. So, at present the crystal structure information on minerals is available both as text files and graphic images of crystal structure models and polycrystal x-ray patterns and the first on-line operations with the above models in Internet are possible.

Mincryst has been registered in Database State Register of Scientific-technical centre "Informregistr" (WWW-version N 0229805169, certificate No 4873, of 11.02.99, Local version N 0229805170, certificate No 4874, of 11.02.99).

At present free on-line access to MINCRYST is provided. URL-reference of MINCRYST: http://database.iem.ac.ru/mincryst

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