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Magmatic systems, fluid-magmatic interaction melts properties

[#]Litvin Yu.A., Matveev Yu.A. Experimental studies of carbonate – silicate melting relations in the $K_2Ca(CO_3)_2$ – diopside – pyrope at 3.8 GPa in connection with genesis of Kokchetav diamond – bearing rocks

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Experimental studies of melting relations of the carbonate – silicate system $K_2Ca(CO_3)_2$ – diopside $CaMgSi_2O_6$ – pyrope $Mg_3Al_2Si_3O_{12}$ were carried out at 3.8 GPa to explore the version that diamonds of Kokchetav metamorphic complex (Kazakhstan) have magmatic origin. The version is based on the findings of diamond – bearing carbonate – silicate rocks composed of dolomite, potassium – rich clinopyroxene and pyrope – grossular garnet [1, 2]. Additional arguments were deduced from high-pressure synthesis of potassium – rich clinopyroxenes in K_2CO_3 – diopside mixtures[3] and $K_2Mg(CO_3)_2$ – $CaSiO_3$ – Al_2O_3 system [4], discovery of potassium – rich fluid - carbonatitic inclusions in Kokchetav diamonds [5], and experimental crystallization of diamonds in multicomponent carbonatitic melts of natural compositions [6]. It was shown that $K_2Ca(CO_3)_2$ composition is most representative of primary fluid inclusions in natural diamonds [7] and effective as a medium for diamond crystallization in melted state [8].

The studies of melting relations of the $K_2Ca(CO_3)_2$ – diopside - pyrope system were carried out in the $K_2Ca(CO_3)_2$ - diopside$_{50}$ pyrope$_{50}$ and $Di_{85}[K_2Ca(CO_3)_2]_{15}$ – $Py_{85}[K_2Ca(CO_3)_2]_{15}$ joins at 3.8 GPa. For the $K_2Ca(CO_3)_2$ – $[CaMgSi_2O_6]_{50}[Mg_3Al_2Si_3O_{12}]_{50}$ join, complete melting was found to occur in the 1200 – 1600°C temperature interval at 3.8 GPa. In the course of quenchimg, the melts form intermitent accretions of phlogopite, montichellite and carbonates. Diopside as a liquidus phase appears at 1200 ° C. No evidence of the effect of carbonate – silicate liquid immiscibility was recognized. For the $Di_{85}[K_2Ca(CO_3)_2]_{15}$ – $Py_{85}[K_2Ca(CO_3)_2]_{15}$ join, garnet of $Mg_{2.0\text{-}1.0}Ca_{1.0\text{-}2.0}Al_2Si_3O_{12}$ composition and clinopyroxene of diopside composition (K_2O content is negligibly small) are formed as liquidus phases at 1200°C. Subsolidus assembly is represented by clinopyroxene, garnet and carbonates.

Taking into account that diamonds crystallize in K-Ca-carbonate melts oversaturated with carbon, it can be seen that the natural diamond – bearing carbonate – silicate assembly is reproducible in high-pressure experiment. This provides new essential grounding in the magmatic version of diamond genesis in Kokchetav – type deposits, the complete geological history of which was influenced by scale processes of the mantle dynamics.

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[#]Litvin Yu.A., Zharikov V.A. Experimental modeling of diamond genesis in multicomponent carbonate – silicate melts (analogous to the primary fluid inclusions)

The question of chemical nature of diamond – producing substratum has been the object of much concentrated attention in the problem of diamond genesis. The data are necessary for experimental recreation of the process of diamond formation in the Earth's mantle as well. Native chemical media in which diamonds crystallized were trapped by them as submicroscopic fluid inclusions. At room temperature these inclusions are heterogeneous mixtures of gaseous CO_2 , liquid H_2O and solid carbonates, silicates, quartz and apatite compressed at 1.5 – 2.1 GPa [1]. Under heating to 1000 – 1300°C (as at the mantle depth 150 – 250 kilometer), pressure inside the inclusions increases to 4 – 7 GPa [2] revealing that the inclusions were trapped at pressures and temperatures associated with the PT – field of diamond stability on the carbon phase diagram. Under these conditions, the heterogeneous substance of the inclusions turns into carbonate – silicate melt which presents a strongly compressed parental medium for diamond growth [2], probably, with properties of deep – mantle carbonatitic magma. Chemical compositions of fluid inclusions are variable in the context of the multicomponent system K_2O – Na_2O– CaO – FeO – MgO – Al_2O_3 – Fe_2O_3 – TiO_2 – SiO_2 – P_2O_5 – CO_2 – H_2O – Cl [2]. It was detected that chemical compositions of fluid inclusions in diamonds may be expressed in terms of two model end members – essentially carbonatitic (K_2O 20.7, Na_2O 2.2, CaO 20.5, MgO 13.2, FeO 19.5, Al_2O_3 0.8, TiO_2 4.6, P_2O_5 2.4, Cl 0.5, wt. %, which is combined with 90 mol.% CO_2 and 10 mol.% H_2O presented

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in the inclusions) and hydro-silicic (K_2O 12.3, Na_2O 0.7, CaO 0.0, MgO 3,3, FeO 7,6, Al_2O_3 6,8, TiO_2 4.3, P_2O_5 0.7, Cl 0.9, SiO_2 58,4 wt.% combined with 10 mol.% CO_2 and 90 mol.% H_2O, correspondingly). This approximation of the fluid inclusion compositions is applicable to the compositions of the carbonate – silicate melts parental for diamond growth and representative as a variable ratio of carbonatitic and silicate (alkali-basaltic) constituents.

The multicomponent system K_2O – Na_2O – CaO – FeO – MgO – SiO_2 – CO_2 - H_2O may represent the closest approach to the compositions of the primary fluid inclusions in natural diamonds. A crucially important for the problem of diamond genesis experiments at 7 – 9 GPa were executed in the system K_2O – Na_2O - CaO – FeO – MgO – CO_2 – C [3] simulating by major components the carbonatitic endmember used for the approximation of the real compositions of fluid inclusions in diamonds by [2]. The objective of this work is the experimental simulating of diamond genesis in multicomponent systems restoring the real compositions of primary fluid inclusions in natural diamonds. The fluid compositions represent essential concentrations of silicate constituents. Data for the compositions of fluid inclusions in natural diamonds from Jwaneng, Botswana [2] were used as the prototypes for experimental compositions. High pressure experiments have been carried out with an “anvil-with-hole” apparatus operating under the action of hydraulic press. Pure graphite sleeves were used as the resistance heaters and capsules (closed with graphite end plugs) simultaneously. Multicomponent starting materials for the experiments (Table) were prepared based on the data for fluid inclusions in the samples JWN 90, JWN91, JWN108 of natural fibrous diamonds from Jwaneng, Botswana, and the model carbonatitic endmember used together with hydrous end-member for approximation of the real fluid compositions [2]. Content of SiO_2 in the natural and experimental compositions varies between 13.6 and 45.1 wt.% showing essential contribution of silicate (alkali – basaltic) constituents. Experimental starting materials were homogeneous mechanical mixtures of high-purity graphite and K, Na, Ca, Mg, Fe carbonates, SiO_2, TiO_2, Al_2O_3, $K_4P_2O_7$, and NaCl. Graphite and carbonate powders were mixed in 1 : 1 weight ratio.

Table. Compositions (wt%) of the starting materials and their natural prototypes

Component	JWN108	JWN90	JWN91	Boundary carbonatite
	Fluid inclusions – prototypes*			
SiO_2	23.9	25.1	45.1	13.6
TiO_2	4.6	4.7	4.9	4.6
Al_2O	2.5	2.5	5.4	0.8
FeO	15.2	16.1	10.7	19.5
MgO	10.9	10.1	5.7	13.2
CaO	13.5	15.6	5.1	20.5
Na_2O	2.2	2.6	1.6	2.2
K_2O	22.2	18.3	16.4	20.7
P_2O_5	2.3	2.4	1.0	2.4
Cl	1.5	1.3	0.8	1.3
Sum	98.8	98.7	96.7	98.8
Experimental compositions**				
SiO_2	23.9	25.1	45.1	13.6
TiO_2	4.4	4.7	4.9	4.6
Al_2O_3	2.5	2.5	5.4	0.8
$FeCO_3$	24.5	25.96	17.4	31.44
$MgCO_3$	22.8	21.18	11..9	27.6
$CaCO_3$	24.1	27.86	9.1	36.6
Na_2CO_3	1.7	1.45	1.6	0.7
K_2CO_3	32.6	26.85	24.1	30.4
$K_4P_2O_7$	5.4	5.6	2.3	5.6
NaCl	1.2	2.1	1.3	2.1

* Oversaturated with CO_2.

** Primary ratio of prototype components is conserved.

High – pressure experiments on diamond crystallization in multicomponent systems which reproduce chemical compositions of the primary fluid inclusions in natural diamonds were carried out at pressures 5 – 7 GPa and temperatures 1200 – 1600^{o}C corresponding to the PT – conditions of diamond stability. Studies of the experimental samples and diamonds synthesized were performed by scaning electron microscopy (SEM) and microprobe analyses with the use of CamScan electron microscope. Figs. 1- 4 depicts experimental samples showing newly formed diamonds in situ in carbonatitic substance (quenched carbonatitic melts) for the conditions of spontaneous nucleation.

Experimental re-creation of diamond crystallization in natural parental media gives physico – chemical insight into the mechanism of diamond nucleation and growth in the mantle conditilons. The results of high – pressure experiments on diamond crystallization in the melts of multicomponent carbonate – silicate systems offer a clearer view of how natural diamonds have formed and give the preference to the carbonatitic version of diamond genesis in the Earth’s mantle. The version is supported by the recent discovery of diamond – bearing magmatic carbonatites of Chagatai Complex, Uzbekistan [5].

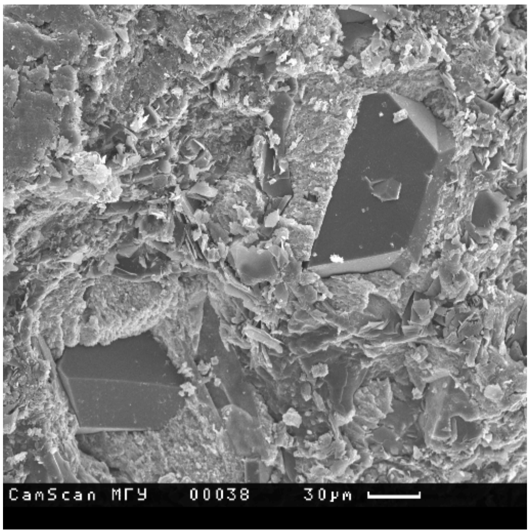

Fig. 1. Sample # 475. JWN108 composition. 5.5 GPa. 1250°C.

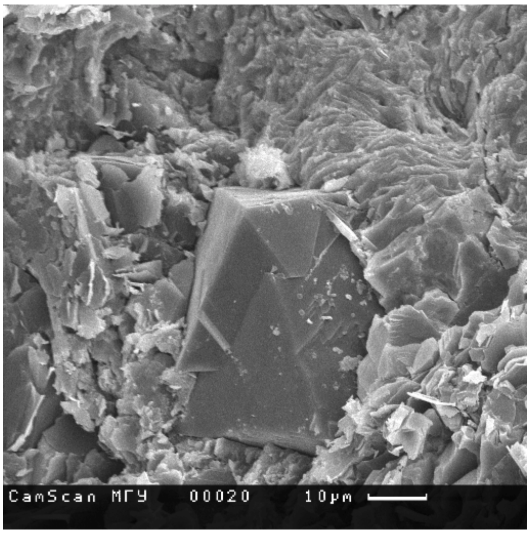

Fig. 2. Sample # 461. JWN90 composition. 5.5 GPa. 1380°C.

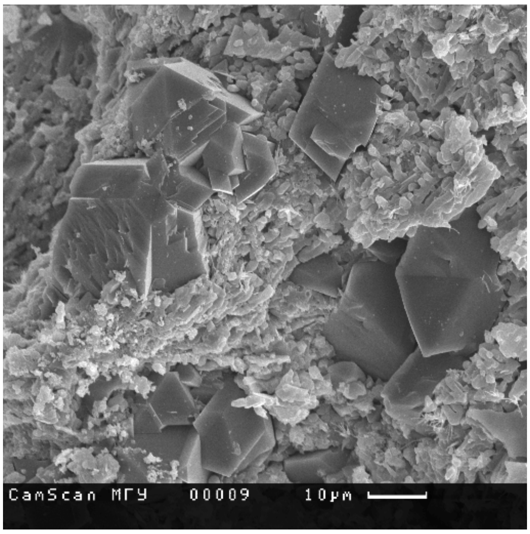

Fig. 3. Sample # 455. JWN9 composition. 6.0 GPa. 1340°C.

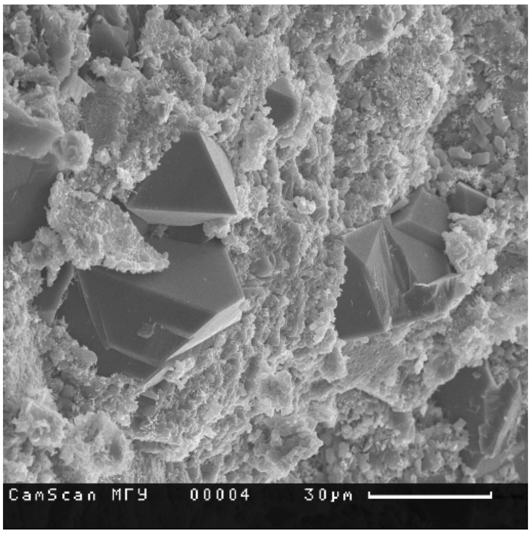

Fig. 4. Sample # 497. Boundary carbonatite composition. 5.75 GPa. 1220°C.

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#Zavel'skii V.O.[1], Salova T.P.[2] Influence of aluminum on an interaction of water with silicate melt (NMR spectroscopy)

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key words [*NMR spectroscopy, water, glass, macrocluster, structure*]

Preliminary experiments on the study of state of water dissolved in aluminosilicate glass were carried out by the method of NMR.

The NMR spectra of all studied aluminosilicate glasses of different aluminum and water content, as well as of different technology of sample preparation, show two characteristic features, which are absent in pure quartz glasses:

1) presence of a narrow (~ 1 kHz) peak, which has more delicate structure at detailed observations (Fig. 1);

2) appearance in the spectrum of an additional extra-wide component, which is more distinct at low temperatures (T ≤ 150 K) (Fig. 2).

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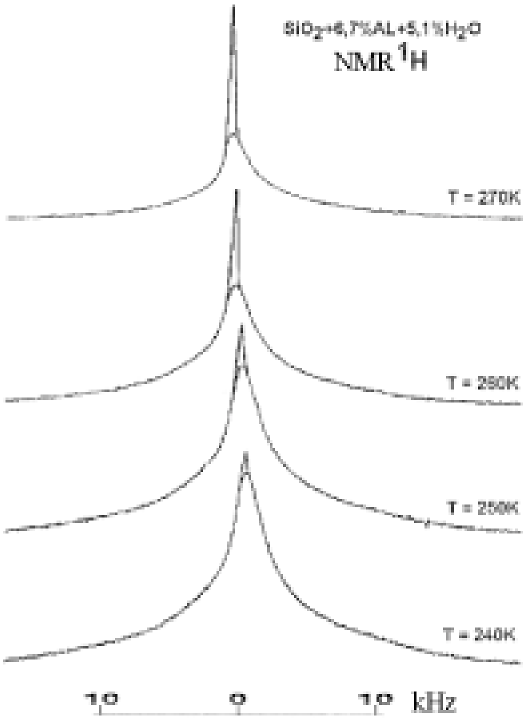

Fig.1. The NMR spectrum of water-bearing aluminosilicate glass at different temperatures.

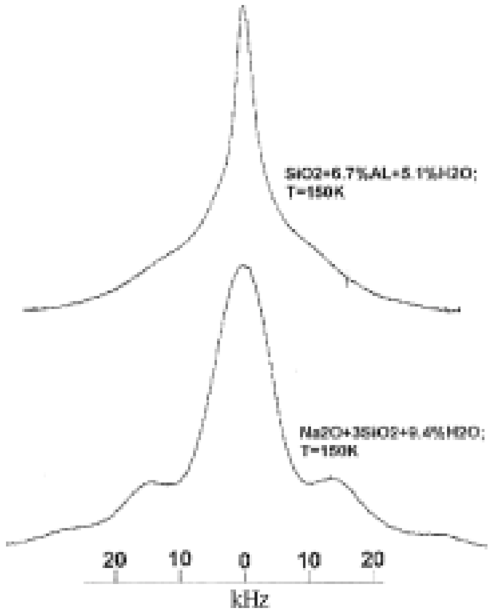

Fig.2. The NMR spectrum of water-bearing aluminosilicate and sodium silicate glasses at 150 K.

Thus, it is found experimentally, that addition of some aluminum into quartz glass causes appearance of two additional peaks in its NMR spectra.

It should be noted, that one of the studied water-bearing quartz glass samples showed the narrow peak, and it was predominant in the spectrum. However, it did not show the fine structure [1]. The sample was prepared at exposition t = 1 hour, that corresponds to the earlier stage of fluid incorporation into melt.

Unfortunately, quantitative calculations of an integration intensity of the narrow peak with respect to other components of the spectrum is impossible by now. However, qualitative regularities in the spectra are distinct.

The narrow peak is very sensitive to the method of sample preparation: its intensity is large if the sample is prepared at T = 1200°C and P = 2 kbar, and decreases by several times at T = 1300°C and P = 4 kbar. An increase of intensity of the narrow peak is observed also at an increase of water content in aluminosilicate glass. The thermal behavior of the narrow peak is characterized by an abrupt hysteresis. The peak exists up to T ~ 240 K (intensity decreases with temperature decrease), whereas it appears by leap at T ~ 275 K. In contrast to quartz glass, where the narrow peak is a singlet, this line is more complex in the proton magnetic resonance spectrum of aluminosilicate (Fig. 3). Refinement of contours by the GRAMS program shows, that the best fit for the line is a superposition of three Gauss-Lorenz curves.

The obtained experimental data allow to assume, that the narrow peak in the NMR spectra of the studied aluminosilicate glasses is formed by water macroclusters, consisting of several hundreds of H_2O molecules. The gradual decrease of its intensity with decrease of temperature could be, apparently, explained by distribution of the macroclusters within the sample: the smaller macrocluster the lower temperature of water freezing in it.

Presence of a chemical shift between the narrow component and the ordinary peak and between the narrow shift itself should be noted. The possible reason for it is changing of a structure of an amorphous material on the interface water-glass caused by incorporation of aluminum. In this case, H_2O molecules of the macrocluster interact with all three types of atoms in glass, i.e. sodium, aluminum, and oxygen. It is not excluded, that the same reason is responsible for displacement of the peak to the weak field with respect to the hydroxyl lines.

Thermal behavior of the narrow peak is different in a pure quartz glass. It exists without changes up to T ~ 240 K upon cooling the sample and appears by leap upon T ~ 275 K at heating. Apparently, there is no distribution of macroclusters by size in this case. Such difference implies different mechanisms of water dissolution in quartz and aluminosilicate glasses.

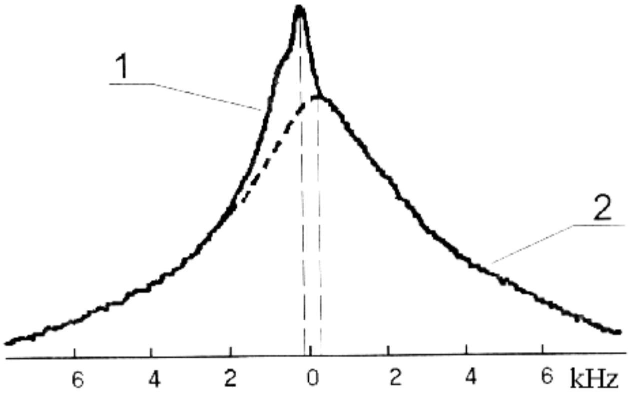

Fig.3. The central portion of the NMR spectrum of water-bearing aluminosilicate glass at 250 K. 1 – peak of water macrocluster; 2 – peak of OH-group.

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[#]Suk N.I. Experimental study of phosphorus and chlorine influence on the silicate-carbonate immiscibility and distribution of some rare and rare earth elements

The possible role of liquid immiscibility in the genesis of carbonatites and associated rocks was discussed by previous authors [1, 2, 3]. Geochemical data estimate the presence of apatite, suphides, phlogopite and other minerals in carbonatites. More over, in massif Tomtor, for an example, there were observed the apatite-carbonate eruptive dykes or tubes and tuff-lavas of phosphate composition [4]. This fact confirms the supplementary fluid components (such as phosphorus and, probably, halogenides) enrichment in latter carbonatites. So, the experimental study of the effect of phosphorus and chlorine on silicate-carbonate immiscibility and behaviour of ore elements in such immiscible systems is an actual problem.

The results of experimental study of liquid immiscibility in carbonate-silicate systems at T=1250°C and P=2 kbar and in phosphate-carbonate-silicate and chloride-carbonate-silicate systems are presented in this paper. The main attention has been paid to the study of distribution of some ore elements (REE, Nb, Ta) between immiscible phases.

The experiments were carried out in a high gas-pressure vessel in sealed platinum capsules (d=3 mm) during 6 h with subsequent quenching. Starting mixtures were prepared from the mixtures of rock-forming minerals (albite, diopside) and the compositions of carbonate model melts were determined by Na_2CO_3 or mixtures of Na_2CO_3 and $CaCO_3$. Phosphorus and chlorine in some special experiments were added as $NaPO_3$ and NaCl respectively. Ore elements were added as La_2O_3, CeO_2, Y_2O_3, Nb_2O_5, Ta_2O_5. The samples obtained were analized on a Camebax microprobe equipment with a Link H.E.D.A. system.

A wide region of layering of the initial melts into two liquids - silicate and carbonate ones was revealed. The carbonate drops in silicate matrix and the silicate drops in carbonate matrix were observed in the samples obtained. There are distinct phase boundaries between both phases.

The study of distribution of REE (La, Ce, Y), Nb, Ta between immiscible silicate and carbonate liquids shows their concentration by silicate melt. The partition coefficients for REE between layering phases ($K=C^{REE}_{carb.}/C^{REE}_{sil.}$) are presented in Fig. They are less than 1. The results obtained and our previous data [5, 6] reveal the dependence of the coefficient of distribution of rare earth elements on temperature: an increase of temperature to 1250°C results in the redistribution of REE in favor of the silicate phase.

The phosphorus influence on the silicate-carbonate layering and distribution of REE between immiscible phases has been well illustrated by the results of our experiments carried out at T=1250°C and P=2 kbar with the addition of $NaPO_3$ (8 and 15 mas.% , which correspond to 5.6 and 10.4 mas.% P_2O_5 respectively). In the studied region of compositions the phosphorus addition does not effect the width of immiscible field in silicate-carbonate systems. But some increase of composition contrast of coexisting phases is likely to be estimated. Salt phase in the studied systems has a phosphate-carbonate composition. An increase of coefficient of distribution of REE between immiscible phases is observed (Fig.), and in alkaline systems they predominantly accumulate in salt melt (K>1). With an increase of phosphorus content in initial melts the salt phase obtained was established to be inhomogeneous and contains the constituents of carbonate and phosphate compositions. The phosphate phase is more effective in concentrating REE than carbonate one, and enriched in these elements. So, our experiments show the positive effect of phosphorus addition on the extraction of rare earth elements by salt melts in the studied systems.

Chlorine influence on the silicate-carbonate layering has been studied at T=1100°C and P=2 kbar with the addition of chloride (NaCl) to the system. In chloride-carbonate-silicate systems the separation of chloride-carbonate melts from the silicate ones is observed. Salt phase occured as a layer in the upper part of the sample or as drops in a silicate melt. Salt liquid is inhomogeneous phase and divided into chloride (NaCl with addition of Ca and Mg) and carbonate phases. Salt phase is depleted in rare earth elements, Nb and Ta, which concentrate in silicate melt. But it is observed that carbonate phase is richer in REE as compared with chloride phase. So, the presence of chlorine does not effect positively the extraction of ore elements by salt melts. On the contrary, in alkaline systems at T=1100°C addition of chlorine promotes a decrease of REE concentration in salt liquids, and REE accumulate in silicate melts. But in pure silicate-carbonate systems according to our previous investigations REE concentrate in carbonate liquids.

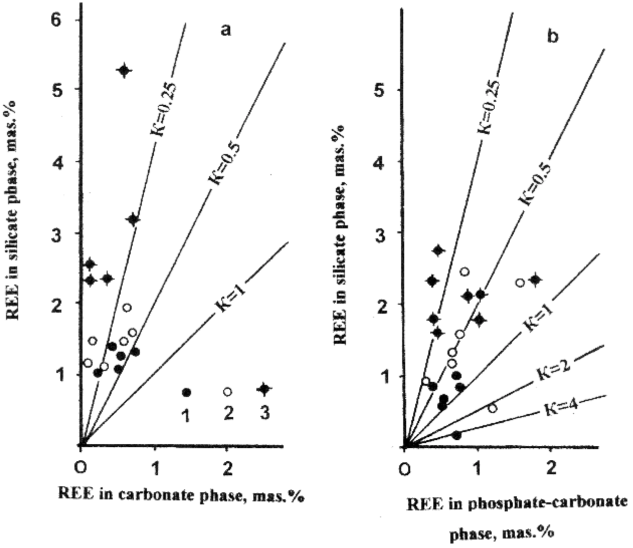

Fig. Coefficients of distribution of rare earth elements between silicate and carbonate melts (a) and between silicate and salt (phosphate-carbonate) melts at T=1250°C and P=2 kbar. 1 - La_2O_3; 2 - Ce_2O_3; 3 - Y_2O_3.

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Lukanin O.A.,[1] Rusakov V.S.[2], Kotelnikova A.A.[2], Kadik A.A.[1] Pressure effect on the Fe^{3+}/Fe^{2+} ratio in basaltic melt (experimental data).

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Using Mössbauer spectroscopy technique, Fe^{3+}/Fe^{2+} ratios and structural positions of ferrous and ferric iron atoms were determined in basaltic glasses synthetised by quenching natural basalt melts at high hydrostatic pressure conditions (P = 0,16-5 kbar, T = 1250 -1350°C). The experiments were conducted in high-pressure vessel with internal heater, in which argon was pressure transmiting medium. The samples of basaltic glasses with various initial ferrous/ferric ratios ($Fe^{3+}/(Fe^{2+} + Fe^{3+})$ = 0,8 - 0,12) were placed in sealed platinum capsules and maintained at given PT parameters from 11 to 130 minutes. Treatment and analysis of Mössbauer spectra of quench glasses were conducted by recovery of two independent distribution functions of hyperfine interactions parameters of the ^{57}Fe nuclei - isomeric shift and quadrupole splitting.

The pressure increase up to 5 kbar does not result in noticeable change in redox state of iron in melts (glasses) after “short” experiments (11-20 minutes duration) at constant temperature. The ratio Fe^{3+}/Fe^{2+} in glasses after these runs corresponds to value Fe^{3+}/Fe^{2+} in initial basaltic melt in error limits. At the same time it is shown, that about 30 % Fe^{3+} is reduced to Fe^{2+} in glass after “long” duration runs up to 120 -130 minutes at pressure 5 kbar with initial oxidised basaltic glass ($Fe^{3+}/(Fe^{2+} + Fe^{3+})$ = 0.8. In these reduced samples ($Fe^{3+}/(Fe^{2+} + Fe^{3+}) \approx 0.5$) the FTIR-spectroscopy detects significantly higher concentrations of H_2O (0.5-0.7 wt. %) in comparison with H_2O concentrations in initial glass and quench glasses after “short” experiments (0.05-0.15 wt. % H_2O). This suggests, that the main reason of partial reduction of Fe^{3+} in “long” runs is the hydrogen penetration in a basaltic melts through platinum walls of the capsule from surrounding gas medium during experiment. The obtained data give the serious basis to doubt, that a pressure increase up to 5-10 kbar can cause strong reduction effect (decrease of Fe^{3+}/Fe^{2+} ratio) in synthetic and natural silicate melts (in closed system conditions), discovered earlier in experiments conducted mainly on the piston-cylinder high pressure apparatus (Mysen, Virgo, 1978, 1983, 1985; Borisov et al.,1985; Mysen, 1991).

The study of Mössbauer spectra of experimental glass samples with an identical iron redox state allows to conclude, that the pressure variation in the range up to 5 kbar does not produce noticeable influence on structural positions of Fe^{3+} and Fe^{2+} in basaltic melts. There is the monomodal distribution of isomeric shift value for each of iron ions in all experimental samples, in other words there is the quasicontinuous distribution of lengths of Fe - O bindings in a near coordination sphere. Thus, in a structure of a glass (melt) for each of iron ions there are no two (or more) preferable structural positions, which would be strictly attributed to tetrahedral and/or octahedral coordination. Obviously, it is possible to speak only about some effective coordination number for each of them. Effective coordination number of Fe^{3+} is within the range between 5 and 6. It is close to 5 in oxidised glasses (melts) with a ratio $Fe^{3+}/(Fe^{2+} + Fe^{3+}) \approx 0.8$ and increases with decreasing of Fe^{3+}/Fe^{2+} ratio. Effective coordination number of Fe^{3+} approaches 6 (deformed octahedron) at $Fe^{3+}/(Fe^{2+} + Fe^{3+}) \approx 0.5$. Effective coordination number of Fe^{2+} is between 4 and 5.

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Mironov N.L.[1], Pletchov P.Y.[1], Portnyagin M.V.[2] The relationships between high-magnesian and high-alumina basalts of the Klyuchevskoy volcano - insight from melt inclusions study.

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key words: [*melt inclusions, high-magnesian and high-alumina basalts, Klyuchevskoy volcano*]

Calc-alkaline basalts of Klyuchevskoy volcano form continuous compositional trend from high-magnesian (HMB - MgO – 11.6, Al_2O_3 – 13.9 wt%) to high-alumina basalts (HAB – MgO – 5.2, Al_2O_3 – 18.2 wt%). To clear up the relationship between HMB and HAB and to compare their mineral-forming melts we studied melt inclusions (MI) in olivines, clinopyroxenes from HMB (flow Bulochka) and olivines, clinopyroxenes, plagioclases from HAB (flow Apakhonchich).

Partially recrystallized inclusions in minerals of HMB consisting of glass, clinopyroxene, spinel and fluid bubble were rehomogenized. Olivines and clinopyroxenes were heated up to 1220 and 1120 °C, kept at these temperatures during 10 and 15 min, respectively, and then were rapidly quenched (~200°/sec). Quenched inclusions contained glass and fluid bubble. MI in HAB phenocrysts were represented by naturally quenched glassy inclusions (glass+fluid phase) and required no experiments.

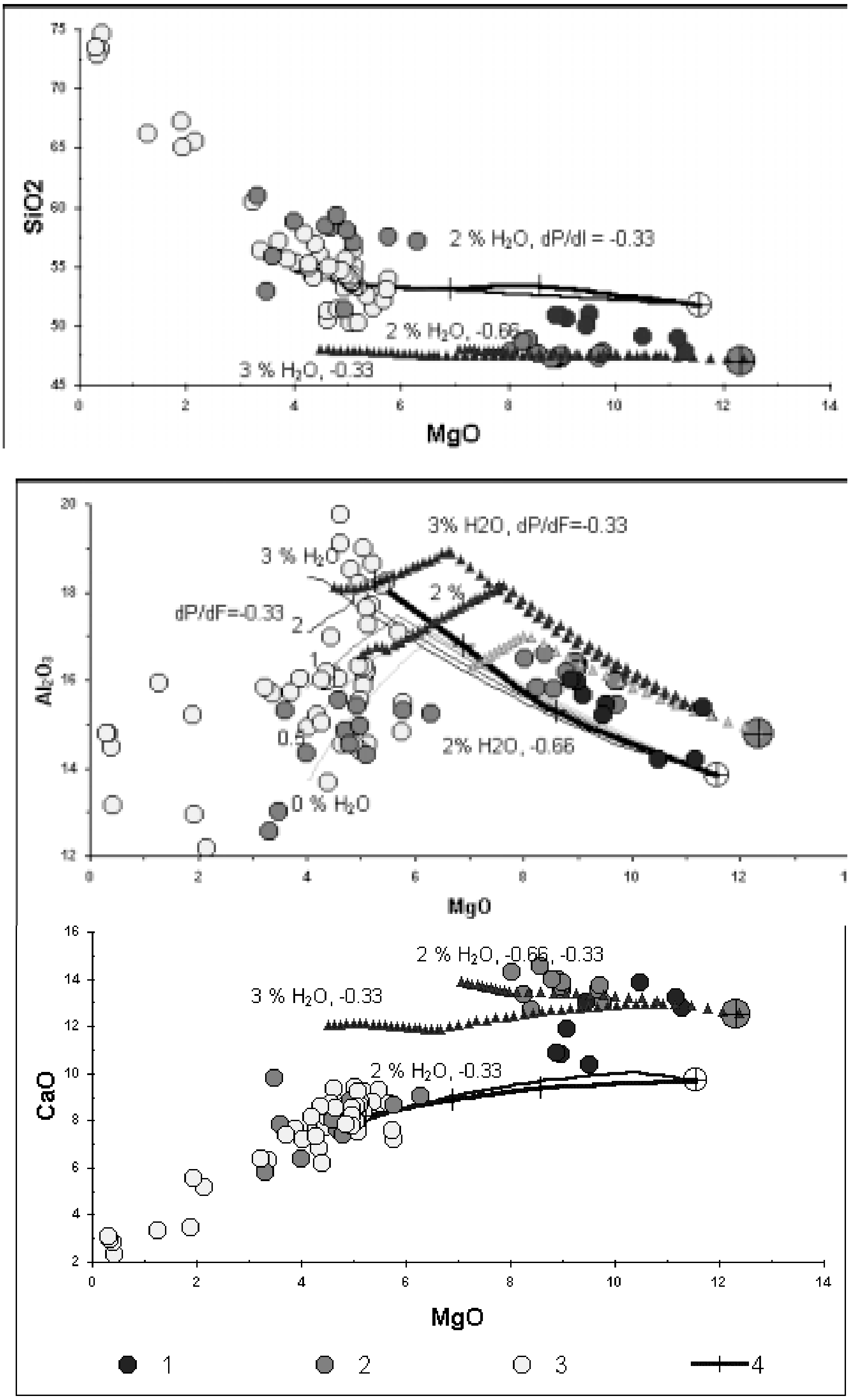

Fig.1 Melt compositions obtained on the base of the melt inclusions study. MI in the minerals of HAB and HMB of Klyuchevskoy volcano: 1) olivines ($Fo_{87-90.5}$) - data of [3,4]; 2) olivines ($Fo_{86-88.5}$), Ol ($Fo_{90.8}$) – average composition, Cpx ($\#Mg_{78-87}$) from HMB flow Bulochka; 3) Ol (Fo_{71-79}), Cpx ($\#Mg_{70-81}$), Pl (An_{47-84}) from HAB flow Apakhonchich [6]; 4 – trend of Klyuchevskoy volcano bulk rock chemistry. Model crystallization trends with two different initial high-magnesian melts are shown by thin lines and triangles (Pinit.=18 kbar). Initial water content and decompression rate are also shown on diagrams (% H_2O, dP/dl).

Estimates of crystallization temperatures (T_{cryst}) were based on calculated "dry" pseudoliquidouse temperatures of mineral-melt equilibria. T_{cryst} of HAB phenocrysts were corrected according to water content in melt. T_{cryst} varied from 1320-1300 °C for Ol (Fo_{91-90}), 1240-1190°C for Ol (Fo_{88-86}) and Cpx $\#Mg_{88-87}$ and 1145-1030 °C for phenocrysts of HAB. Crystallisation pressure was estimated not to exceed 3-3.5 kbars on the basis of Cpx - geobarometer [1] applied to the composition of Cpx from HAB ($\#Mg_{70-81}$). Water content was estimated for melts, in equilibrium with Ol and Pl according to method [2]. Estimated water content in HAB melts varied from 0 to 5 wt.% with the maximum content in high-alumina melts. Minimum water content in HMB melts, which are undersaturated in Plag, is estimated to be 1.1 wt.% on average. These results are in a good agreement with the direct measurements of water content in olivine-hosted MI from HMB ($Fo_{87-90.5}$) [3,4], which indicate values between 1.5 and 2.5 wt.%.

The composition of studied MI is shown on fig.1. Magnesian melts (MgO > 8 wt.%) (a part of melts from group 2) were obtained from the studied MI in HMB olivines ($Fo_{86-88.5}$) taking into account the post entrapment effect of "Fe-loss" [5].Parental melts of HMB contain 12 wt.% MgO and are in equilibrium with olivine $Fo_{90.8}$. These compositions were obtained by modelling the reverse fractionation of olivine from magnesian MI. Melts of group 1 (data of [3,4]) are in equilibrium with olivine $Fo_{87-90.5}$. It's important to point out that obtained compositions of primitive melts differ significantly from bulk rock compositions of Klyuchevskoy volcano by elevated CaO, Al_2O_3 and low SiO_2 content (Fig.1). Melts with MgO < 6 wt.%, recorded in MI from minerals of HAB form a wide compositional field (group 3) and characterize the final stage of magma evolution at Klyuchevskoy volcano [6]. It is interesting to note that melts from MI in Cpx ($\#Mg_{78-87}$) of HMB are similar in composition to some of melts of group 3 (Al_2O_3 < 16, MgO < 6 wt.%). This observation seems to confirm a genetic link between melts, from which HMB and HAB minerals crystallized.

The study of crystal inclusions in minerals also confirms such relationships [7]. However our data on the composition of MI in minerals of HAB and HMB do not allow to be confident about the existence of single continuous trend of melt evolution from HMB to HAB compositions. This is because sor far we found no melts with MgO –6-8 wt.% and no melts in minerals of HAB overlapping in composition those of HMB.

Modeling of decompression fractional crystallization with initial melts identical to HMB allows to obtain the observed composition spectrum with MgO < 6 wt.% [6](Fig.1). However, when average composition of MI in HMB olivine is taken as a parental melt, the model crystallization trends can not explain observed variations of HAB melts (Fig.1).

The discrepancy between composition of high-magnesian melts (MgO>8 wt.%) from inclusions in HMB olivines and bulk HMB and HAB chemistry can be caused by two reasons: 1) variation of initial melts composition and 2) partial decrepitation of MI. The first reason appears to be not suitable, because there are no rocks on Klyuchevskoy volcano corresponding in composition to melts found in MI.

The influence of natural partial decrepitation of MI could be an alternative explanation for the observed discrepancy [9]. This is a characteristic feature not only of basalts from Klyuchevskoy volcano but also of some other objects, for example, basalts of Avacha volcano [9]. As it was shown in [9], decrepitation leads to decrepancy between bulk inclusion and initially trapped melt compositions. As a result bulk inclusion composition is shifted to that of “daughter” mineral (Cpx in our case) after reheating in experiment.

Thus the problem of genetic relationships between melts, from which minerals of HMB and HAB crystallized, is still under discussion. Direct data on the composition of melts in HMB minerals reported in this paper and [3,4] show that there are no melts among them corresponding to HABm and the most primitive melts in MI can not be linked with high-alumina magmas by fractional crystallization of Ol and Cpx. Investigations on this subject will be continued and we hope it will allow us to resolve the paradox in near future.

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[#]Portnyagin M.V.[1], Plechov P.Yu.[2], Osipenko A.B.[3] Influence of natural decrepitation on the composition of melt inclusions in olivine: a study of melanocratic basalts from Avacha volcano, Kamchatka

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key words [*melt inclusions decrepitation island-arc magmatism Kamchatka*]

Natural decrepitation of melt and fluid inclusions in minerals typically occurs in response of magma ascent at crystallisation and volcanic eruptions leading to significant difference between pressure inside inclusion and external pressure around host mineral **[1,2]**. In fact, decrepitation is a way of decompression of inclusion, and this may

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[#] This work is supported by RFBR (Grant № 00-05-64384) proceed by partial lost of initial content of melt inclusion. The degree of the leakage depends largely on compressibility of inclusion content **[2]**. Due to the weak compressibility, inclusions of magmatic melts undergo typically partial decrepitation when a primary inclusion is visually preserved but accompanied by numerous secondary inclusions accommodating excess of volume. In this paper we address some geochemical consequences of partial decrepitation on the composition of melt inclusions illustrated by the study of exotic olivine-clinopyroxene rich lavas from Avacha volcano named previously as "avachites" **[3]**.

Avachites were first described in paper **[3]**. These rocks are basaltic in composition and contain 35-50 vol.% of large (up to 2 cm) phenocrysts of high magnesian olivine (Fo$_{91-85}$) and clinopyroxene (Mg#92-87) in hyalo-ophitic high-alumina andesite-basaltic groundmass (Table 1). Abundant xenoliths of volcanic and intrusive rocks were also described **[3]**. The olivine phenocrysts contain numerous fluid and melt inclusions, crystal inclusions of clinopyroxene and chrome-rich spinel. The assemblage of inclusions is indicative of magmatic origin of the olivine crystals and suggests an origin of phenocrysts in avachites by cotectic crystallisation of olivine, clinopyroxene and spinel from high magnesium parental melt. At room temperature melt inclusions consist of dacitic glass, high calcium pyroxene (Table 1), spinel and fluid bubble. Melt inclusions in forsterite-rich olivines (Fo$_{>87}$) are typically built by few well-shaped daughter crystals and are partially decrepitated as indicated by the aureole of a small secondary melt and fluid inclusion around the large primary inclusion (Fig.1a). Inclusions in relatively iron-rich olivines (Fo$_{85-87}$) are finely crystallised and do not display features of decrepitation (Fig.1b).

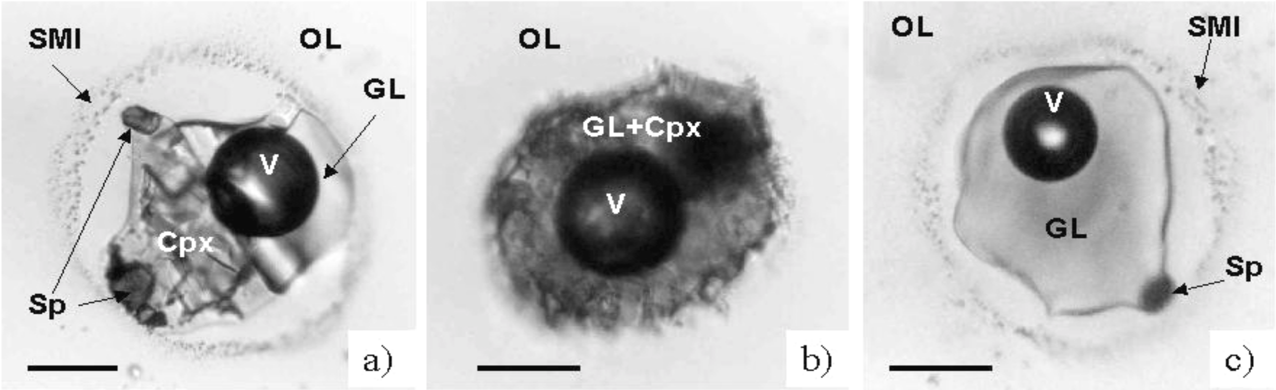

Fig.1. Melt inclusions in olivine from avachites: a) inclusion in high magnesian olivine; b) inclusion in iron-rich olivine; c) melt inclusion in high magnesian olivine quenched at 1250 ^{o}C. Abbreviations: OL – host olivine, GL - glass, Cpx - clinopyroxene, Sp - spinel, V- fluid bubble, SMI – secondary melt inclusions. Scale bar is 30 mkm.

In order to determine the bulk composition of recrystallised melt inclusions we have carried out a series of heating experiments.

During the runs single grains of olivines containing inclusions were heated in He-atmosphere up to the melting point of last daughter clinopyroxene or some 10-30 degrees above and then rapidly ($\sim 200^{o}$/c) quenched. A low-inertia heating stage with optical control **[4]** was employed for the study. No complete homogenization was achieved in any of 15 experiments. Fluid bubble was always present in inclusions regardless the temperature approached. Quenched inclusions contained glass, fluid bubble and rare spinel crystal. If existed before experiment, an aureole of secondary inclusions was also observed after quenching (Fig.1c). No correlation was found between the temperature of daughter clinopyroxene melting and composition of host olivine.

Representative compositions of partially homogenized melt inclusions are shown in Table 1. All analyzed inclusions have basaltic *Ne*-normative composition, whereas lavas of Avacha volcano are *Hy*-normative basalts approaching *Qz*-normative andesites and dacites. In comparison to host rock inclusions are characterized by low FeO and MgO, similar SiO_2 and elevated CaO, Al_2O_3, Na_2O, K_2O, TiO_2 content. Ratios of elements incompatible with olivine vary significantly. CaO/Al_2O_3 in melt inclusions tend to decrease with increasing iron content in the host olivine. However, up to 2-fold variations of the ratio are observed for co-genetic melt inclusions within a single olivine grain (e.g., analyses no 7-9 in Table 1). Na_2O/K_2O and K_2O/TiO_2 ratios in opposite remain almost constant for cogenetic inclusions but vary significantly for different grains. The variations of melt inclusions composition and their peculiarities when compared to host rocks can hardly be explained by a single process and more likely resulted from a complex of different processes, such as (1) diffusive re-equilibration of melt inclusions and host olivines, (2) mixing of compositionally variable parental melts and (3) partial decrepitation of melt inclusions.

Re-equilibration of melt inclusions and host olivines at low temperatures is a common feature of melt inclusions in minerals of island-arc rocks and readily explains systematically lower FeO content in inclusions compared to host rocks **[5]**. However, this process can not account for *Ne*-normative and high-Ca composition of the majority of melt inclusions in avachites. This is because of olivine hosted melt inclusions, diffusive re-equilibration should decrease calcium in melt due to referable partition of calcium into olivine with decreasing temperature **[6]**. Normative nepheline content should also decrease to compensate an increase of normative hyperstene proportion in the melt. The melt inclusions studied demonstrate reverse compositional trends. Clearly, this observation call into question a very genetic link between rocks of Avacha volcano and melts found in high magnesian olivines from avachites. Mass balance calculations and thermodynamic modeling of olivine and clinopyroxene crystallisation from compositions of melt inclusions further support this conclusion.

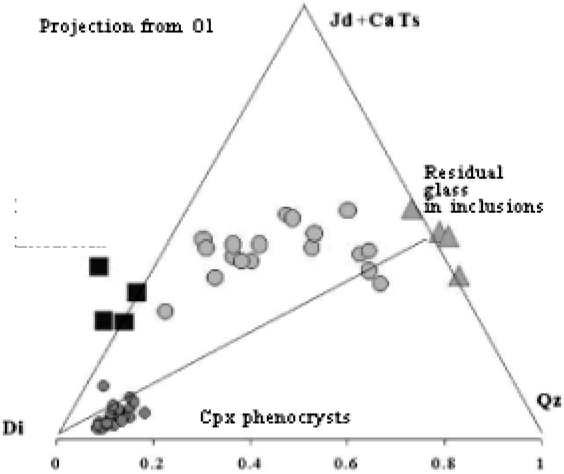

Fig.2 The compositions of partially homogenized melt inclusions, daughter phases in recrystallised melt inclusions and clinopyroxene phenocrysts from avachites plotted in CIPW normative tetrahedron, projected from olivine onto base jadeite plus calcium tschermak's molecule (Jd+CaTs) - quartz (Qz) - diopside (Di) **[9]**.

A straightforward explanation for the observed relationships between melt inclusions and rock chemistry is that olivine was crystallised from a specific type of primitive *Ne*-normative high-Ca melts, which were not found so far among lavas erupted on the surface **[7]**. However, when applied to avachites, this explanation seems to contradict the data obtained. Host olivines of the melt inclusions have restricted CaO content (0.15-0.20 wt.%), which does not correlate with the composition of trapped melts. In more general view, high-Ca melts could not be equilibrated with typical mantle sources **[7]**, and assimilation of common clinopyroxenites by ascending magmas was shown not to produce *Ne*-normative melts **[8]**. Thus, if large volumes of silica undersaturated high-Ca melts really existed in nature, one should imply origin of these magmas by involvement of "exotic" low-Si pyroxene component of unknown provenance in mantle melting or assimilation process. Fractionation from parental silica-undersaturated melts to typical basalts and andesites seem to be not simple as well and should involve amphibole as fractionating phase **[7]** or silica-rich contaminant. Clearly, the idea of primary nature of silica undersaturated high-Ca melts found in melt inclusions meets a large number of unknowns.

Table 1. Major elements content in samples studied (wt.%)

	1	2	3	4	5	6	7	8	9	10	11
Sample	WR	GM	Gl-i	Cpx-i	Av1	Av3	Av4-a	Av4-b	Av4-c	Av10a	Av14
SiO_2	50.6	54.5	64.8	44.3	48.6	47.8	49.5	49.7	50.2	47.8	50.5
TiO_2	0.72	0.57	0.47	1.48	0.73	1.18	1.22	1.14	1.02	0.74	1.33
Al_2O_3	10.3	18.6	21.1	13.5	13.6	13.7	14.3	16.6	12.0	18.2	18.7
FeO	8.46	6.20	0.72	6.49	6.70	5.57	6.00	5.71	6.33	6.62	5.49
MnO	0.14	0.14	0.05	0.09	0.10	0.13	0.10	0.11	0.36	0.23	0.28
MgO	16.2	4.90	0.40	10.9	11.1	13.2	10.4	9.90	10.8	8.98	8.67
CaO	11.5	10.3	2.25	22.6	15.3	14.5	14.5	12.5	15.4	13.4	9.24
Na_2O	1.77	3.65	8.37	0.67	3.20	3.02	3.15	3.31	3.03	3.56	4.79
K_2O	0.30	0.58	1.56	-	0.43	0.81	0.71	0.82	0.73	0.45	0.88
Cl	-	0.07	0.29	-	0.12	0.08	0.12	0.19	0.17	0.10	0.18
Fo, mol%	-		-	-	90.7	89.4	88.6	88.6	88.6	86.0	85.0
CaO/Al_2O_3	1.12	0.55	0.11	1.68	1.12	1.06	1.01	0.75	1.28	0.73	0.49

1 - avachite bulk composition **[3]**; 2- groundmass composition of avachite (average of 5 broad beam EMP analyses) ; 3-4 - average composition of daughter phases in 4 recrystallised melt inclusions in olivine Fo_{87-89} (3 - glass, 4 - clinopyroxene);
5-11 - partially homogenized melt inclusions. Fo - host olivine Mg-number. All compositions are normalized to 100 wt.%.

Compositional variability of primitive melts is proved to exist in nature. However, alternative and intuitively more realistic explanation for the origin of silica undersaturated high-Ca melts from this study is the influence of partial decrepitation on the composition of melt inclusions as microscopic observations provide strong evidence for the suggestion (Fig.1). Let us assume that decrepitation took place at the moment when large daughter clinopyroxene in inclusions had been already crystallised. Then, predominant leakage of residual melt from an inclusion will shift the bulk composition of the inclusion to the enrichment in a component of daughter clinopyroxene composition. In general case, the shift of bulk inclusion composition will be controlled by the chemistry of daughter phases existed inside inclusion at the moment of decrepitation. The data of this work appear to support this assumption. The geochemical effect of decrepitation is demonstrated in Fig.2, where normative compositions of reheated melt inclusions fall along the trend between compositions of major daughter phases in inclusions. The composition of daughter clinopyroxene in melt inclusions is highly unusual for basaltic magmas and differs significantly from composition of clinopyroxene phenocrysts in the same rocks. The most important peculiarities are low SiO_2 and high Al_2O_3 and TiO_2 contents. These features reflect high proportion of Ca- и Ca-Ti- tschermak's molecule in pyroxene composition which amounts ~20 mol.% whereas majority of magmatic pyroxenes contain around 2-5 mol.% tschermak's molecule. These compositional peculiarities of daughter pyroxene seem to be responsible for the shift of bulk inclusion chemistry to silica undersaturated high-Ca field.

Based on the data obtained one may conclude that partial decrepitation of melt inclusions influenced strongly the composition of melt inclusions in the most magnesian olivines which probably crystallised at highest pressure. An origin of silica-undersaturated high-Ca melts is explained by an excess of daughter low-Si high-Al clinopyroxene in melt inclusions, which were remelted in high-temperature experiments. Pyroxene of similar composition is described in melt inclusions from many olivine-bearing primitive samples of different provenance [10, unpublished data]. Thus, one may expect that geochemical effect of decrepitation will be also similar in many cases especially when clinopyroxene is an early liquidus phase of melts. Taking into account wide spread of naturally decrepitated magmatic inclusions [1,2], our results emphasize an importance of detailed microscopic study of magmatic inclusions in order to avoid erroneous results.

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Shchekina T.I., Gramenitskii E.N. Processes of Ta, Nb, Zr and Hf concentration connected with the granitoide magmatism on the base of experimental research.

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key words: [*element partitioning and concentration, partition coefficient, silicate, fluid (aluminofluorine) melts, geochemical indicators*]

The problems of relationships of ore formation with intrusions and a source of ore material are actual during the whole lifetime of geology. The way to solve these problems in present is seen owing to admittance of a role of aqueous-salt liquid phases (fluidized melts), which are able to effectively extract ore components. A study of model systems including fluorine is most interesting for rare metal granites and nepheline syenites.

Phase relations in the liquidus of the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2-H_2O, where some portion of oxygen is substituted by fluorine [1], were experimentally studied. Partitioning of Ta, Nb, Zr, Hf, Ba, and P between immiscible silicate and aluminofluorine melts in the system are also considered. All experiments were carried out at temperature 800°C and pressure 1 kbar using hydrothermal apparatus (Tuttle bomb type) during 3-4 days. The experiments on element partition were performed for 12 starting systems: K-, K-Na, and Na, corresponding to the model granite composition; Na-Al, alumina oversaturated; Li-bearing composition, which models Li-F granites; and nepheline-normative composition (designated as Ne). The obtained results were compared with natural objects.

On the basis of the experimental data, the boundaries of an immiscibility gap in the agpaitic plumasite and silica-rich portions of the system were specified. The immiscibility gape is shown to be extended towards the nepheline-normative portion of the system.

In the case of an equilibrium of aluminosilicate and aluminofluorine melts, Ta, Nb, Zr, and Hf are concentrated in the former melt. The data support a leading role of the crystallization differentiation in concentrating the above elements. Separation of the aluminofluorine melt reinforces this effect. The partition coefficient between silicate and fluidized melts significantly decreases in addition of lithium into the system [2], especially for Zr and Hf (the coefficient becomes close to unit for Hf). In addition to lithium, the values of the partition coefficients are influenced by the variations of K and Na content in the system, saturation of the system in silica, its agpaite character, and substitution of some fluorine by carbon dioxide. The tendencies of variation are not similar, right up to reverse, for chemically similar elements. It causes changes in the values of their ratios (geochemical indicators). The obtained experimental results allow to explain the regularities of a decrease of Zr/Hf and Nb/Ta ratios in the later phases of granite complexes; accumulation of Nb and Zr in sodic granites, while Ta and Hf in potassic granites; lack of Zr accumulation (in contrast to Nb and Ta) in residual melts of Li-F granites. Within the nepheline-normative region, the experimental data are in accordance with the general features of Nb and Ta geochemistry. The former element is accumulated mainly in nepheline syenites, while the latter element enriches granites. Nb plays a greater role in agpaitic rocks, whereas enrichment in Ta is characteristic only of plumasite rocks.

The experimental data do not point to the possible concentrations of the above elements in post-magmatic process. However, addition of carbon dioxide into the system causes a systematic decrease of Nb partition coefficient for agpaite nepheline-normative compositions and an increase of the coefficient for quartz-normative compositions (see Figure). In fact, carbonatites with commercial concentrations of Nb are always associated with agpaitic nepheline syenites.

Data on Ba and P partitioning are also obtained in the experiments. Geochemistry of Ba in magmatic process is, in general, in direct opposition to the geochemistry of Nb, Ta, Zr, Hf. Similar features are characteristic of partition of these elements between silicate and fluorine melts. The common decrease of Ba clark in leucocratic granites and alaskites can be explained both by its isomorphic dissipation in feldspars on the earliest stages of crystallization and by an extraction into fluorine liquid with the partition coefficient of 0.03-0.15. At the same time, the partition coefficient is above unit for the sodic portion of the system. That is in agreement with Ba enrichment in plagiogranites. The partition coefficient of P and Ba abruptly decreases down to 0.02-0.05 in the lithium-bearing potion of the system. These elements are not characteristic for Li-F granites. They are practically completely extracted by the fluorine melt. The Ba partition coefficient is above 1 in the nepheline-normative portion of the system. That agrees with an increase of Ba content in nepheline syenites.

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[#]Almeev R.R., Rusakov V.S.* Mossbauer spectroscopy of amphiboles from andesites of the bezymyanny volcano (Eastern Kamchatka)

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Amphibole fractionation and high DAmph-Liq for REE and HFSE are the important factors of evolution of island arc magmas at intermediate and late stages of crystallization. It is evidenced by geochemical trends of major and trace elements in many calc-alkaline series [1-4]. In particular, our investigations of mutual mineral inclusions in lavas of the Bezymyanny volcano show, that hornblende and magnetite are in cotectic relations with plagioclase and pyroxenes. It means amphibole fractionation should be taken into account during development of realistic computer models simulating crystallization of hydrous basalt melts.

Before develop a quantitative hornblende-melt phase equilibria model the amounts of FeO, Fe_2O_3, and H_2O must be measured or estimated in order to characterize a hornblende solid solution [5]. Definition of the ferric-ferrous ratio and H_2O content in amphiboles is a problem because 1) such information is commonly absent among experimental data on phase equilibria; 2) no normalization scheme based on chemical and stechiometric limits of the given microprobe data alone consistently replicates the measured FeO, Fe_2O_3, and H_2O. To estimate the Fe^{3+}/Fe^{total} ratio with reference to the amphiboles of a Bezymyanny volcano, Mossbauer spectroscopy of hornblende was caried out. We used hornblende crystals from andesites of directed blust eruption of 1956 as a starting material. These crystals were obtained as a result of magnetic separation, excretion in a bromoform and subsequent selection under binocular microscope of minerals from fractions of andesites of 2-1 mm and 1-0.5 mm.

The Mossbauer absorption measurements were performed on a MS1101E spectrometer (the MOSTEK Company, RUSSIA) in a constant-acceleration mode at room temperature. The source of γ-quanta was the 57Co isotope in the Rh matrix.

As a result we observed, that about 14 % of total Fe is presented in the form of magnetite. This is despite of the use of a magnetic separator which reduces to a minimum possible hit of crystalline joint of hornblende with magnetite. The presence of fine-dyspersated (cotectic) magnetite in the amphibole is consistent with presence of magnetite inclusions investigated earlier on a microprobe. This fact should be taken into account at interpretings total chemical analysis of hornblende, obtained by "wet" chemistry.

The proportions of Fe^{3+} in hornblende is to about 39 %, that allows us to assume oxidizing conditions during crystallization of the mineral. Values of isomeric shifts for Fe^{2+}, and Fe^{3+} uniquel specify an octahedral environment for both cations.

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Pletchov P.Y., Trousov S.V. The influence of boundary layer effects on the melt inclusions compositions.

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key words: [*melt inclusions, experiment, diffusion, boundary layer effect*]

Introduction. It is well known that the melt composition at the surface of growing crystal is very different from the bulk melt composition owing to the boundary effects of redistribution of a substance between the melt and the crystal. The observed width of this layer

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[#] The work was supported by the Russian Fund of Basic Research (grants 99-05-64875 and 00-05-64466)

varies from 10-15 μm (for basalt melts of low viscosity) to 100-150 μm (for rhyolite melt) in dependence on melt viscosity and growth conditions. Taking into account that melt inclusions form from the melt portion adjacent to the growing crystal, it can be assumed that their composition is distorted in comparison to the bulk composition. Smith et al. [1] first showed that the melt in the boundary layer would be depleted in compatible components and enriched in incompatible components.

The experimental reproduction of the boundary effects

In order to distinguish an influence of the boundary effects on the composition of melt inclusions, the experiment on growth of alkali feldspar (Fsp) crystal in the haplogranitic system (Q-Ab-Or) was performed. The system was cooled during 6 days from 760 to 700°C with a rate of 10°day, and subsequently quenched. As a result, diffusion profiles around Fsp crystals were produced (Fig. 1). The profiles show an enrichment of the boundary layer at the crystal surface in the components, whose concentration in Fsp is lower, then in the melt (for example, SiO_2). However, a depletion in SiO_2 and an enrichment in Al_2O_3 are observed in the portion of the profile remote from the surface. This effect is difficult to explain by simple diffusion transport of the components from the growing face.

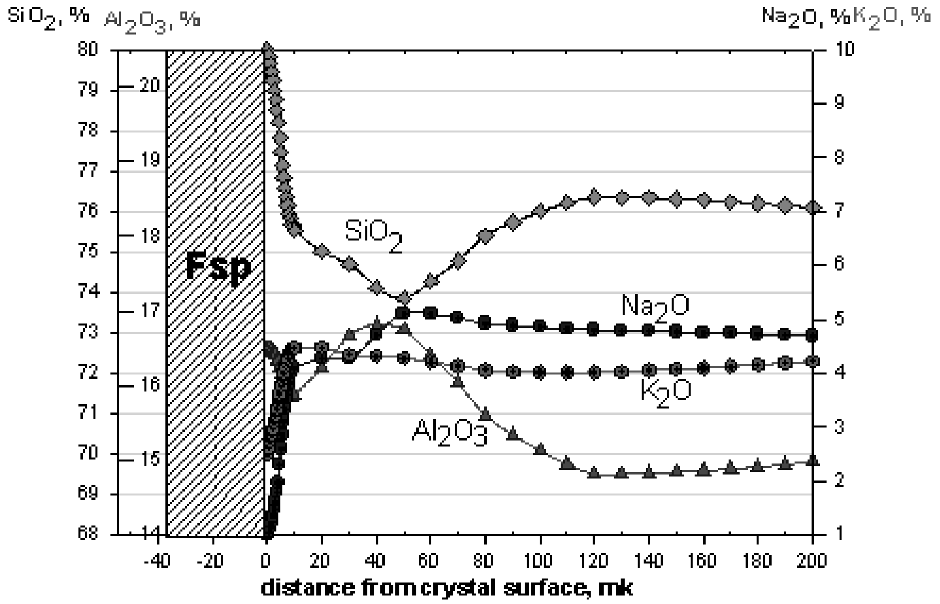

Fig.1. Distribution of melt species on the boundary of Fsp crystal

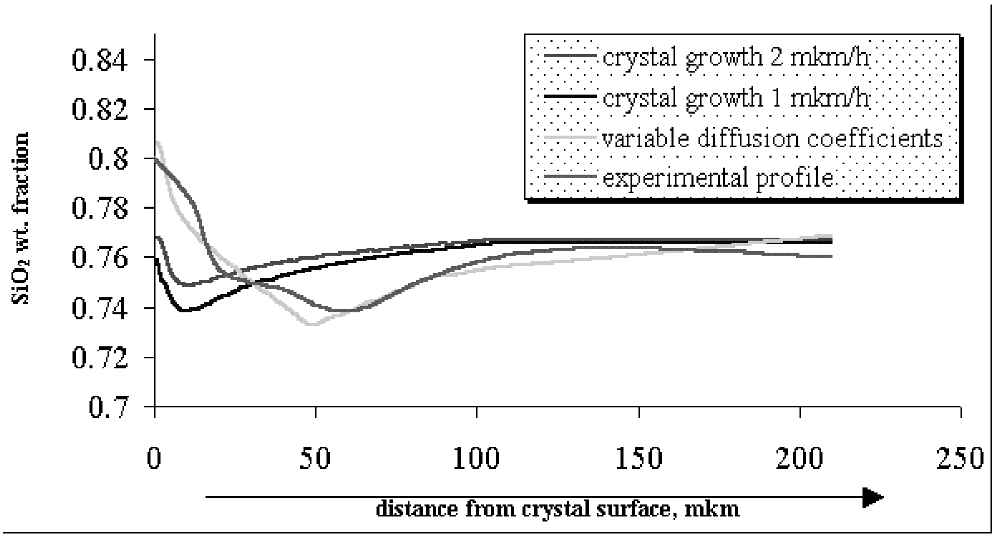

Fig.1a. Modeling of the boundary effects during Fsp growth. **1**. growth rate 2 μm/h; **2**. growth rate 1 μm/h; **3**. arbitrary diffusivities; **4**. the experimental profile; **5**. SiO_2, wt. %; **6**. distance from the crystal, μm.

Computer modeling of the boundary effects

The authors carried out a computer modeling of the growth of Fsp crystal in the granite melt. We used an equation of a multicomponent diffusion and an algorithm of Oishi [2]. The crystal growth was modeled by the mechanism of the layer-by-layer growth. Diffusion coefficients were taken from [3, 4]. The major difficulty was to model the portion of the profile, which is remote from the growing face. The profile configuration (Fig. 1) implies head diffusion fluxes, which transport component to the opposite sides. It means that these components would be present in the melt as different species. The flux directed to the crystal would be exhausted by the growing face, in order to form a concentration gradient. An assumption that component transportation toward the growing face occurs by species, whose composition is similar to the growing mineral, allowed to obtain satisfactory results of modeling.

Fig.1a shows two calculated diffusion curves for silica during Fsp growth with rates 1 and 2 µm/hour and a curve calculated with changing diffusivities (a dependence of diffusivity on concentration was added). It should be noted, that the calculated diffusion profiles are not stationary in time and can be considered as an oscillatory system (a period of oscillations depends on frequency of new layer production). Uncertainty of some parameters, such as diffusivities of complexes in the melt, their sizes, chemical interaction between them etc., does not allow to create a complete numerical model of the process.

Estimation of an influence of the boundary effect on melt inclusion composition

If we suggest, that melt inclusions partially capture the boundary layer, then composition of small inclusions would correspond to an average composition of the trapped portion of the boundary layer. The larger inclusion the weaker its influence on the boundary layer.

Fig.2 shows the calculated curves of an average composition of the boundary layer in dependence on inclusion size. Points on the diagram show a composition of melt inclusion, whose diameter corresponds to the dimension of the X-axis. Generally, good correlation between the predicted and the measured compositions of melt inclusions is observed.

Thus, study of diffusion profiles gives a possibility to calculate a correction for composition of melt inclusions. Theoretical modeling of crystal growth in synthetic systems reproduces the experimental profiles through the boundary layer and probably can be used for the prediction of composition of melt inclusions.

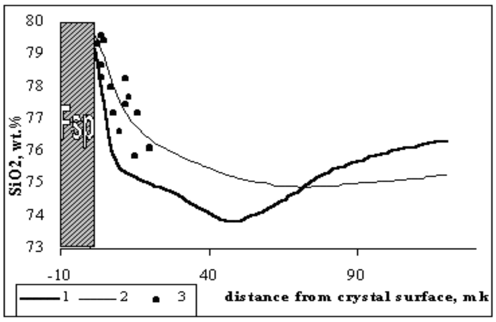

Fig.2. Compositional relations of melt inclusions with the calculated average composition of the boundary layer. 1 – the experimental diffusion profile, 2 – the average composition of the boundary layer, 3 – compositions of melt inclusions. 1. SiO_2 content, wt. %; 2. distance from the crystal

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[#]Maximov A.P. The effect of water on the stability temperature of amphibole in melts.

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key words: [amphibole, melt equilibrium,water]

The investigation has been carried out to elucidate the regularities in the behavior of melting curves of water-free silicates. These regularities are well described by an ideal model of the dissolution of water particles in melts [1]. The theoretical analysis of the effect of water concentration in melts on the crystallization of water phase is given in the work on an example of amphibole (Amph).

Peculiarities of the behavior of amphibole stability curves. The Amph stability curve under constant pressure has a maximum in the H_2O undersaturated region whereas liquidus temperature of water-free phases continuously decreases. There are also temperature and pressure maxima on the P-T curves of Amph melting whereas water free silicates have a temperature minimum only.

The existence of isobaric maximum on T is accounted by changing the hydration reaction controlling amphibole stability for melting one with increasing water activity [2], or by changing the character of melting reaction in the maximum point where water concentration in a melt corresponds to that in Amph [3].

The schematic equation and results of its analysis.

To describe the behaviour of water phase in melts the latter was approached as an ideal solution. Based on the schematic reaction of Amph crystallization and using a conventional expression for the reaction equilibrium constant we obtained the equation describing in a general view the effect of water on the Amph-melt equilibrium temperature. The equation obtained allows to predict and estimate the existence and position of a maximum. Water concentration in the maximum point does not depend on the form of its occurrence in a melt. The existence of an isobaric temperature maximum of Amph stability is explained by the two-fold effect of water on Amph-melt equilibrium: on the one hand, according to the crystallization reaction water increases Amph stability, on the other hand when dissolving in a melt, water decreases mole fractions of silicate components in Amph composition decreasing, thus, its stability. This is to note that M. Giorso [4] has recently been engaged in the similar

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[#] This research was supported by grant RFBR 99-05-65495.

investigation. His analysis although performed in a different way by and large confirms our conclusions.

Quantitative application in terms of the system pargasite-H_2O-CO_2.

For the quantitative estimation of the above approach we used experimental results on the system pargasite - water-CO_2 [5]. Pargasite stability curves at 5 and 8 kbar (water concentrations in a melt are given in [5]) were used as a basis for the calculation of equation coefficients. The results of calculations from 2 to 10 kbar are presented on the diagrams (fig. 1 and 2). The model of water solubility in melts was borrowed from [5]. Calculation curve adequately reproduces all the peculiarities of experimental curves behavior and well agrees with them from the standpoint of absolute position.

Experimental data processing.

This work is aimed at deriving equations describing the behavior of real Amphs in natural melts. First we applied the above approach to derive crystallization equations of tremolite and pargasite using experimental data from the INFOREKS database [6]. The estimation of mole fractions and activities of end members of Amph offers the major difficulty in the analysis of its equilibria. An ambiguity of this estimation forced us to make some assumptions in the hope that a unified scheme of calculation at deriving and solving the equation would level the error. Water concentrations in melts were calculated by the modified Bernem's model. Several versions of Amph-melt equilibrium have been analyzed. Average deviations of calculated temperatures from the experimental ones were about 35°C. Calculations on hydroxyl and molecular forms of water in melts yielded about identical results. Changing the supposed number of silicate particles in melts gave no improvement. It is noteworthy that calculated equilibrium temperatures for tremolite and pargasite are commonly close.

Conclusions. The analysis results show that Amph behavior in melts could be described by an ideal model of water dissolution. In the first approximation the effect of activity coefficients of melt components is negligible. Insufficient accuracy of the results for natural systems is likely to be related to the calculation error of the Amph structural formulas. The model, thus, requires significant corrections. Major attention should be paid to the existence of pressure and temperature maxima of Amph stability on P-T projections which are probably due to changing reaction volume effect with pressure.

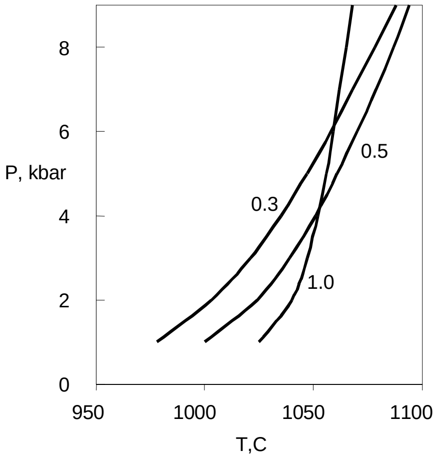

Fig. 1. Calculated P-T melting curves of pargasite.

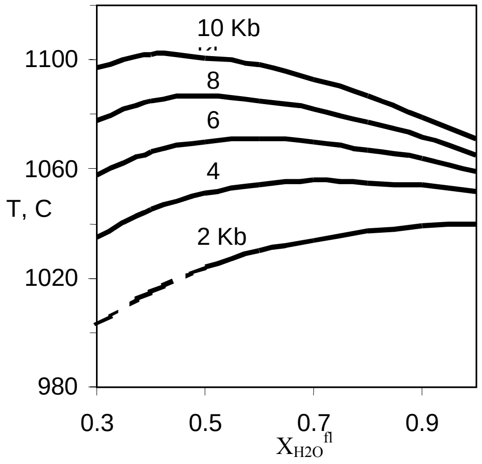

Fig.2. Calculated isobaric melting curves of pargasite vs. various mole fractions of water in the fluid

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Karzhavin V.K. About a correctness of thermodynamic properties of a components melts

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Many practical problems of crystallization of simple and complicated melt systems are considered in view of phase transition, degree of cooling, rate of temperature decrease in the medium, possibility of vitrification, etc. A great number of papers have been published on the given problem. The majority of them present the results of the studies of crystallization conditions, the related redistribution of substance between coexisting phases, and the character of chemical reactions in view of thermal conductivity, diffusion, the effects similar to self-organization phenomena, which are described by equations of thermodynamics of irreversible processes. Some theoretical studies are devoted to approximate methods of solutions of the problems connected with crystallization of multicomponent melts through empirical or quasi-theoretical models, which included simple oxide ideal systems, polymeric models, quasi-chemical models, complicated models for mixtures of ideal components and complex models for regular solutions. A magmatic melt was considered both as a separate phase consisting of differentiated liquid components (cybotactic groups) with a polymeric structure of solid minerals, but with preservation of only near-order connections.

A major problem at the modeling of the crystallization process in any natural mineral-melt system is the lack of data on thermodynamic properties of both simple and complicated components of siliceous melts. The available information obtained by the modeling of synthetic siliceous systems is not correct for an automatic transfer immediately to natural systems. The modern reference media on thermodynamic properties of substances (elements, chemical compounds, minerals) are based practically completely on thermochemical definitions. The information about thermodynamic properties of substances is given in some papers and reference media as intercoordinated data on temperature-dependence of thermal capacity, entropy, enthalpy of formation and Gibbs energy. There are, however, great discrepancies in the data on the number of substances [1-3]. They concern thermodynamic properties of compounds in a metastable state under standard conditions, which are offered, or used, for the study of crystallization of complex magmatic systems or for a construction of phase diagrams.

The phase transition is the extreme form of manifestation of intermolecular interaction resulting in a radical reorganization of a system. On both sides of the point for phase transition in melt systems there can exist both phases, the Gibbs energy of which reaches a minimum and is equal. This situation occurs in melts and represents a corollary of the known principle about the correspondence of chemical potentials of components in a heterogeneous system to those of a homogeneous saturated solution at other identical phase parameters. As the temperature decreases, the heat capacity and entropy of a metastable phase over the entire temperature interval should exceed (by an insignificant value) the heat capacity and entropy of a stable crystalline phase, and this is proved by experimental and theoretical investigations of liquid, glassy and crystalline state of a series of minerals [4,5]. In addition, the temperature of vitrification (Tg) is found to be dependent on the rate of cooling (tempering) of the melt. The temperature of vitrification of individual compounds is not a constant. A similar regularity has been also established for metal glasses.

To substantiate the applicability of the discussed thermodynamic properties of chemical compounds, we have considered sodium tetraborate as a representative example. The given chemical compound is one of the most thoroughly investigated experimentally (calorimetry) in a wide temperature interval, and the thermodynamic properties of this compound in liquid, glassy and crystalline states have been determined [6]. The calculation of a temperature assotiation of a heat capacity, entropy, enthalpy of formation and Gibbs energy was carried out under condition decribed by Smith [6], reference edition [7] and theoretical approach at an evaluation of a metastable melt condition [8]. The carried out research has allowed us to establish a definite relationship between thermodynamic functions of phases in a wide temperature interval. So, the difference in the entropy, enthalpy of formation and Gibbs energy between glassy and crystalline phases of a substance is described by the following equations:

$$\Delta G\text{gl.} - \Delta G\text{crys.} = \Delta H\text{gl.} - \Delta H\text{crys.} - (\Delta S\text{gl.} - \Delta S\text{crys.})\cdot T$$

or

$$\Delta G_T^* = \Delta H_T^* - T\cdot\Delta S_T^*$$

The melts are thermodynamically nonequilibrum and metastable. Depending on conditions of phase transformations (crystallization, vitrification), metastable phases are formed along with the stable ones. The analysis and registration of their properties when constructing an objective picture of phase transformations in multisystems contributes to the study of crystallization paths of a liquid phase both in equilibrium and nonequilibrum conditions. For solution of these problems it is necessary to have a minimum scope of information about the studied systems, which will allow one to come to an unambiguous solution.

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#Chevychelov V.Yu., Simakin A.G., Chevychelova T.K., Bondarenko G.V. The effect of composition and phase state of chloride fluid on chlorine solubility in a model granodiorite melt at T= 1000°C, P=1kbar.

key words: [*granodiorite melt chlorine solubility chloride fluid melt structure*]

The effect of changing composition and phase state (mono- and heterophase state included) of chloride fluid on chlorine solubility in an aluminosilicate melt has been investigated on an example of model granodiorite melt composed of oxides of five metals: Si, Al, Ca, Na, K. Experiments were carried out at $P_{H2O}=P_{tot.}=$ 1 kbar, T=1000°C for 4 days using an internally heated gas pressure vessel. Chlorine was introduced in the system melt-fluid through fluid as chlorides of Na, K, Ca, and Al. Varying the total content of chlorides in the starting fluid we simultaneously matched the ratio of different metal chlorides in the fluid so that the composition of quenched granodiorite melt remained about constant. Chlorine dissolution in an aluminosilicate melt was realized by diffusion from fluid. The integral pieces of granodiorite glass preliminary saturated with water were used in the experiments.

Fig. 1 presents the dependence of chlorine solubility in an aluminosilicate melt on the total content of chlorides (recalculated to chloride of a one-valent metal with no account of SiO_2) in the fluid. Shown on fig.1 are the regions of low-dense vapor (L1) and salt (L2) fluids as well as the region of these fluids coexistence (L1+L2).

As it is shown on the figure, chlorine solubility in a melt in the region of vapor fluid (L1) is relatively low (0.1-0.4%) but it is increasing fairly rapidly. Chlorine partitioning in this region (D fluid/melt) can be in favor of a melt. Chlorine solubility in a melt reaches the highest value (0.9-1.0%) at the equilibrium with two-phase fluid, total chlorides content in the fluid being relatively low (7-10wt%). With further increase of the total chlorides content in the fluid, chlorine solubility in a granodiorite melt decreases up to 0.5-0.6 wt%.

Lastly, in the stability field of homogeneous water-depleted salt fluid (L2) Cl solubility in aluminosilicate melt seems to decrease notably, for example at 94wt% of chlorides in the fluid Cl content in the melt is about 0.3%.

The dependence of the “total” coefficient of chlorine partitioning (D fluid/melt) on the total content of chlorides in the fluid is presented in fig.2. The regions of vapor (L1) and salt (L2) fluids as well as the region of the both fluids coexistence (L1+L2) are shown. The “total” coefficient of chlorine partitioning in the system is shown to increase routinely with increasing chlorides content in the fluid. In the region of vapor fluid (L1) the coefficient of chlorine partitioning may be below 1, i.e. in favor of the melt. In the region of heterophase fluid this “total” coefficient increases from 2-3 up to 50 in favor of the fluid. And at last in the region of homogeneous salt fluid it increases up to 60-80 and higher.

Presented in fig.3 is the dependence of chlorine solubility in a melt on the mole ratio Al_2O_3/ ($CaO+Na_2O+K_2O$) (reverse to the agpaitic coefficient). The strait line stands for the well pronounced negative (because we refer to the region of subalkaline compositions of a melt) correlation between chlorine and $Al_2O_3/(CaO+Na_2O+K_2O)$ ratio in the presence of a two-phase fluid (L1+L2). So, chlorine solubility in the melt increases with the distance of this mole ratio from 1(Chevychelov, 1999).

So, dependence of the content of Ca, Na, and K chlorides in the fluid on chlorine solubility in the equilibrium with the fluid melt is non-linear. Chlorine solubility in the melt increases notably with the appearance of a second fluid phase in the system, i.e. at the layering of the chloride fluid. The above dependence is likely to be related to a sharp increase in Cl- activity in the fluid and agree well with the data of other authors (Malinin, Kravchuk, 1995, et al.). But the conclusion about the existence of the maximum (extremum) on the curve of chlorine solubility in an aluminosilicate melt vs total chlorides concentration in the fluid is not so trivial. This effect is likely to be related to the formation of an alkaline salt melt and HCl separation (transformation) into a vapor phase. The effect of the hydrolysis reaction is fairly well studied experimentally (Shmulovich, 1999).

The samples of the quenched granodiorite glasses with different contents of chlorine, water, and cations of alkaline and alkaline-earth metals have been studied by the method of IR spectroscopy. The complicated absorbtion bands of the IR spectra obtained in the frequency range 300-700 cm-1 were approximated by two contours related to the oscillations of three- four- and six- membered aluminosilicon and silicon rings (the GRAMS program was used for the spectra treatment).

Chlorine in the melt structure is known to be bound only with cations-modificators (Na, K, Ca, Fe etc.) as contrasted to fluorine which can interact with the network-forming elements: Al and Si. We suggest that chlorine may be present in a melt in two positions: either in the coordination sphere of free cations or in the coordination sphere of cations still connected with the aluminosilicate network. The granodiorite melt is mainly composed by elements of quartz (6-membered rings) and feldspar (4-membered rings) structures. The elements of feldspar structure are stabilized by the connected with them cations of alkaline and alkaline-earth metals.

[#] The work has been supported by the RFBR (projects 99-05-65439 and 99-05-64106).

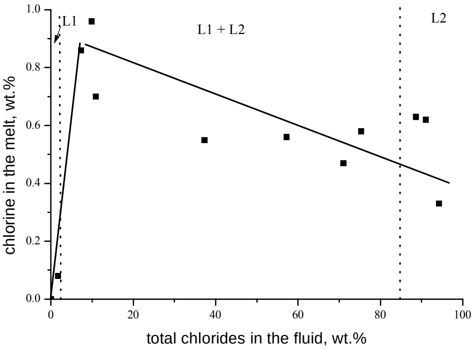

Fig.1. Correlation between chlorine solubility in an aluminosilicate melt and total content of chlorides (recalculated to the chloride of a one-valent metal with no account of SiO_2) in a fluid.

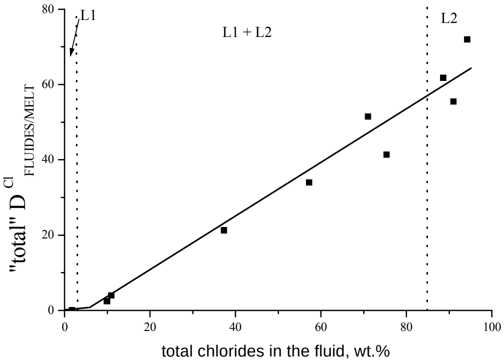

Fig.2. Correlation between "total" partitioning coefficients of chlorine (D fluid/melt) and total concentration of chlorides (recalculated to the chloride of a one-valent metal) in a fluid.

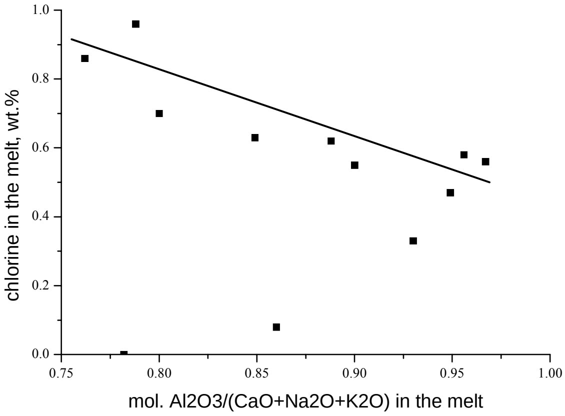

Fig.3. Correlation between chlorine solubility in a melt and mole ratio $Al_2O_3/(CaO+Na_2O+K_2O)$ in the melt composition.

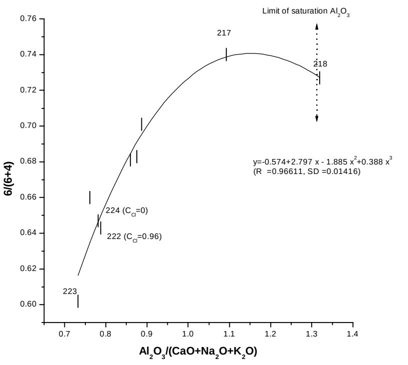

Fig.4. Dependence of a relative fraction of six-membered aluminosilicon and silicon rings in the melt structure on the mole ratio $Al_2O_3/(CaO+Na_2O+K_2O)$ in the melt composition.

The experimental data obtained suggest that the influence of the total content of alkaline and alkaline-earth metals on the medium range ordering of the melt structure is comparable with that of the dissolved water. As we reported earlier, water dissolution leads to the systematic decrease of the portion of 4- membered feldspar rings (Simakin et al., 1998).

Shown in fig. 4 is the ratio of six-membered to the sum of four- and six-membered aluminosilicon rings in the melt structure vs mole ratio $Al_2O_3/$ $(CaO+Na_2O+K_2O)$ in the melt composition . An increase in the ratio $Al_2O_3/$ $(CaO+Na_2O+K_2O)$ from 0.7 to 1.1 increases a relative part of six-membered rings. Thus, an excess of alkalies and calcium stabilizes the feldspar structural components. Granodiorite glasses of two experiments of the same composition differing only in chlorine content have the same ratio of six- and four-membered rings. According to the available data, the effects of chlorine and water are very close which may be well related to the fact that water and chlorine dissolutions are followed by their interaction with alkaline and alkaline-earth metals by the similar mechanism. The interaction of cations with the network, herewith, weakens providing destruction of its feldspar configuration.

The preliminary analyses of water content evidence that chlorine dissolution probably decreases water solubility. This may be related to the fact that chlorine competes with OH groups for free cations not bound with the network and a decrease in water content occurs at the expense of hydroxyl groups. For the interpretation of the dependence obtained we envisage to determine the fraction of hydroxyl water and summary H_2O content in quenched glasses by the method the local precision FTIR-IR spectroscopy.

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