EXPERIMENT

In

Mineralogy	Crystallography
Petrology	Geophysics
Geochemistry	Isotopy

GeoSciences

EXPERIMENT in

Mineralogy Petrology Geochemistry

Crystallography Geophysics Isotopy

GeoSciences

EXPERIMENT IN GEOSCIENCES is the only journal in English that gives you the latest, most reliable information on advances in experimental mineralogy, petrology, geochemistry, crystallography and geophysics in Russia. The coverage of the journal includes:

- original research and review articles
- abstracts of scientific papers
- proceedings, abstracts and announcements of national and international conferences, symposia and workshop
- information about the leading experimental centers in Russia
- advertisement of new techniques and equipment

TRANSLATED into ENGLISH by:
the authors

KdF monotonically decreases. As the pressure increases to 2 kbar, the behavior of Na, Al and F changes. The partition coefficients of Na and F at concentrations of water up to 30 wt. % give the lowest values (5 and 6.8), and at 50 wt. % water – range of about 9. KdAl begins monotonically increase to a value of 1.6. KdK and KdSi decreased by 0.1. This is probably due to the beginning of crystallization of K-Na cryolite from aluminofluoride melt. And also, it is possible that with increasing pressure and water content, the structure of the silicate melt changes, contributing to the transition of the Al part from tetrahedral to octahedral coordination.

REE behavior depends on the temperature, pressure and water fluid content in the melt. According to the experiments carried out at 800 °C, there is a decrease in KdREE(LF/L) from light to heavy, both at 1 and at 2 kbar (Fig. 4a,b). Sc is always distributed in favor of an aluminosilicate melt, however, its low values of separation coefficients in comparison with rare earths indicate a relatively higher affinity of Sc to aluminosilicate melt, compared with most REE. And the separation coefficients of yttrium are greater than one, which indicates its greater affinity to the salt melt. Also, there is a tendency that as the water concentration in the system increases, the KdREE (LF/L) increases. When the temperature decreases to 700 °C, the separation coefficients increase (Fig.4b,d). There are differences in Kd depending on the water introduced into the system, but they are not natural. The tendency to decrease the coefficients of REE separation at 800 °C with an increase in pressure from 1 to 2 kbar is maintained. It is experimentally obtained that all rare earth elements, yttrium, scandium and lithium are distributed in favor of the salt aluminofluoride melt, regardless of the specified experimental conditions. The separation coefficients between salt and aluminosilicate melts at 2 kbar are significantly reduced compared to those for 1 kbar. According to ICP MS, the aqueous fluid is the most depleted phase in Li, REE, Sc and Y.

As a result of the new data obtained at lower temperatures, it is shown that the salt phase enriched with rare earth elements remains in equilibrium with the silicate melt and fluid up to a temperature of 600 °C at a pressure of 1 kbar. Quartz begins to crystallize from the silicate melt, and from the salt – phase of LiNaK - cryolite. Rare earth elements form fluorides of LnF3 composition or complex fluorides with alkaline elements during salt melt quenching.

As a result of the data obtained, the following conclusions were made:

1) It's shown that when the temperature decreases from 800 to 600 °C, the phase composition of the system changes: at 700 °C, P = 1 and 2 kbar, a partial crystallization of the salt melt occurs with the formation of large crystals of aluminofluorides that practically do not contain rare earths. The residual salt melt, even more enriched with rare earth elements and casting, is stored in the system up to 600 °C. With a water content of more than 10 wt. % there was a free water fluid in the system.

2) At T = 600 °C and P = 1 kbar, quartz crystallizes from the aluminosilicate melt (L) and the phase composition of the system becomes: L+LF+Crl+Qtz.

3) Regardless of the given experimental conditions, all rare earth elements and lithium with large separation coefficients (several times) are distributed in a salt aluminofluoride melt.

4) REE separation coefficients between salt and aluminosilicate melts depend on temperature, pressure and volatile (water) content in the system.

5) Experimental data confirm the assumptions (Gramenitsky et al., 2005, Alferieva et al., 2011, Shchekina et al., 2013) about the formation of cryolite-containing granites at late stages of formation of large granite massifs as a result of separation from magma of salt alkaline fluoride melts rich in rare elements and capable of crystallizing much later than aluminosilicate melt at lower temperatures.

References:

Alferyeva Ya.O., Gramenitsky E.N., Shchekina T.I. Experimental study of phase relations in the lithium bearing fluorine-rich gaplogranite and nepheline-syenite systems. Geochemistry (7). 2011. P. 713-728 (in Russian).

Gramenitsky E.N., Shchekina T.I., Devyatova V.N. Phase relations in fluorine-containing granite and nepheline-syenite systems and distribution of elements between phases. Moscow: GEOS. 2005. P. 186 (in Russian).

Shchekina T.I., Gramenitsky E.N., Alferyeva Ya.O. Leucocratic magmatic melts with fluorine limit concentrations of fluorine: experiment and natural relations. Petrology 21 (5). 2013. P. 499 – 516 (in Russian).

Manning D. The effect of Fluorine on liquidus phase bonds in the system Qz-Ab-Or with excess water at 1 kb // Contrib. Mineral. Petr. V. 76. 1981. pp. 206-215.

Shchekina T.I.[1], Rusak A.A.[1], Alfereva Ya.O.[1], Gramenitsky Ye.N. [1], Kotelnikov A.R.[2], Zinovieva N.G.[1], Bychkov A.Yu.[1], Akhmedzhanova G.M.[2] The role of lithium in the differentiation of granite melts with extreme concentrations of fluoride and distribution of rare earth elements at a

pressure of from 1 to 5 kbar UDC 552.11, 550.42.

[1]Lomonosov Moscow State University, Department of Geology, Russia, Moscow, [2] Institute of Experimental Mineralogy RAS, Russia, Chernogolovka (t-shchekina@mail.ru, aleks7975@yandex.ru; *yanaalf@yandex.ru*, engramen@geol.msu.ru, kotelnik@iem.ac.ru, nzinov@mail.ru, andrewbychkov@rambler.ru, akhm@iem.ac.ru). 119991, Russia, Moscow, Lenin Hills, 1, aud. 607. +7 (495) 939-20-40.

Introduction to the model granite system Si-Al-Na-K-F-O-H lithium in an amount of about 2 at.% at 800 ºC and 1 kbar leads to the appearance of a wide area of incompressibility between aluminosilicate and LiKNa-aluminofluoride (salt) melts in the system (Gramenitsky et al., 2005; Alferyeva et al., 2011). It is shown that the salt melt enriched with lithium in comparison with silicate is stable at 800 °C in the pressure range from 1 to 5 kbar and up to 600 ºC at 1 kbar. Rare earth elements, yttrium and scandium, along with lithium, accumulate with high separation coefficients >>1 in the salt melt in the range of 800 – 600 ºC at 1 kbar. They remain in it until its complete crystallization in the form of complex compounds of REE, Y and Sc, forming fluorides and LiKNa-fluorides during quenching. It was found that the pressure increase from 1 to 5 kbar leads to the convergence of the concentrations of Li, REE, Y and Sc in silicate and salt melts and a significant decrease in their separation coefficients.

Keywords: lithium; granite system; rare earths; separation factor; aluminosilicate; aluminofluoride; salt melts; water content; influence of pressure.

The main mechanism of differentiation in the magmatic process considered in Petrology and Geochemistry of elements is the mechanism of crystallization differentiation with fractionation of crystalline phases. This mechanism does not explain a number of processes occurring in granite melts at the latest stages of their differentiation. This refers to the melts from which ongonites, elvans, Li-F and cryolite-containing granites and their pegmatites are formed. They are enriched with fluorine and often lithium – incompatible elements that undoubtedly affect the formation of these rocks. Our experiments are aimed at explaining the Genesis of such rocks and the associated ore concentrations of rare elements. At the first stage of experimental work in the model granite system, Si-Al-Na-K-Li-F-O-H (Gramenitsky et al., 2005), we set ourselves the task of obtaining a silicate melt saturated with water and fluorine as an analogue of pegmatite magma in the assumption that it will be separated from granite magma by the mechanism of liquid incompressibility. We have not obtained such a silicate melt. With an increase in the fluorine content of more than 3 wt. % we consistently obtained alkaline-aluminium-fluoride phases corresponding to the composition of K-Na cryolite (Crl or Cry) on the liquidus of the system. Only in a narrow high-alumina region of the compositions of the system

was found a salt fluoride melt, equilibrium with silicate, close in composition to the chiolite. Introduction to the Li system (in an amount of more than 1 wt. %) led to a significant expansion of the field of the salt melt in the system by reducing the field of cryolite (Alfereva et al., 2011). Aluminum fluoride melt, has a variable composition depending on the part of the system. The ratio of Al/Na in it ranges from 20/80 to 40/60. We had been delineated by an extensive region of immiscibility in the system Si-Al-Na-Li-F-O-H. An experimental study of the system showed that for the explanation of the origin of pegmatites and leucocratic, rich in fluorine and lithium species, inevitably the involvement of physico-chemical systems involving not only fluid (volatile), and salt components. The mechanism of liquid incompressibility in natural systems can play a significant role in the differentiation of granite melts. In the 2000s, there was an increased interest in experimental work in this area due to the detection of salt melts in melt inclusions in granitoid minerals (Badanina et al., 2006; Andreeva et al., 2007; Solovova et al., 2010). In this paper (Peretyazhko et al., 2010) melt of cryolite and fluorite composition is described in inclusions. Inclusions of silicate-salt melts were also obtained in artificial inclusions in minerals (Kotelnikova, Kotelnikov, 2008). Largely due to the study of melt inclusions, magmatic deposits now include large rare-metal deposits of Zashikhin and Katuginskoye, which are confined to cryolite-containing granites. Previously, they were fully or partially ranked as metamorphogenic-metasomatic. We believe that all manifestations of cryolite-containing granites, including the exclusive Ivigtut Deposit and smaller formations, should be attributed to magmatic ones with the participation of fluoride melts during their differentiation (Shchekina T. et al, 2013). Salt and, in particular, high-fluoride aqueous fluids and fluoride melts are of particular importance in explaining the nature of the distribution of rare earth elements in the differentiation of granite magmas and subsequent metasomatosis and ore formation in granites (Irber, 1999, Gusev A.I., Gusev A.A., 2011).

In this paper, special attention is paid to the behavior of lithium in the silicate-salt high-fluoride system Si-Al-Na-K-Li-F-O-H. Along with fluorine, lithium manifests itself as an important element that affects the phase relations in the system and provides a manifestation of the liquation separation of the salt melt from the aluminosilicate. Its influence on the distribution of rare-earth elements between melts is known (Gramenitsky, Shchekina, 2005; Veksler, 2005). Before this work the task was to investigate the influence of pressure on the nature of the distribution of Li between the silicate and salt phase and the distribution of rare earth elements between them.

Conditions and methods of experiments. The initial materials for the experiments were a fluoride-silicate mixture consisting of chemical reagents SiO_2, NaF, LiF, AlF_3, Al_2O_3, K_2SiF_6, and distilled water. Rare earth elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, as well as Y and Sc were introduced into the system in the form of oxides of 0.5 wt.% element's. The experiments were carried out on the installation of high gas pressure with internal heating. The duration of the experiments was 5-7 days. Platinum ampoules with a diameter of 3 mm were used as containers for the substance of the experiments. Experimental conditions: temperature 800 ° C and pressure 1, 2, 3 and 5 kbar. The experiments were carried out with a certain reference composition of the model granite, similar in composition to granite eutectic at 1 kbar and 4 mass. % F (Manning D., 1981), under H2O saturation conditions. The experiments also differed in the content of injected water from 2 to 50 %. The study of phase relations and chemical composition of solid products of the experiments was carried out in the Laboratory of local methods of substance research of the Department of Petrology of the geological faculty of Moscow state University. Electronic images are obtained in the mode of reflected electrons (BSE). Analysis of the main elements and fluorine in phases was performed using a scanning electron microscope Jeol JSM-6480LV (Japan) with energy dispersion Oxford X-MaxN and crystal diffraction INCA Wave-500 (Oxford Instrument Ltd., UK) spectrometers. Shooting conditions: voltage 20 kV, current 0.7 nA. The accuracy of the estimation of the main elements in the synthesized phases was 2 – 5 comparative %. Instrument error in the measurement of fluorine was ±1 % of the element concentration. In a number of samples the main and rare-earth elements in silicate glasses were studied using the electron probe microanalyzer Superprobe JXA-8230 (Japan). Analysis of rare earth elements, Y, Sc and Li was performed by inductively coupled plasma mass spectrometry in the laboratory of experimental Geochemistry of the Department of Geochemistry of the geological faculty of Moscow state University. Measurements were carried out on a mass spectrometer with ionization in inductively coupled plasma with double focusing Element-2. The measurement error was 1-3 comparative %.

Conclusion. The study of phase relations showed that at a temperature of 800 °C, a pressure of 1-5 kbar and a different water content from 2 to 50 wt. % is the balance of two melts aluminosilicate (L) and aluminofluoride (salt LF). With a water content of more than 10 mass.% the fluid phase is in equilibrium with two melts, that is the system passes to the 3-phase equilibrium. It is macroscopically seen that the increase in water content contributes to a significant increase in porosity and increase in the size of the pores themselves, especially in silicate melts. Increasing the pressure to 5 kbar leads to a more uniform distribution of quenching REE fluorides in the globules of the salt phase. The content of Li in the silicate phase ranged from ~ 1 to 1.5 wt. %, and salt - from 1 to 11 wt. %. The separation coefficients in all experiments exceed 1, i.e. Li is always distributed mainly in the salt phase (Fig.1a).
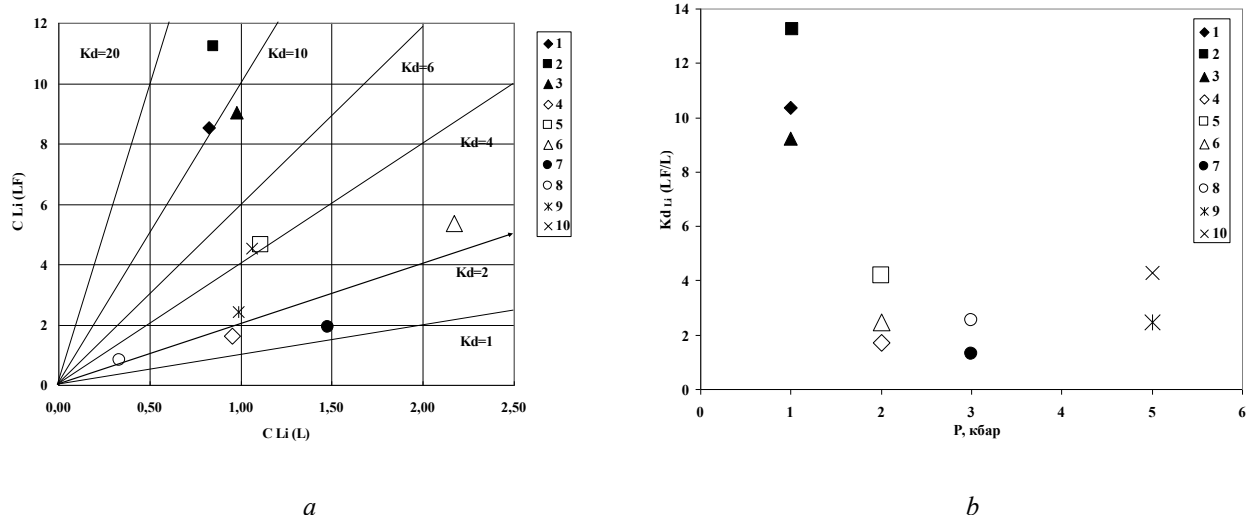

a

b

Fig. 1. a. The distribution of Li (wt. %) between aluminosilicate (L) and salt (LF) melts at 800 °C, 1 - 5 kbar. Symbols: experiment numbers at 1 kbar pressure– 1 - 776, 2 – 778, 3 – 777 with 2,06, 5,12 and 9,3 wt. % H_2O, respectively; at a pressure of 2 kbar– 4 – 785, 5 – 786, 6 – 787 with 2,4, 4,9, 11,1 wt. % H_2O, respectively; at a pressure of 3 kbar – 7 - 817, 8 – 718 with 30 and 50 wt. % H_2O, respectively; at a pressure of 5 kbar – 9 - 811, 10 - 812 with 5 and 10 wt. % H_2O, respectively. Lines correspond to the partition coefficients (LF/L) is equal to from 1 to 16. b. The dependence of the lithium separation coefficients KdLi(LF/L) between the salt and silicate melts on the pressure from 1 to 5 kbar at T=800 °C. The designations are the same as in Fig. 1a.

In the experiments carried out with 1кбар, observed the most high (8,5-11,2 wt. %) Li concentrations in the salt phase compared with experiments at higher pressures at water content in the system from 2.06 to 9, 34 wt. %. Li concentrations in aluminosilicate glass in experiments at 1 kbar not higher than 1 wt. %, while in samples obtained at higher pressures, it reaches 1.5-2 wt.%. Accordingly, the lithium separation coefficients $Kd_{Li}^{(LF/L)} = C_{Li}^{LF}/C_{Li}^{L}$, where the C_{Li}^{LF} - concentration of Li in the salt melt and the C_{Li}^{L} - concentration of Li in the silicate melt are significantly higher for samples obtained at a pressure of 1 kbar (from 9.23 to 13.24) than at higher pressures. Points corresponding to pressures 2, 3 and 5 kbar (Fig. 1a) overlap and occupy the field in the interval between Kd=1 to Kd=4. Thus, it was found that the separation coefficients of Li decrease with increasing pressure (Fig.1b).

The study of the distribution coefficients of rare earth elements, yttrium and scandium between salt and silicate melts showed that they have a direct relationship with the nature of lithium distribution. For fig.2 it can be seen that the higher $Kd_{Li}^{(LF/L)}$, the higher $Kd_{REE, Y, Sc}^{(LF/L)}$.
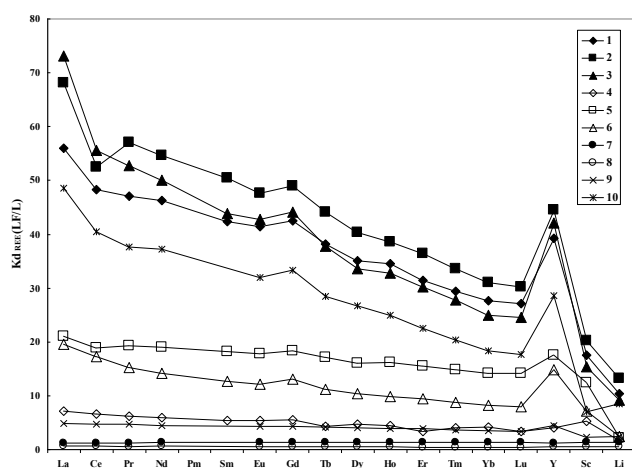

Fig. 2. Dependence of separation coefficients $Kd_{REE, Y, Sc}^{(LF/L)}$ and $Kd_{Li}^{(LF/L)}$ between salt and silicate melts on pressure at 800 °C. Designations as in Fig. 1 a,b.

The highest coefficients of separation of REE, Y and Sc are typical for experiments at 1 kbar. Their spectra are located at the top of the graph (Fig.1b). Below are the spectra for the experiment at 5 kbar and 10 % H_2O, then the spectra of samples obtained at 2 kbar with different water contents and the spectrum at 5 kbar and 5 % H_2O and below all – spectra at 3 kbar. More research is needed to explain these data. However, the trends in the distribution of elements in all experiments are similar. The shape of REE, Y and Sc spectra has a great similarity. The separation factors decrease relatively smoothly from light to heavy REE, forming a small maximum in the

Gd region. Yttrium manifests itself as a light REE, and Sc – like heavy. There is a dependence on the water content in the system, but it is not natural. It should be noted that against the background of weak changes in the composition of silicate and salt melts, depending on the pressure, rare earth elements and lithium react to changes in pressure and water content. Our data confirm that the entry of Li into the granite system acts in the same direction as fluorine and water, providing, apparently, a decrease in the viscosity of the melt and a decrease in the temperature of its crystallization. New results are obtained indicating a decrease in the coefficients of separation of REE, Y, Sc and Li between the salt and silicate melts with increasing pressure in the system. It is assumed that the presence of three components in the system – H_2O, F and Li causes a change in the structure of the silicate melt, contributing to the transition of part Al from tetrahedral to octahedral coordination, and this, apparently, affects the distribution of rare elements. Trivalent rare-earth elements, Y and Sc are readily included in the salt aluminum fluoride melt, forming complex compounds with F and probably c Li. The undoubted fact of Li influence on the phase relations, namely, the appearance of a wide area of incompressibility between silicate and salt melts in the granite system, determines its great influence on the behavior of rare elements.

Summary.

1. It is shown that the equilibrium of aluminosilicate and aluminofluoride (salt) melts in the model granite system was found at a temperature of 800 °C and 1 kbar, 4-10 mass.% H_2O, stored up to a pressure of 5 kbar at a water content of 2 to 50 wt. %.

2. The separation coefficients of rare earth elements, yttrium and scandium between salt and silicate melts increase with increasing lithium separation coefficients.

3. Increasing the system pressure from 1 to 5 kbar reduces the separation coefficients of REE, Y, Sc and Li between the salt and silicate melts.

References:

Alferyeva Ya.O., Gramenitsky E.N., Shchekina T.I. Experimental study of phase relations in the lithium bearing fluorine-rich gaplogranite and nepheline-syenite systems. Geochemistry (7). 2011. P. 713-728 (in Russian).

Andreeva I.A., Kovalenko V.I., Yarmolyuk V.V., Listratova E.N., Kononkova N.N. Incidence of silicate and salt (Li, Na, F) melts in the comendits of the occurrence of the Dzarta-Huduk (central Mongolia): data of the study of melt inclusions.

Doklady Earth Science. 414 (4). 2007. P. 528-534 (in Russian).

Gramenitsky E.N., Shchekina T.I., Devyatova V.N. Phase relations in fluorine-containing granite and nepheline-syenite systems and distribution of elements between phases. Moscow: GEOS. 2005. P. 186 (in Russian).

Kotelnikova Z.A., Kotelnikov A.R. NaF-bearing fluids: experimental study at T = 500-800 °C and P = 2000 bar by the synthetic fluid inclusion method in quartz. Geochemistry (1). 2008. P. 54-68 (in Russian).

Peretyazhko I.S., Savina E.A. Tetrade-effects in the spectra of distributions of rare earth elements of granitoid as the indicator of the fluoride-silicate liquid incidence in the magmatic systems. Petrology 18 (5). P. 536-566 (in Russian).

Solovova I.P., Girnis F.A., Kovalenko V.I. Liquid incidence in the system pantellerite liquid-F-Cl. Doklady Earth Science 433 (3). 2010. P. 390-393 (in Russian).

Shchekina T.I., Gramenitsky E.N., Alferyeva Ya.O. Leucocratic magmatic melts with fluorine limit concentrations of fluorine: experiment and natural relations. Petrology 21 (5). 2013. P. 499 – 516 (in Russian).

Badanina E. V., Trumbull R. B., Dulski P., Wiedenbeck M., Veksler I. V., Syritso L. F. The behavior of rare earth and lithopile trace elements in rare-metal granites: a sudy of fluorite, melt in clutions and host rocks from the Khangilay complex, Transbaikalia, Russia. Can. Mineral. 44. 2006. P. 667-692.

Irber W. The lanthanide tetrad effect and its correlation with K/Rb, Eu/Eu*, Sr/Eu, Y/Ho, and Zr/Hf of evolving peraluminous granite suites. Geochim. Cosmochim. Acta63 (3/4). 1999. P. 489-508.

Manning D. The effect of Fluorine on liquidus phase relationships in the system Qz-Ab-Or with excess water at 1 kb // Contrib. Mineral. Petr. V. 76., 1981. P. 206-215.

Veksler I. V., Dorfman a.m., Kamenetcky M., Dulskii P., Dingwell D. B. Partitioning of lanthanides and Y between immiscible silicate and fluoride melts, fluorite and cryolite and the origin of the lanthanide tetrad effect in igneous rocks. Geochim. Cosmochim.Acta 69 (11). 2005. P.2847-2860.

Suk N.I. Interphase distribution of elements in silicate-phosphate systems UDC 550.89:553.062

Institute of Experimental Mineralogy RAS (IEM RAS), (sukni@iem.ac.ru)

Abstract. The results of an experimental study of liquid immiscibility occurring in alkaline silicate-phosphate systems at T = 1250°C and P=2 kbar under water pressure are presented. The experiments were carried out in high gas pressure vessel. The distribution of petrogenic and ore elements between silicate and phosphate melts was studied. It is shown that the phosphate melt concentrates Ca, Mg and Na, the nature of the separation of Al and K between silicate and phosphate melts depends on the initial composition of the system, decreasing with increasing ratios (Ca+Mg)/(Na+K) and (Ca+Mg)/(Si+Al) of silicate melt. High efficiency of phosphate extraction was revealed in relation to REE, Ti, Nb, Ta, W, Sn. The partition coefficients of zirconium vary from 2.15 to 0.76, decreasing with an increase in the ratio Ca/(Na+K) and Ca/(Si+Al) and an increase in agpaiticity ((Na+K)/Al) of silicate melt.

Keywords: liquid immiscibility, silicate melt, phosphate melt, experiment, elements distribution

The liquid immiscibility that occurs in alkaline silicate-phosphate systems and the distribution of petrogenic and ore elements between silicate and phosphate melts has been experimentally investigated.

The experiments were carried out on a high gas pressure vessel at T = 1250 ° C and P = 2 kbar under dry conditions and in the presence of water (12% **by** weight of the sample). The compositions of model systems were specified by mixtures of natural minerals (nepheline, albite, diopside, potassium feldspar, apatite) and $NaPO_3$. Ore components were added in the form of oxides of rare-earth elements, Ti, Zr, Nb, Ta, as well as Na_2SnO_4 and Na_2WO_4. The obtained samples were analyzed on a Camebax X-ray microanalyzer (Cameca, France) with a Link AN-10000 energy dispersive spectrometer (Oxford Instruments, England).

In the systems studied, wide field of splitting into two immiscible liquid phases – silicate and alkali-phosphate melts, which form either droplets of one melt in another, or stand out in the form of a layer with a clear phase boundary between melts, were established (Fig. 1). Experiments conducted in dry and water-containing systems demonstrate an inversion of densities: dissolving a fluid in a phosphate melt leads to a decrease in its specific gravity compared to a silicate melt, as a result of which the salt melt floats up, which in this case is located in the upper part of the sample (Fig. 1).

The compositions of coexisting liquids are well illustrated by the diagram in coordinates ($Na_2O + Al_2O_3$) – P_2O_5 – SiO_2. Fig.2 shows the liquid immiscibility areas of melts for the various systems studied (Suk, 1993). These data reflect a narrowing of the liquid separation zone when CaO and MgO are added to the alkaline melt in diopside composition, which indicates an increase in the mutual solubility of phosphate and aluminosilicate melts (Fig. 2a, c) and is consistent with the data (Delitsyna et al., 1989). The same trend is observed when adding the first percent of TiO_2 to the system (Fig. 2b). A regular change in the compositions of coexisting melts is observed: the more the salt component is contained in the system, the more acidic the immiscible silicate phase has.