Na (Table 2). The mineral becomes impregnated with granitoid melt like a sponge. The melt flows into among the small "islands" of loparite, and it dissolves the mineral (Fig. 4).

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Kotelnikov A.R., Korzhinskaya V.S., Suk N.I., Van K.V., Virus A.A. Experimental study of zircon and loparite solubility in silicate melts UDC 550.89

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Abstract. The solubility of zircon in an aluminosilicate melt was experimentally investigated at T = 1000°C and P=2 kbar in the presence of water or a solution of 1M KF. In the experiments, zircon synthesized under hydrothermal conditions and previous melted aluminosilicate glasses with different agpaiticity (from 0.81 to 2.5) were used. It is shown that with an increase in the agpaitic coefficient (K = (Na + K) / Al) of the melt, the solubility of zircon increases 10 or more times (with maximum agpaiticity). The solubility of loparite in an aluminosilicate melt of different composition was studied experimentally at T=1200 and 1000°C and P=2 kbar in dry conditions and in the presence of 10 wt.% H_2O. The initial material was synthetic glass of malignite and eutectic albite-nepheline composition, as well as natural loparite of the Lovozerskiy massif. It is established that the solubility of loparite depends on the composition of the aluminosilicate melt.
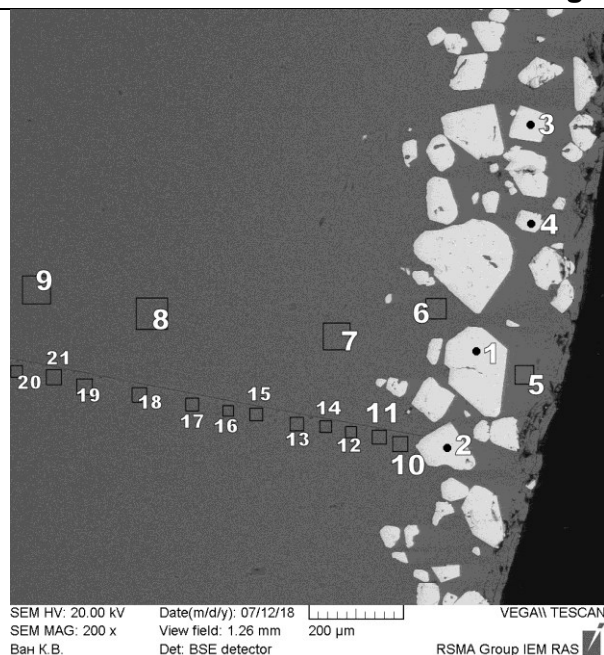
Keywords: *silicate melt, zircon, loparite, solubility, experiment*

Experimental method The solubility of zircon and loparite in an aluminosilicate melt was experimentally investigated at T=1000°C and P=2 kbar in a high gas pressure vessel. The installation is characterized by the accuracy of setting and determining the temperature and pressure, large working volume, high performance and considerable duration of experiments. A heater with tungsten-rhenium or molybdenum wire as a heating element allows experiments to be carried out at temperatures up to 1400°C. The temperature was controlled and monitored with Pt-PtRh10 thermocouples with an accuracy of ± 2°C, the pressure was measured with a spring pressure gauge with an error of ± 1%. The gradient free zone is 50 mm, the working diameter of the furnace is 15 mm. The experiments were conducted in welded platinum ampoules, where the sample was placed and, if necessary, the initial solution was poured.

The solubility of zircon was studied in the presence of water or a solution of 1M KF. The duration of the experiments was 5 days. In the experiments, zircon synthesized under hydrothermal conditions and granite (Orlovka deposit, well 42) of the following composition were used (mas.%): SiO_2 – 72.10; TiO_2 – 0.01; Al_2O_3 – 16.14; Fe_2O_3 – 0.68; MnO – 0.09; CaO – 0.30; MgO – 0.01; Na_2O – 5.17; K_2O – 4.28; P_2O5 – 0.02; F – 0.32; H_2O – 0.18, which was previously melted at atmospheric pressure and a temperature of 980°C. Also aluminosilicate glasses with different agpaitic coefficient $K_{agp}=(Na+K)/Al$ (from 0.80 to 2.5) were previously prepared by melting. The experiments were carried out in 7x0.2x50 mm platinum ampoules, into which about 50 mg of granite glass, 5 mg of zircon crystals and about 15 mg of water or 1 M KF were loaded. Ampoules were hermetically sealed and placed in a "gas bomb" for the experiment. The duration of such experiments was 5 days.

The solubility of loparite was studied under dry conditions and in the presence of 10 wt.% H_2O. The duration of the experiments was 1 day. The initial material was synthetic glass of malignite, urtite and eutectic albite-nepheline composition, previously melted at T=1450°C in a furnace with chromite-lanthanum heaters in platinum crucibles for 2 hours, and also natural loparite of the Lovozerskiy massif.

The compositions of all samples after experiments were determined by electron probe X-ray spectral analysis (EZRSA) using a Tescan Vega II XMU scanning electron microscope (Tescan, Czech Republic) equipped with the INCA Energy 450 X-ray microanalysis system with energy-dispersion (INCAx-sight) and crystal diffraction (INCA wave 700) X-ray spectrometers (Oxford Instruments, England) and software platform INCA Energy +.

SEM HV: 20.00 kV | Date(m/d/y): 07/12/18 | VEGA\\ TESCAN
SEM MAG: 200 x | View field: 1.26 mm | 200 µm
Ван К.В. | Det: BSE detector | RSMA Group IEM RAS

Fig. 1. Diffusion profile in the study of zircon solubility in an aluminosilicate melt in the presence of 1 M KF (T=1000°C, P=2 kbar).
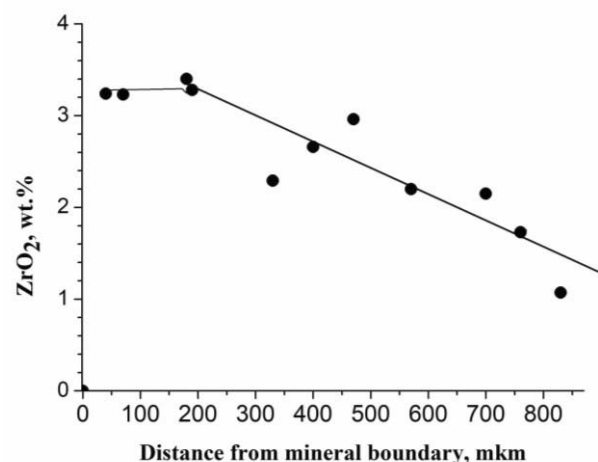
Zircon solubility in an aluminosilicate melt at T= 1000°C, P=2 kbar To estimate the solubility of zircon in an aluminosilicate melt, we used the method of measuring the diffusion profile of the ZrO_2 content in quenching glass from the boundary of the zircon crystal. Figure 1 shows the selected diffusion profile, and fig. 2 shows an example of the measured diffusion distribution profile of ZrO_2 when zircon is dissolved in a granitic melt in the presence of 1 M KF. The figure clearly shows that at a distance of ~ 200 μm, the ZrO_2 content in the glass remains constant and then begins to decrease. This gives grounds to take these maximum values as the solubility of ZrO_2 in the melt.

To determine the effect of agpaiticity on the solubility of zircon in an aluminosilicate melt, experiments were carried out in systems with different K_{agp}=(Na+K)/Al: from 0.80 to 2.5 in the presence of water. The dependence of the solubility of ZrO_2 in the melt on agpaiticity was revealed: with an increase in K_{agp} from 0.8 to 2.08, the solubility of ZrO_2 in glass increases from 0.2 wt.% to 6.54 wt.%. (Fig. 3).
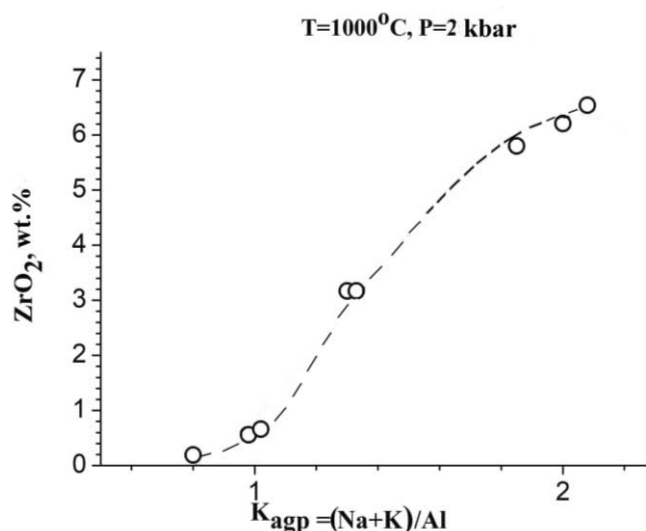
Loparite solubility in an aluminosilicate melt at T=1000°C, P=2 kbar In the course of the experiments, the aluminosilicate melt was saturated with elements characteristic of loparite. At the same time, the formation of titanium-silicates of rare earths was observed, and in water-containing systems – the growth of rims depleted in titanium and enriched in rare-earth elements on loparite crystals. Apparently, this may indicate incongruent dissolution of loparite.

The solubility of loparite can be estimated by determining the sum of oxides of rare earths (La_2O_3, Ce_2O_3, Nd_2O_3) and oxides of elements inherent only in loparite (TiO_2, Nb_2O_5, SrO) in glass obtained as a result of the experiment. The presence of water on the solubility of loparite had almost no effect. It is established that the solubility of loparite depends on the composition of the aluminosilicate melt (Fig. 4, 5): it increases with increasing agpaiticity ((Na+K)/Al) and decreases with increasing Ca/(Na+K) ratio. According to preliminary data, the solubility of loparite in the melt of the malignite composition according to estimates is on average ~ 6.58 wt. %, in the melt corresponding to the composition of albite-nepheline eutectic – on average ~ 5.19 wt. %, and in the melt corresponding to the composition of urtite – 3.7.


Fig. 2. An example of the measured profile of the diffusion ZrO_2 distribution upon dissolution of zircon in the granite melt with 1 M KF (Kagp=0.80, T=1000°C, P=2 kbar).

Fig. 3. Dependence of zircon solubility in an aluminosilicate melt in the presence of water on agpaiticity (Kagp=(Na+K)/Al).
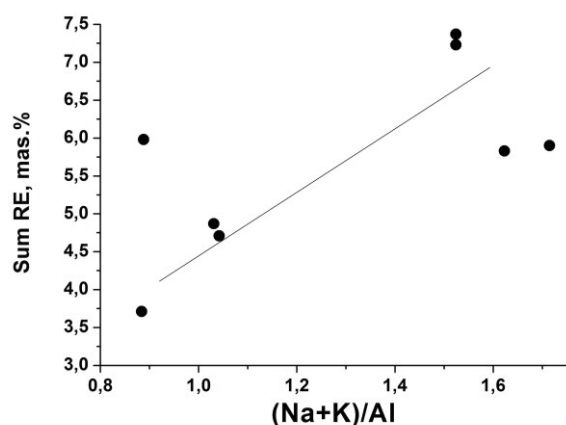
Fig. 4. Dependence of loparite solubility on agpaiticity of aluminosilicate melt ((Na+K)/Al). Sum RE = TiO_2 + Nb_2O_5 + SrO + La_2O_3 + Ce_2O_3 + Nd_2O_3.
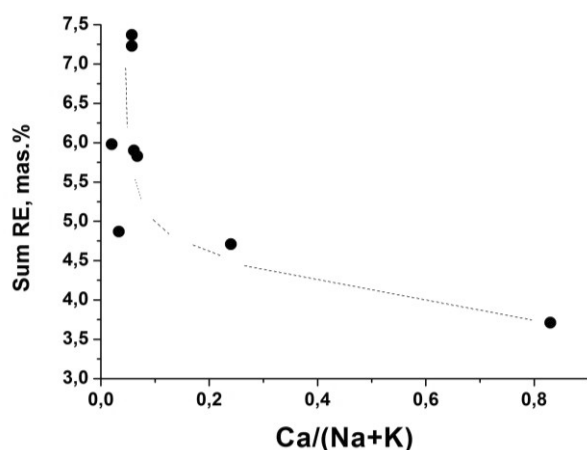
Fig. 5. Dependence of loparite solubility on Ca/(Na+K) of aluminosilicate melt. Sum RE = TiO_2+Nb_2O_5+SrO+La_2O_3+ Ce_2O_3+ Nd_2O_3.

Such values of solubility are not enough to explain the content of loparite in the malignite horizon, to which rich loparite ores are confined. The content of loparite in malignite reaches 20-25%. The data obtained may explain the presence of accessory loparite in the rocks.

In water containing systems, the formation of an emulsion is also observed, which is expressed in the presence of small droplets enriched with elements characteristic of loparite. Apparently, this is a manifestation of titanate-silicate liquid immiscibility (Suk, 2007), which was previously obtained in water containing aluminosilicate systems containing ore elements (Ti, Nb, Sr, REE).

Thus, the formation of rich loparite ores can be explained only by the appearance of titanate-silicate immiscibility, as a result of which the magmatic melt is significantly enriched in ore components.

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Kotelnikov A.R.[1], Shapovalov Yu.B.[1], Suk N.I.[1], Kotelnikova Z.A.[2], Korzhinskaya V.S.[1] Liquid immiscibility and problems of ore genesis UDC 550.89:553.062

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Abstract. The results of an experimental study of phase relations and distribution of elements in the systems of silicate melt – salt (carbonate, phosphate, fluoride, chloride) melt, silicate melt I – silicate melt II, as well as in fluid-magmatic systems in the presence of alkali metal fluorides are presented. Salt extraction of a number of ore elements (Y, REE, Sr, Ba, Ti, Nb, Zr, Ta, W, Mo, Pb) was studied in liquid immiscibility processes in a wide temperature range of 800–1250°C and pressure of 1–5.5 kbar. It is shown that the partition coefficients are sufficient for the concentration of ore elements in the quantity necessary for the genesis of ore deposits. In the fluid-saturated trachyrhyolite melt, separation into two silicate liquids was obtained, and the partition coefficients for a number of elements (Sr, La, Nb, Fe, Cr, Mo, K, Rb, Cs) between phases L1 and L2 were determined. The processes of interaction of a heterophase fluid in the granite (quartz) - ore mineral - heterophase fluid (Li, Na, K-fluoride) system were studied at 650–850°C and P =1 kbar. The formation of a phase of a highly alkaline fluid-saturated silicate melt – Ta and Nb concentrator – is shown as a result of the reaction of the fluid with the rock and ore minerals.

Keywords: liquid immiscibility, silicate melt, salt melt, experiment, ore genesis

The problem of liquid immiscibility in natural endogenous processes was studied by many prominent scientists in petrology (F.Yu. Levinson-Lessing, A.A. Marakushev, D.S. Korzhinskiy, V.A. Zharikov, E. Roedder, etc.). To date, an extensive petrological and geochemical material has been accumulated, which indicates phase heterogeneity of natural melts and solutions. However, the question of the connection of this heterogeneity with the processes of magmatism and ore formation remains relevant. Works for example (Marakushev, 1979; Marakushev et al., 1983; Gramenitskiy, 1986) are devoted to solving this problem.

According to numerous experimental data, magmas are concentrators of ore metals with respect to equilibrium with them aqueous fluids of the most diverse composition. The data on the study of the