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GEOCHEMISTRY

Experimental Study of Alkaline Magmatic Aluminosilicate Systems: Implication for the Genesis of REE–Nb Loparite Deposits

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The study of the formation mechanism of alkaline intrusive and related deposits is of great theoretical and applied significance. The alkali magmatic complexes often host large deposits of rare and radioactive elements (Sr, REE, Ti, Nb, Zr, Th, U, and others). In this respect, the Lovozero alkaline massif (Kola Peninsula) with loparite and eudialyte mineralization is one of the most productive bodies. The loparite deposits localized in the urtite horizon were taken as the modeling object. For many years, they have been studied in different aspects, including experimental modeling [3, 9].

The experimental study of phase equilibria in the loparite–nepheline [3] and melting in the lujavrite–loparite [9] systems without the participation of volatile components showed wide fields of loparite crystallization in the agpaitic melt. We carried out experiments under virtually natural conditions of magma and ore formation strongly defined by fluid–magma interaction [8, 10, 11].

To reveal the impact of fluid on the magmatic systems, we investigated the aluminosilicate alkaline magmatic systems containing Ti, REE (La, Ce, Y), Sr, and Nb in the fluid-present (10 wt %) and fluid-absent conditions at 1200°C and 2 kbar. The starting charge was made from natural minerals (albite and nepheline) or their gels. The albite accounted for 60–62 wt % of the silicate component. In addition, TiO_2, La_2O_3, CeO_2, Y_2O_3, and Nb_2O_5, as well as CaO and $SrCO_3$ occasionally, were added as ore components. The spectrum of ore elements was variable, with the total oxide content ranging from 10 to 25 wt %. The experiments were performed in sealed Pt ampoules (3 mm across) by treating the charge in a high-pressure apparatus for 1 day and its quenching. Run products were analyzed on a digital scanning CamScan MV2300 (VEGA TS 5130MM) microscope equipped with YAG secondary and back-scattered electron detectors and a Link INCA Energy energy-dispersive microprobe equipped with a Si (Li) semiconductor. Results of microprobe analysis were recalculated with the INCA Energy 200 program and subsequently recalculated with a software package developed at the Institute of Experimental Mineralogy.

The fluid-present experiments with aluminosilicate systems with addition of only TiO_2 (10 and 20 wt % of charge) produced silicate glass with rutile crystals. The TiO_2 content in the silicate glass varied from 3.9 to 4.9 wt %. In the fluid-absent experiments with systems containing Ti, REE (La, Ce, Y), Sr, and Nb, we obtained loparite crystals in a silicate matrix (Fig. 1a).

Under fluid-present conditions, the same systems yielded basically different results owing to the immiscible splitting into two liquids [13]: (i) the predominant aluminosilicate liquid (matrix) and (ii) drops enriched in Ti, REE (La, Ce, Y), Sr, and Nd (Fig. 1b). The drops are compositionally close to the loparite solid solutions with silicate admixture (table, Fig. 2). Crystals of loparite or REE titanoniobates also formed, probably due to the initial composition of the charge and additions of ore elements. The drops vary from 1 to 3 μm in size, which is comparable with the X-ray generation region. Therefore, the compositions of small drops were corrected by subtraction of the silicate component (admixture of aluminosilicate matrix entrained by microprobe beam) from the obtained analysis and the recalculation of results to 100%. The correction was made proportional to the amount of drops of potassium, which is present only in the aluminosilicate melt. The table lists the representative analyses of immiscible phases. Figure 2 shows the results of fluid-present experimental immiscible splitting of the melt into two phases at 1200°C and 2 kbar. For comparison, the figure also presents the average compositions of urtites and lujavrites from different layers of the differentiated

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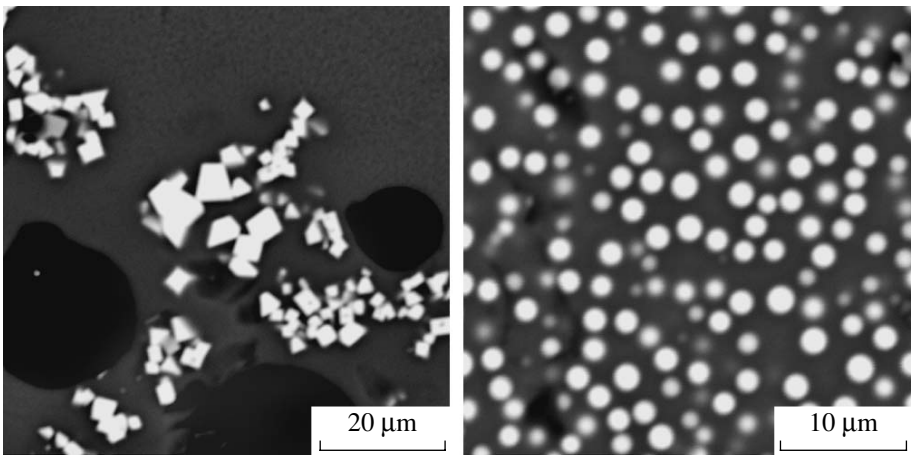

Fig. 1. (a) Loparite crystals formed without the participation of volatile components in the aluminosilicate matrix and (b) drop layering in the same system under the pressure of aqueous fluid at 1200°C and 2 kbar. Back-scattered electron images.

complex of the Lovozero alkaline massif [5] and the average compositions of loparites from urtites, malignites, and lujavrites [2]. It is seen that the natural rock compositions are similar to those of experimental phases produced by the liquid immiscibility under the pressure of aqueous fluid.

The liquid immiscibility was previously obtained by many researchers in both silicate–salt (silicate–phosphate, silicate–fluoride, silicate–carbonate, silicate–chloride, and others) and salt-free silicate systems. The possibility of the existence of two liquid phases in the

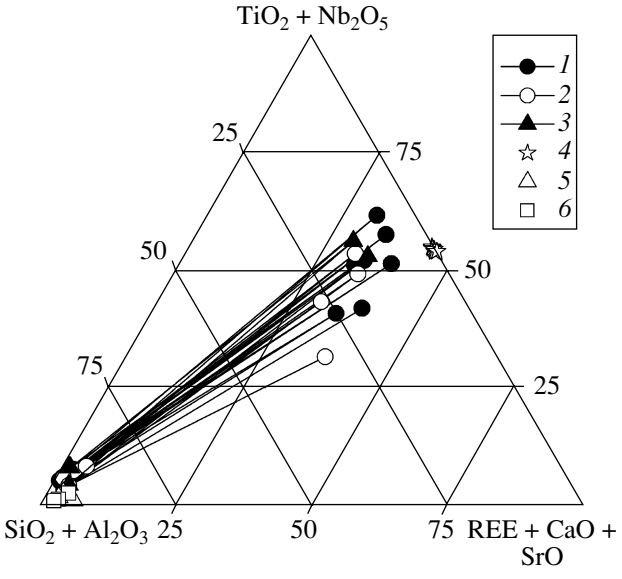

Fig. 2. Results of experimental splitting of the melts into two phases at 1200°C and 2 kbar in the presence of aqueous fluid (wt %). The tie lines connect the coexisting phases. (*1*) Nb-bearing systems; (*2*) Nb-free systems; (*3*) Nb-, Sr-, and Y-bearing systems; (*4*) compositions of loparites of the Lovozero Massif [2]; (*5*) urtites [5]; (*6*) lujavrites [5] of the Lovozero Massif.

experimental silicate systems $CaO–SiO_2$, $MgO–SiO_2$, and $FeO–SiO_2$ (without salt components) was first shown in the fluid-absent experiments by Greig [14]. However, the compositions of these systems were too different from those of natural rocks to explain the genesis of natural objects. At the same time, the liquation temperature was extremely high (about 1700°C). Later, Roedder [12] found a stable immiscibility field in the $K_2O–FeO–Al_2O_3–SiO_2$ system that is split into two (Fe-rich and Si-rich) immiscible liquids. Grigor'ev and Iskyul [6] detected splitting into two immiscible liquids in the $SiO_2–MgO–CaO–Al_2O_3$ system at temperatures close to those of natural magmas (1200–1250°C). It was noted that fluorine plays a significant role in this process, significantly increasing the immiscibility field as compared to fluid-absent systems. The authors also found that boron and water facilitated liquid immiscibility of the melts. The immiscibility in simple silicate systems is attributed to the combination of network-modifying cations (hereafter, modifier cations) into independent cation–oxygen groups, which differ from silica–oxygen (network-forming) ones [4, 1]. The distribution of network-forming cations and modifier cations in the melt structure leads to the differentiation between polymerized and depolymerized areas and, correspondingly, to the unmixing into two phases. In terms of influence on the melt structure, all elements can be subdivided into three groups [7]: (1) network-forming cations (Si, P, Ti^{4+}), (2) modifier cations (K, Na, Ca, Fe^{2+}, Mg, and others), and (3) cations that can serve as both modifiers and network-forming ones (Al^{3+}, Fe^{3+}, Cr^{3+}, Ti^{3+}). The introduction of oxide to splitting silicate melts containing a weaker cation prevents immiscibility [1]. In particular, the addition of Na_2O and K_2O to the $SiO_2–CaO$ system decreases the liquation temperature [1]. Decrease in the liquidus temperature due to the introduction of fluorides and water should foster liquid immiscibility.

Compositions of layered phases in the ore-bearing aluminosilicate systems at 1200°C and 2 kbar in the presence of aqueous fluid (wt %)

Oxides	L-31		L-33		L-40		L-41		L-42	
	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2
SiO_2	49.16	10.28	50.42	9.63	52.24	4.85	46.79	8.54	47.75	5.89
TiO_2	4.24	41.71	4.40	34.41	5.04	33.66	6.28	50.53	4.05	38.11
Al_2O_3	18.56	3.44	20.05	3.14	21.08	4.45	18.96	5.84	19.43	1.59
Na_2O	9.72	3.92	7.55	3.57	9.74	3.82	8.62	5.79	7.94	1.25
K_2O	1.97	–	1.88	–	2.08	–	1.76	–	1.83	–
CaO	1.03	4.96	1.11	5.66	–	–	1.55	6.64	1.39	7.00
SrO	1.21	7.60	–	4.98	–	–	–	–	–	–
Nb_2O_5	1.09	12.38	1.87	16.74	1.19	15.87	–	–	1.40	18.84
La_2O_3	–	4.09	–	6.35	1.03	16.88	0.84	10.71	0.50	14.11
Ce_2O_3	–	5.85	–	9.39	1.25	20.47	0.81	11.95	0.46	13.21
Y_2O_3	–	5.77	–	6.13	–	–	–	–	–	–
Total	86.98	100	87.28	100	93.65	100	85.61	100	84.75	100

Oxides	L-43		L-49		L-50		L-51	
	L1	L2	L1	L2	L1	L2	L1	L2
SiO_2	54.87	8.73	51.15	3.77	52.81	7.99	53.13	7.85
TiO_2	4.85	45.84	3.06	40.08	3.94	34.79	3.51	36.33
Al_2O_3	21.73	7.04	21.09	2.20	21.29	7.42	21.41	6.20
Na_2O	10.74	6.99	8.42	2.88	9.17	7.47	10.74	2.11
K_2O	2.11	–	2.00	–	1.94	–	2.03	–
CaO	–	0.94	1.29	8.44	0.18	1.01	–	0.78
SrO	–	–	–	–	–	–	–	–
Nb_2O_5	–	–	0.93	19.22	0.77	12.54	0.69	14.71
La_2O_3	–	13.87	0.26	12.66	0.32	13.45	0.26	13.58
Ce_2O_3	–	16.59	0.21	10.75	0.35	15.33	0.36	18.44
Y_2O_3	–	–	–	–	–	–	–	–
Total	94.30	100	88.41	100	90.77	100	92.13	100

Note: (L1) Aluminosilicate melt (matrix); (L2) melt enriched in ore metals (drops). Composition of the drops is adjusted to 100%.

The aluminosilicate alkaline systems with ore metals investigated in the fluid-present conditions are also ascribed to the aforementioned systems, in which splitting is probably caused by the immiscibility of phases during the separation of network-forming cations and modifier cations in the melt (Si and Al, on the one hand, and Ti and Nb, on the other hand). The presence of Na, Ca, Sr, and REE provides favorable conditions for liquid immiscibility. Aqueous fluid in these systems also facilitates splitting into unmixed phases, thus decreasing the liquidus temperature and increasing the depolymerization of the melt.

The most important result of our experiment is the splitting of the melt into two immiscible liquids with compositions corresponding to aluminosilicate and loparite, respectively. The experimental splitting can be used to simulate the loparite mineralization and elucidate the genesis of REE–Nb loparite deposits.

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REFERENCES

1. B. G. Varshal, in *Study of Structure of Magmatic Melts* (Sverdlovsk, 1981), pp. 41–51 [in Russian].
2. K. A. Vlasov, M. V. Kuz'menko, and E. M. Es'kova, *The Lovozero Alkaline Massif* (Akad. Nauk SSSR, Moscow, 1959) [in Russian].
3. I. V. Veksler, L. N. Kogarko, and L. D. Krigman, Geokhimiya, No. 8, 1203 (1983).
4. F. Ya. Galakhov and B. G. Varshal, in *Phenomena of Liquation in Glasses* (Leningrad, 1969) [in Russian].
5. V. I. Gerasimovskii, V. P. Volkov, L. N. Kogarko, et al., *Geochemistry of the Lovozero Alkaline Massif* (Nauka, Moscow, 1966) [in Russian].
6. D. P. Grigor'ev and E. V. Iskyul, Izv. Akad. Nauk SSSR, Ser. Geol., No. 1, 77 (1937).
7. V. M. Kalugin, Candidate's Dissertation in Geology and Mineralogy (Novosibirsk, 2002) [in Russian].
8. L. N. Kogarko, *Problems of the Genesis of Agpaitic Magmas* (Nauka, Moscow, 1977) [in Russian].
9. L. N. Kogarko, in *The Russian Arctic: Geological Evolution, Metallogeny, and Geoecology* (St. Petersburg, 2002), pp. 773–787 [in Russian].
10. F. A. Letnikov, I. K. Karpov, A. I. Kiselev, and B. O. Shkandrii, *Fluid Regime of the Earth's Crust and Upper Mantle* (Nauka, Moscow, 1977) [in Russian].
11. A. A. Marakushev, E. N. Gramenitskii, and M. Yu. Korotaev, Geol. Rudn. Mestorozhd., No. 1, 3 (1983).
12. E. Roedder, in *The Evolution of the Igneous Rocks. Fiftieth Anniversary Perspectives*, Ed. by H. S. Yoder (Princeton Univ., Princeton, 1979; Moscow, Mir, 1983).
13. N. I. Suk, *Proceedings of Annual Seminar on Experimental Mineralogy, Petrology, and Geochemistry, Moscow, Russia, 2006* (Moscow, 2006), pp. 70–71 [in Russian].
14. I. W. Creig, Am. J. Sci. **13**, 1 (1927).