Vestnik Otdelenia nauk o Zemle RAN, VOL. 3, NZ6093, doi:10.2205/2011NZ000223, 2011

Liquid immiscibility in alkaline silicate systems containing Ti, Nb, Sr, REE and Zr (experiment)

N. I. Suk
Institute of Experimental Mineralogy RAS, Chernogolovka
sukni@iem.ac.ru, fax: 8 (496) 524 4425, tel.: 8 (496) 524 4425

Key words: Liquid immiscibility, alkaline magmatic systems, fluid.

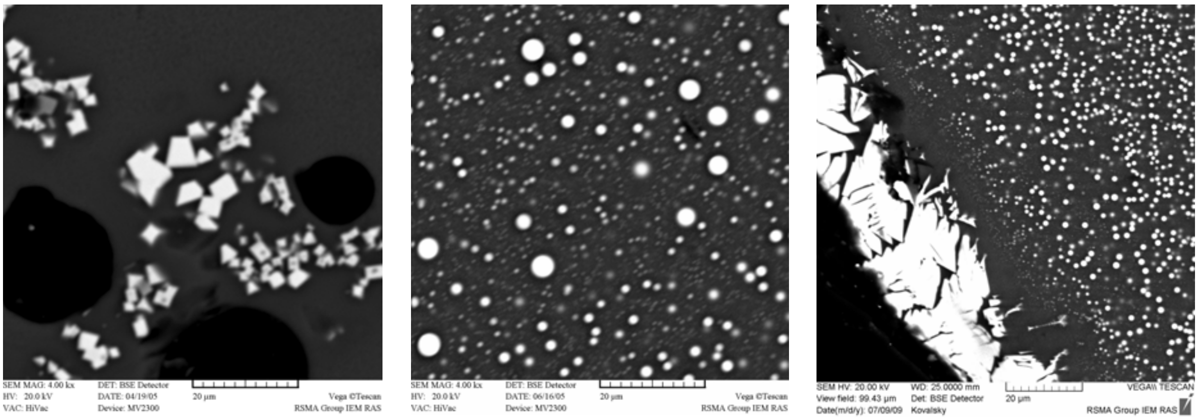
Citation: Suk, N. I. (2011), Liquid immiscibility in alkaline silicate systems containing Ti, Nb, Sr, REE and Zr (experiment), *Vestn. Otd. nauk Zemle, 3*, NZ6093, doi:10.2205/2011NZ000223.

This experimental study has been produced to close their conditions to natural ones of magmatism and ore-forming which are connected with fluid effect on the magmatic systems. Different authors have noted the role of this effect [*Letnikov et al*, 1977; *Kogarko,* 1977; *Marakushev et al*, 1983].

To reveal the fluid effect on the magmatic systems the experiments have been carried out at T=1200 and 1250°C, P=2 kbar without volatile components (in dry conditions), under water fluid pressure (the part of fluid was 10 wt.% concerning the charge) and in presence of alkaline fluid (10 wt.% and 27 wt.% NaOH solution, 1 M Na_2CO_3 or 0.5 mol NaF solution, the part of which was ~17 wt.% concerning the charge). In these regimes the aluminosilicate alkaline systems containing Ti, REE (La, Ce, Y), Nb, Sr and Zr have been investigated. The initial mixtures consisted of natural minerals (or gels) of albite and nepheline. Albite quantity in silicate part was 60-62 wt.%. Ore elements were added by oxides TiO_2, La_2O_3, CeO_2, Y_2O_3 and Nb_2O_5, sometimes CaO, $SrCO_3$ or ZrO_2 were added too. The list of ore elements was various, and sum contents of added oxides in the system was changed from 10 to 25 wt.%. The experiments were conducted in sealed platinum capsules (3 mm in diameter) in high gas pressure vessel. The duration of experiments was 1 day with subsequent quenching. The experimental samples were analyzed on an X-ray micro analyzer.

In dry systems containing Ti, REE (La, Ce, Y), Sr and Nb we observed crystallization of loparite in silicate matrix (fig. 1a). In the same systems under water fluid pressure we obtained basically different results [*Suk*, 2007] owing to the immiscible splitting into two liquids: aluminosilicate one, which formed matrix, and droplets, enriched in Ti, REE (La, Ce, Y), Sr and Nb mixed with silicate (fig. 1b). At 1200°C sometimes crystals of loparite or REE titanoniobates also formed, probably due to the initial composition of the charge and additions of ore elements.

In the systems containing alkaline fluid (10 wt.% NaOH solution) analogical droplet splitting into silicate matrix and droplets enriched in Ti, REE (La, Ce, Y), Sr and Nb have been obtained. In alkaline environment ore metals solution in silicate melt increases and loparite crystals don't form. So, content of NaOH solution in the system have positive influence on arising of liquid immiscibility.

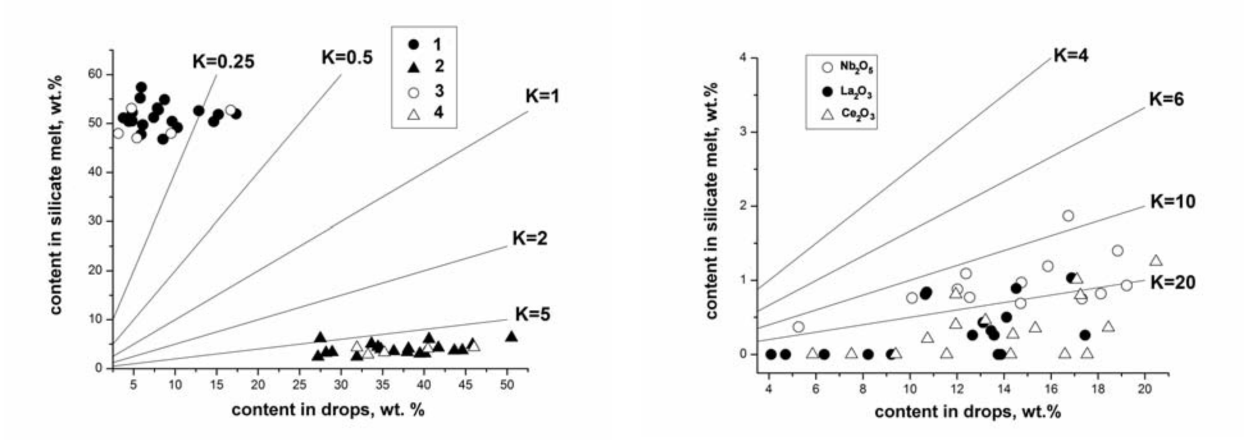


a **b** **c**

Fig. 1. Loparite crystals in aluminosilicate matrix formed without volatile components (a) and droplet splitting in the same system under water fluid pressure at T=1200, P=2 kbar (b) and at T=1250°C, P=2 kbar (c). BSE images

In experiments at T=1250°C, P=2 kbar in presence of water or alkaline fluid crystals don't form, and there are only two phases in the system: aluminosilicate melt forming matrix and the melt enriched in Ti, REE (La, Ce, Y), Sr and Nb, forming droplets. The letter can be pressed out to the sample rims and form thin layer (fig. 1c).

Based on the immiscible phases compositions obtained at 1200 and 1250°C and P=2 kbar in presence of water and alkaline fluid the diagrams of some elements partition between immiscible phases have been produced (fig. 2).



A **b**

Fig. 2. Partition coefficients of some elements between immiscible phases in the systems studied: a – for SiO_2 (1, 3), for TiO_2 (2, 4), full symbols – at T=1200°C, uncovered symbols – at T=1250°C; b – for Nb_2O_5, La_2O_3 and Ce_2O_3 at T=1200°C in presence of water or alkaline fluid

The data obtained indicate that droplets melt enrich in Ti, REE, and Nb and is depleted in Si and Al. The diagrams (fig. 2) allow to estimate the partition coefficients ($K=C_{drop}/C_{sil}$) of these elements between droplets melt and aluminosilicate melt of matrix approximately. The partition coefficients for TiO_2 are more than 5, for $SiO_2<0.35$, for Nb_2O_5 are 10-20 approximately, and for REE >15.

In the systems containing Ti, REE (La, Ce), Ca and Zr under water fluid pressure the micro droplets enriched in ore components were presented as well as ZrO_2 crystals (sometimes mixed with REE and Ti). Analogical microemulsion was observed in the systems containing 10 wt.% NaOH solution or 0.5 mol NaF solution.

The investigations in analogical system at T=1250°C, P=2 kbar show the possibility of arising of droplet layering without crystal forming at this parameters. Herewith, zirconium contents in droplet melt were significant (up to 6.5 wt. %).

Based on the analysis of immiscible phase's compositions in the presence of water or alkaline fluid the diagrams of some elements partition between these phases have been produced (fig. 3). The data obtained show the possibility of zirconium concentrating together with Ti and REE due to the process of liquid immiscibility of this type. The diagram (fig. 3) allow to estimate the partition coefficient of ZrO_2 ($K=C_{drop}/C_{sil}$) between droplets melt and aluminosilicate melt of matrix approximately. It is from ~3.5 to 9.

Investigated in this study in the presence of water fluid aluminosilicate systems containing ore metals apply to the same systems in which separation is likely to be explained by phase immiscibility arising as a result of the separation of net forming kations and kation-modificators in the melt structure [*Varshal*, 1981; *Galakhov & Varshal*, 1969]. Content in the system of Na, Ca, Sr, REE oxides have positive influence on the arising of liquid immiscibility. Fluid (water or alkaline) in these systems is the factor of melt separation into immiscible phases by decrease of liquidus temperature and increase of melt depolimerization.

Obtained droplet splitting into two immiscible liquids one of which have aluminosilicate composition and another one have composition close to that one loparites may modeling the loparite ore forming at the magmatic stage and have grate significant for explanation of genesis of REE-Nb (loparite) deposits. Moreover, the experiments demonstrate the possibility of zirconium concentrating together with Ti and REE due to the process of liquid immiscibility of this type. It can have grate significant for explanation of genesis of eudialyte ore mineralization.

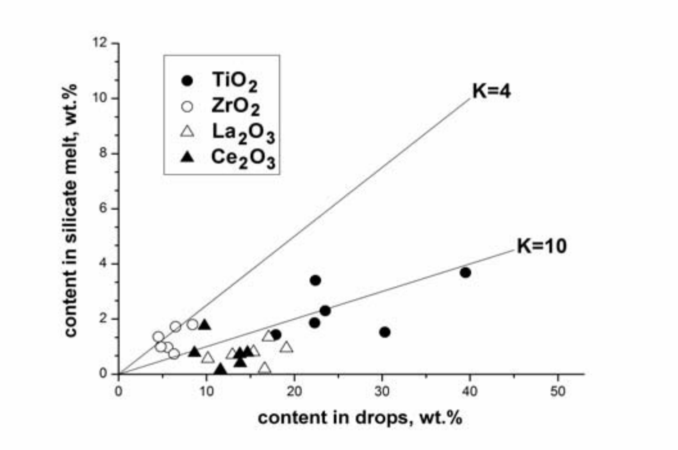


Fig. 3. Partition coefficients of some elements between immiscible phases in the systems containing ZrO_2 at T=1200 and 1250°C and P=2 kbar in presence of water or alkaline fluid

This study was supported by RFBR, project № 07-05-00217 and NS-3634.2010.5.

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