

**Experimental study of systems alkaline silicate melt – low concentrated water-sulphate fluid at T=1250°C and P=2 kbar**

N. I. Suk, A. R. Kotelnikov

Institute of Experimental Mineralogy RAS, Chernogolovka  
[sukni@iem.ac.ru](mailto:sukni@iem.ac.ru), fax: 8 (496) 524 4425, tel.: 8 (496) 524 4425

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The investigation of process of ore material selective concentration in magmatic systems remains of interest at this time. In previous works on the granite systems example it was shown that the role of hydrothermal solutions in the ore deposits formation is not sufficient effective [Marakushev, et al, 1983; Chevychelov, 1992], and important ore-forming role is obtained by heavy salt phases which arise during fluid systems evolution separating as a result of extension of liquid inhomogeneity in them.

In this work the results of study of the system silicate melt – low concentrated water-salt (carbonate, sulphate, fluoride) fluid and distribution of ore metals (Ba, Sr, REE) between coexisting phases at T=1250°C and P=2 kbar are presented. The experiments were carried out in the system albite – diopside and albite – nepheline with the addition of BaCO<sub>3</sub> and SrCO<sub>3</sub> (or SrO) or CaO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub> and fluid (as 1M Na<sub>2</sub>SO<sub>4</sub>, 1M Na<sub>2</sub>CO<sub>3</sub> or 0.5M NaF solutions) in sealed platinum capsules in high gas pressure vessel with subsequent quenching.

The experimental aluminosilicate glass was analyzed on an X-ray micro analyzer. Water-salt fluid was collected and analyzed by atomic absorption method (for Na, Sr and Ba), emission method (for Ca and Mg) and ICP-MS method (for REE).

The systems studied are applied to multicomponent systems water–salt of P-Q type (as carbonate and sulphate are) – silicate [Ravich, 1974; Valyashko, 1990]. It shows that at magmatic parameters in this systems fluid phase may be heterogeneity with formation of two (or more) phases.

In experimental systems studied containing fluid during the experiment aluminosilicate glass enriches in Na and becomes poorer in Si and in the less degree in Al, Ca and Mg as compared with initial charge composition. Solution obtained after runs has pH near neutral which connects with decrease of Na concentration and perhaps with some increase of Al and Si concentrations in solution composition.

In the system silicate melt – water-carbonate fluid Sr, Ca and Mg contents in solution are insignificant (0.010, 0.063 and 0.007 wt.% respectively) and Ba by the method used don't detected. In glass average content of BaO is 3.35 wt. % and of SrO – 3.80 wt. %. The fine crystalline phase probably containing from carbonates of this elements is observed. This evidences that Ba, Sr, Ca and Mg essentially enriches the silicate melt relatively the fluid.

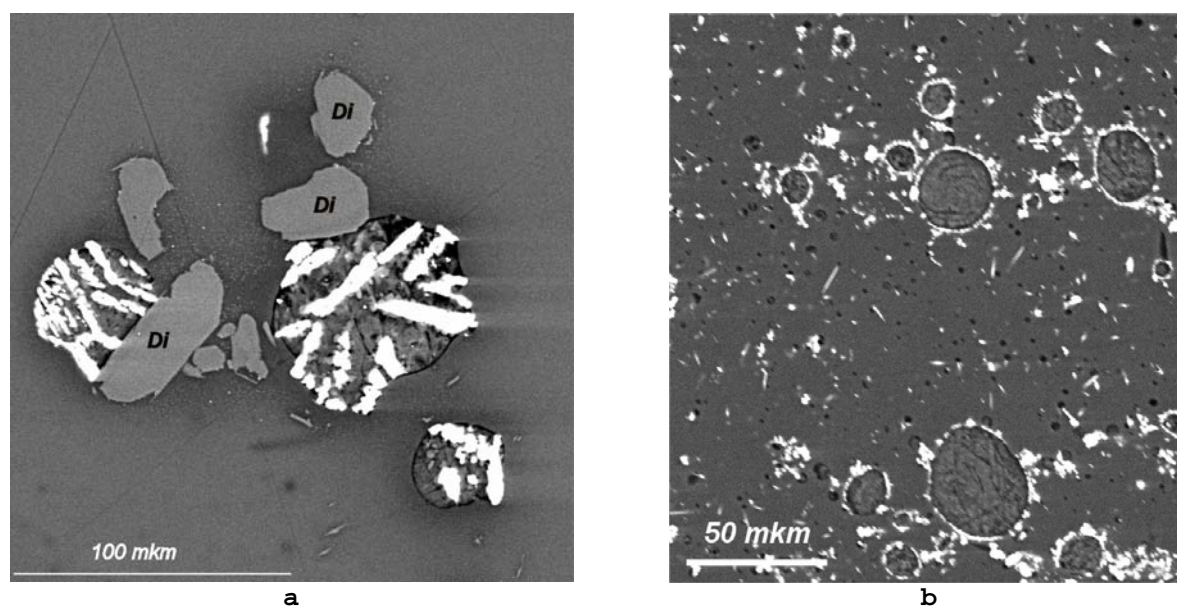
In the system silicate melt–water-fluoride fluid REE (La, Ce, Y, Dy) contents in solution are insignificant (0.00022, 0.00032, 0.00008 and 0.000084 wt. % respectively). In glass REE contents are insignificant (as phone means). The fine crystalline phases probably containing from silicates and fluorides of this elements are observed.

Investigations of Sr and Ba distribution between phases in the system silicate melt–water-fluoride fluid show that silicate melt has high contents of SrO (~3.3 wt. %) and BaO (~3.9 wt. %). Balance estimations testify that low concentrated water-fluoride fluid does not contain significant concentrations of Sr and Ba.

In the system silicate melt–water-sulphate fluid at the parameters of experiments it has been observed three phases: aluminosilicate melt, low concentrated water phase and sulphate melt forming the droplets in the silicate matrix (fig. 1). It evidences that at this parameters fluid was in heterogeneity state.

In these systems, containing REE, sulphate phase and low concentrated water-sulphate fluid don't content significant concentrations of REE which concentrate in fine crystalline phase in silicate melt (fig. 1b). In solution average REE contents are: La – 0.015 wt.%, Ce – 0.017 wt.%, Y – 0.0076 wt.%, Dy – 0.0085 wt.%. In the systems with water-sulphate fluid, containing Sr and Ba, in solution Sr content is insignificant (~0.034 wt. %) and Ba does not reveal. In glass average contents of BaO are 2.97 wt. % and SrO – 2.22 wt. There are the diopside crystals in the sample too. In droplets there is a heterogeneity observed. This is

reflects in existence of crystal aggregates of Ba and Sr sulphate which are placed in matrix having alkaline composition (sodium sulphate) (fig. 1a). Bulk compositions of droplets are characterized by average contents of BaO 14.06 wt. % and SrO – 7.65 wt. %. This sulphate phase is the concentrator of Sr and Ba. The average partition coefficient sulphate phase/silicate melt for Sr is 3.45 and for Ba – 4.7. The results obtained indicate the efficiency of sulphate ore extraction for recovery from the melt such ore elements as Sr and Ba.



**Fig.1.** Sulphate droplets in aluminosilicate matrix experimentally obtained in the system silicate melt – water-sulphate fluid at  $T=1250^{\circ}\text{C}$  and  $P=2$  kbar: a – in the system with Ba, Sr; b – in the system with REE. BSE image

Obtained data in the systems silicate melt – low concentrated water-carbonate, water-sulphate or water-fluoride fluid at  $T=1250^{\circ}\text{C}$  and  $P=2$  kbar has shown that low concentrated water fluids of studied compositions cannot be effective concentrators and transporters of such ore elements as REE, Sr and Ba. But our experiments show the efficiency of heavy sulphate phase for recovery from the melt such ore elements as Sr and Ba.

In previous works the liquid immiscibility in alkaline silicate-phosphate and silicate-carbonate systems has been studied. It has been determined the extraction of REE and Ti by phosphate melt [Suk, 1997] and extraction of Ba, Sr and at some conditions REE by carbonate melt [Freestone, Hamilton, 1980; Kjarsgaard, Hamilton, 1988; Veksler et.al., 1998; Suk, 2001, 2003 and others]. The study of equilibrium of granite melt with salt melts, fluorides as an example [Marakushev, Shapovalov, 1994], have detected the efficiency of fluoride ore extraction for recovery of ore elements as W and REE from the melts.

This confirms that the role of hydrothermal solutions in the ore deposits formation is not sufficient effective, but important ore-forming role is obtained by heavy salt phases arising during extension of liquid inhomogeneity in fluid-magmatic systems.

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