# Distribution of REE, Nb, Ta, Ba and Sr between immiscible phases in silicate-carbonate systems (experiment)

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Liquid immiscibility and distribution of REE, Nb, Ta, Ba and Sr between immiscible phases in silicate-carbonate systems at 1100 and 1250°C and P=2 kbar has been experimentally studied. It has been shown that Ba and Sr enrich the carbonate melt, and Nb and Ta – silicate melt.

It has been shown that partition coefficients ( $K=C^{REE}_{carb}/C^{REE}_{sil}$ ) of REE between immiscible silicate and carbonate phases depend on the initial magmatic melt composition and correlate with coexisting silicate melt composition: the magnification of  $K_{REE}$  with increase of (Al+Si)/(Na+K+Ca) relation and decrease of Ca/(Na+K) and Ca/(Si+Al) relations in silicate melt is observed.

Key words: experiment, liquid immiscibility, silicate-carbonate systems, partition coefficients

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The possible role of liquid immiscibility for the formation of carbonatites and related rocks was pointed out by a number of authors [*Koster van Groos, Wyllie, 1966, 1973; Wyllie, Tuttle, 1960; Kjarsgaard, Hamilton, 1988 and others*]. These experimental investigations demonstrated the existence of a wide field of liquid immiscibility of carbonate and silicate melts at various temperatures and pressures [*Koster van Groos, 1975; Wedlandt, Harrison, 1979; Freestone, Hamilton, 1980; Hamilton et al., 1989; Kjarsgaard, Hamilton, 1988 and others*].

We have experimentally studied the silicate-carbonate melt layering at T=1100 and  $1250^{\circ}C$  and P=2 kbar which corresponds to the superliquidus region of the systems considered. Special emphasize was placed on the character of some ore element (REE, Nb, Ta, Ba, Sr) distribution between immiscible phases.

The experiments were carried out in a high gas pressure vessel in sealed platinum capsules (3 mm in diameter) at a duration of 6 h with subsequent quenching. Dry systems were investigated. The initial mixtures consisted of natural minerals (albite, diopside, potassium feldspar, nepheline) in different with addition of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) or its mixture with calcite (Na<sub>2</sub>CO<sub>3</sub> + CaCO<sub>3</sub>). Ore elements were introduced as oxides La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub> and barium and strontium as carbonates BaCO<sub>3</sub> and SrCO<sub>3</sub>. The initial charge was 100 mg in weight and was preliminary dried at T=100°C for 18–20 h. The experimental samples were analyzed on a Camebax X-ray microanalyzer with an energy-dispersive system Link and on a digital scanning electron Tescan Vega TS5130MM microscope.

The experimental investigation of silicate-carbonate systems at T=1100 and  $1250^{\circ}C$  and P=2 kbar shows the wide field of liquid immiscibility with separation of starting silicate-carbonate melts into two liquids – silicate and carbonate [*Suk*, 2001, 2003]. Sharp phase boundaries between the melts are remarkable. These melts can form layers and drops of one liquid in another and fluidal textures (fig. 1). The relations between carbonate and silicate melts experimentally obtained model textural peculiarities observed in natural carbonatic complexes.

The heterogeneities of obtained carbonate liquids showed in the separation of carbonate phase into alkaline (mainly, sodic) and calc-alkaline (mainly, calcic) fractions is observed.

Comparison of previous experimental data with our results shows a good agreement and confirms that pressure increase and temperature decrease promotes the extension of immiscibility field.

Previous experimental investigations [*Koster van Groos, 1975; Veksler et al., 1998*] show that Ba and Sr concentrate in carbonate melt, and some rare elements, such Nb, Ta, Zr,

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Hf, enrich silicate melt with respect to carbonate melt [*Veksler et al., 1998*]. It has been shown that REE enrich carbonate melt with temperature decrease [*Hamilton et al., 1989*], pressure increase [*Hamilton et al., 1989*; *Jones et al., 1995*] and increase of coexisting silicate melt polymerization [*Hamilton et al., 1989*]. But distribution of rare and rare earth elements was studied in local field of more alkaline compositions. We studied the distribution of some ore elements in wide composition diapason involving the whole immiscibility field.



**Fig. 1.** Liquid immiscibility of silicate-carbonate melts at  $T=1100^{\circ}C$  and P=2 kbar: a – with structure "drop in drop", b – with fluidal texture (light – silicate melt, dark – carbonate melt). BSE images

Our experimental study reveals the dependence of the character of rare earth partitioning on the temperature, too. At  $T=1250^{\circ}C$  and P=2 kbar REE concentrate in silicate melt. At  $T=1100^{\circ}C$  and P=2 kbar the character of their distribution depends on the initial melt composition.

Because the compositions of coexisting carbonate and silicate melts are connected we can consider the dependence of REE partition coefficients ( $K=C^{REE}_{carb}/C^{REE}_{sil}$ ) on the compositions of silicate melt coexisting with carbonate melt and correlating with initial composition of the system. So we have made some diagrams. At 1100°C the magnification of K<sub>REE</sub> with increase of (Al+Si)/(Na+K+Ca) relation (Fig. 2c) is observed. This relation is likely to reflect the balance of net work cation and modifying cation [Galakhov, Varshal, 1969] in the melt and the polymerization degree pointed by Hamilton [Hamilton et.al., 1989]. But we can observed more strong dependence of K<sub>REE</sub> on the Ca/(Na+K) and Ca/(Si+Al) relations in coexisting silicate melt (Fig. 2 a, b). At T=1100°C and P=2 kbar in alkaline silicate-carbonate systems (where in silicate melt Ca/(Na+K)<0.5 and Ca/(Si+Al) <0.25) the light REE (La, Ce) accumulate in carbonate phases: their partition coefficients  $(K_{REE})$  are more 1. Thereby it is observed their predominant concentration in the calcium-rich fractions of carbonate phases as compared with sodium ones which don't content REE. In the lime silicatecarbonate systems (where in silicate melt Ca/(Na+K)>0.5 and Ca/(Si+Al)>0.25) inverse regularity is observed: rare earth elements are accumulated in the silicate melt (fig. 2). For Y (which is considered as a model of hard (HREE) rare earth elements) partition coefficients become more 1 only in the systems where  $Ca/(Na+K) < \sim 0.05$  and  $Ca/(Si+Al) > \sim 0.03$  (Fig. 2 b, c). For comparison of obtained data of REE distribution between silicate and carbonate melts the experimental data of Hamilton et al [Hamilton et.al., 1989] for La, Ce, Yb and Gd (1150°C, 2 kbar) and data of Veksler et al [Veksler et.al., 1998] for La and Y (for 965°C and ~940 bar and 1015°C and ~850 bar) were plotted. These data are in a good agreement.

At T=1250°C and P=2 kbar the predominant concentration of REE in silicate melt is observed: the partition coefficients ( $K=C^{REE}_{carb}/C^{REE}_{sil}$ ) are lower than 1. But for the light REE (LREE) the analogical dependence ( $K_{REE}$ ) on Ca/(Na+K) and Ca/(Si+Al) is estimated. For Y the dependence of partition coefficient on these relations practically does not observe.





**Fig. 2.** The dependence of partition coefficients ( $K=C^{REE}_{carb}/C^{REE}_{sil}$ ) of REE between silicate and carbonate melts on composition of coexisting silicate melt. a - Ca/(Na+K), b - Ca/(Si+Al) and c - (Al+Si)/(Na+K+Ca) in silicate melt. Our data: 1 - La, 2 - Ce, 3 - Y (at T=1100°C and 2 kbar); literature data: 4 - La, 5 - Y ([*Veksler et.al.*, 1998] at 965°C and ~940 bar and 1015°C and ~850 bar); 6 - La, 7 - Ce, 8 - Yb, 9 - Gd ([*Hamilton et.al.*, 1989]; at 1150°C and 2 kbar)

Our experimental investigation have shown that Nb and Ta in the systems studied at T=1100 and 1250°C are concentrated in silicate melt and Ba and Sr at T=1250°C and P=2 kbar are accumulated in carbonate phases. [*Suk, 2001, 2003*]. This is in a good agreement with previous experimental investigations [*Koster van Groos, 1975; Veksler et.al., 1998*]. But the dependence of partition coefficients of Nb and Ta on the initial system composition is in contemplation as aforesaid for REE.

Our experimental results on REE partitioning between immiscible liquids in alkalic systems at  $T=1100^{\circ}C$  and P=2 kbar demonstrated the extraction of these elements by carbonate melts allow us to conclude that the carbonatite deposits of rare earth elements could be formed in connection with alkalic (agpaitic) magmatism only.

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