Crystallization of bastnäsite and burbankite from carbonatite melt in the system La(CO₃)F-CaCO₃-Na₂CO₃ at 100 MPa

Anna M. Nikolenko^{1,2,3,*}, Konstantin M. Stepanov^{3,4}, Vladimir Roddatis¹, and Ilya V. Veksler^{1,3,†}

¹Helmholtz Centre Potsdam—German Research Centre for Geosciences GFZ, Telegrafenberg, 14473 Potsdam, Germany ²University of Potsdam, Institute of Geosciences, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany ³V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Akad. Koptyuga, 3, Novosibirsk 630090, Russia

⁴Vereshchagin Institute for High Pressure Physics RAS, Troitsk, 142190 Moscow, Russia

ABSTRACT

Bastnäsite [REE(CO₃)F] is the main mineral of REE ore deposits in carbonatites. Synthetic bastnäsite-like compounds were precipitated from aqueous solutions by many different methods, but previous attempts to model magmatic crystallization of bastnäsite from hydrous calciocarbonatite melts were unsuccessful. Here we present the first experimental evidence that bastnäsite and two other REE carbonates, burbankite, and lukechangite, can crystallize from carbonatite melt in the synthetic system La(CO₃)F-CaCO₃-Na₂CO₃ at temperatures between 580 and 850 °C and a pressure 100 MPa. The experiments on starting mixtures of reagent-grade CaCO₃, Na₂CO₃, La₂(CO₃)₃, and LaF₃ were carried out in cold-seal rapid-quench pressure vessels. The studied system is an isobaric pseudoternary join of a quinary system where CO₂ and fluorides act as independent components. Liquidus phases in the run products are calcite, nyerereite, Na carbonate, bastnäsite form a eutectic in the boundary join La(CO₃)F-CaCO₃ at 780 ± 20 °C and 58 wt% La(CO₃)F. Phase equilibria in the boundary join La(CO₃)F-Na₂CO₃ are complicated by peritectic reaction between Ca-free end-member of burbankite solid solution petersenite (Pet) and lukechangite (Luk) with liquid (L):

 $Na_4La_2(CO_3)_5$ (Pet) + NaF (L) = $Na_3La_2(CO_3)_4F$ (Luk) + Na_2CO_3 (Nc).

The right-hand-side assemblage becomes stable below 600 ± 20 °C. In ternary mixtures, bastnäsite (Bst), burbankite (Bur), and calcite (Cc) are involved in another peritectic reaction:

 $2La(CO_3)F(Bst) + CaCO_3(Cc) + 2Na_2CO_3(L) = Na_2CaLa_2(CO_3)_5(Bur) + 2NaF(L).$

Burbankite in equilibrium with calcite replaces bastnäsite below 730 \pm 20 °C. Stable solidus assemblages in the pseudoternary system are: basnäsite-burbankite-fluorite-calcite, basnäsite-burbankite-fluorite-lukechangite, bastnäsite-burbankite-lukechangite, burbankite-lukechangite-nyerereite-calcite, and burbankite-lukechangite-nyerereite-natrite. Addition of 10 wt% Ca₃(PO₄)₂ to one of the ternary mixtures resulted in massive crystallization of La-bearing apatite and monazite and complete disappearance of bastnäsite and burbankite. Our results confirm that REE-bearing phosphates are much more stable than carbonates and fluorocarbonates. Therefore, primary crystallization of the latter from common carbonatite magmas is unlikely. Possible exceptions are carbonatites at Mountain Pass that are characterized by very low P₂O₅ concentrations (usually at or below 0.5 wt%) and extremely high REE contents in the order of a few weight percent or more. In other carbonaties, bastnäsite and burbankite probably crystallized from highly concentrated alkaline carbonate-chloride brines that were found in melt inclusions and are thought to be responsible for widespread fenitization around carbonatite bodies.

Keywords: Experimental petrology, carbonatite melts, REE ore deposits, Mountain Pass, Bayan Obo