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Experimental study of phase equilibria between bastnäsite, burbankite and La phosphates in the system $\text{La}(\text{CO}_3)\text{F} - \text{CaCO}_3 - \text{Na}_2\text{CO}_3 - \text{Ca}_3(\text{PO}_4)_2$ at 100 MPa

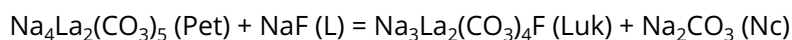
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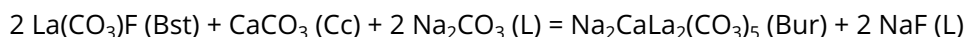
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Bastnäsite $[\text{REE}(\text{CO}_3)\text{F}]$ is the main mineral of REE ore deposits in carbonatites. Synthetic bastnäsite-like compounds have been precipitated from aqueous solutions by many different methods but previous attempts to model magmatic 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 $\text{La}(\text{CO}_3)\text{F} - \text{CaCO}_3 - \text{Na}_2\text{CO}_3$ at temperatures between 580 and 850 °C and pressure 100 MPa. The experiments on starting mixtures of reagent-grade CaCO_3 , Na_2CO_3 , $\text{La}_2(\text{CO}_3)_3$ and LaF_3 were carried out in cold-seal rapid-quench pressure vessels. The studied system is an isobaric pseudoternary join of a quinary system where CO_2 and fluorides act as independent components. Liquidus phases in the run products are calcite, nyerereite, Na carbonate, bastnäsite, burbankite solid solution $(\text{Na,Ca})_3(\text{Ca,L a})_3(\text{CO}_3)_5$ and lukechangite $\text{Na}_3\text{La}_2(\text{CO}_3)_4\text{F}$. Calcite and bastnäsite form a eutectic in the boundary join $\text{La}(\text{CO}_3)\text{F} - \text{CaCO}_3$ at 780 ± 20 °C and 58 wt% $\text{La}(\text{CO}_3)\text{F}$. Phase equilibria in the boundary join $\text{La}(\text{CO}_3)\text{F} - \text{Na}_2\text{CO}_3$ are complicated by peritectic reaction between Ca-free endmember of burbankite solid solution petersenite (Pet) and lukechangite (Luk) with liquid (L):



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



Burbankite in equilibrium with calcite replaces bastnäsite below 730 ± 20 °C. Stable solidus assemblages in the pseudoternary system are: bastnäsite-burbankite-fluorite-calcite, bastnäsite-burbankite-fluorite-lukechangite, bastnäsite-burbankite-lukechangite, burbankite-lukechangite-nyerereite-calcite and burbankite-lukechangite-nyerereite-natrite. Addition of 10 wt% $\text{Ca}_3(\text{PO}_4)_2$ to 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 P_2O_5 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 carbonatites, bastnäsite and burbankite probably crystallized from highly concentrated alkaline carbonate-chloride brines that have been found in melt inclusions and are thought to be responsible for widespread fenitization around carbonatite bodies.

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