## **RARE-EARTH RICH CARBONATITES: A REVIEW AND LATEST RESULTS**

F. WALL<sup>1</sup>, A. ZAITSEV<sup>2</sup>, A. P. JONES<sup>3</sup>, A. N. MARIANO<sup>4</sup>

<sup>1</sup>Department of Mineralogy, The Natural History Museum, Cromwell Road, London, SW7 5BD, United Kingdom
<sup>2</sup>Department of Mineralogy, University of St Petersburg, St Petersburg 199034, Russia
<sup>3</sup>Department of Geology, University College London, Gower Street, London WC1E 6BT, United Kingdom
<sup>4</sup>48 Page Brook Road, Carlisle, MA 0174, USA

Carbonatites contain some of the highest concentrations of REE in the Earth's crust. Levels of hundreds of ppm REE are characteristic but concentrations can exceed 10 wt. %. Such rare-earth rich carbonatites are common minor components of carbonatite complexes. They are often ferrocarbonatites and, even if only minor components of a carbonatite complex, can still host the majority of the REE. When, more rarely, the rare-earth rich carbonatites occur in larger quantities they are of economic importance.

Rare earth minerals form in the final stages of carbonatite emplacement and during subsequent alteration. Unambiguous igneous textures are rare but part of the Mountain Pass carbonatite, the best known rare-earth rich carbonatite, consists of calcite carbonatite containing up to 20 % bastnäsite (La,Ce)CO<sub>3</sub>F, plus barite and fluorite, which texturally does seem to have crystallized from a magma. Published experimental data at 1 kbar and 550 °C support this hypothesis and suggest that such extreme concentrations can be produced by differentiation of carbonatites in the crust. Other possible candidates for primary RE minerals are carbocernaite ((Ca,Na)(Sr,Ce,Ba)(CO<sub>3</sub>)<sub>2</sub>) and burbankite ((Na,Ca)<sub>3</sub>(Sr,Ba,Ca)<sub>3</sub>(CO<sub>3</sub>)<sub>5</sub>) for which there are reports of igneous textures and estimates of crystallisation temperatures above 500 °C. We are currently conducting some experiments in the range 0.5 to 5 kbars and up to 900 °C to see if it is possible to crystallize these minerals.

Most RE-rich carbonatites are, however, the result of sub-solidus processes involving carbonatite-derived fluids which may precipitate rare earth minerals directly, or may alter earlier minerals such as apatite, and are variously described as "hydrothermal", "carbothermal" or combinations of the two. Much of the mineralisation is pervasive, producing polycrystalline aggregates. Published studies have concluded that there is an external component to some of these fluids and certainly they can transport REE outside of the carbonatites to produce mineralization in the country rock; examples occur at Araxá and Catalão I, Brazil, Chiriguelo, Paraguay, and Kangankunde Malawi. Reworking and transport of the REE can modify the typical carbonatite light REE-enriched patterns and remove the lightest REE or precipitate the mid REE. An extreme example is the presence of mckelveyite-(Y) (Ba<sub>3</sub>Na(Ca,U)Y(CO<sub>3</sub>)<sub>6</sub>.3 H<sub>2</sub>O) and ewaldite (Ba(Ca,Y,Na,K)(CO<sub>3</sub>)<sub>2</sub>) in carbonate–zeolite veins at Khibina, Russia. Care must be taken in interpreting mineral chemistry as being indicative of changes in fluid because crystal chemical effects can be important. For example, sector zoning in monazite can produce 10 wt. % variation in La<sub>2</sub>O<sub>3</sub> within single crystals.

Weathering concentrates the REE which are released from primary hosts such as apatite and calcite and reprecipitate in weathering products such as monazite, rhabdophane and particularly crandallite-group minerals.

The action of pervasive fluids derived directly from the carbonatite magma is particularly important and we are presently studying several examples in which the RE assemblages, including ancylite ( $SrCe(CO_3)_2(OH).H_2O$ ), strontianite, synchysite ( $Ca(Ce,La)(CO_3)_2F$ ), calcite, barite, quartz, monazite ((La,Ce)PO<sub>4</sub>) and apatite, now form pseudomorphs after a hexagonal prismatic mineral. Localities include Kangankunde, Malawi; Wigu Hill, Tanzania; Adiounedj, Mali; Bear Lodge, Wyoming and Gem Park, USA. By analogy with occurrences at Khibina and Ozernyi, Russia, we are investigating the hypothesis that the original mineral was burbankite. This would require alteration by fluids containing F,  $SO_4^{-2}$ ,  $OH^-$ , and/or  $PO_4^{-3-}$ , removal of Na, and introduction of Sr.