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REE minerals at the Songwe Hill carbonatite, Malawi: HREE-enrichment in late-stage apatite

Sam Broom-Fendley [a,b,*], Aoife E. Brady [c,1], Frances Wall [a], Gus Gunn [b], William Dawes [c]

[a] Camborne School of Mines, University of Exeter, Penryn Campus, Penryn, Cornwall TR10 9FE, UK
[b] British Geological Survey, Keyworth, Nottinghamshire NG12 5GG, UK
[c] Mkango Resources Ltd., 706 27 Avenue NW, Calgary, Alberta, T2M 2J3, Canada

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ABSTRACT

Compared to all published data from carbonatites and granitoids, the fluorapatite compositions in the Songwe Hill carbonatite, determined by EPMA and LA ICP-MS, have the highest heavy (H)REE concentration of any carbonatite apatite described so far. A combination of this fluorapatite and the REE fluorocarbonates, synchysite-(Ce) and parisite-(Ce), which are the other principal REE bearing minerals at Songwe, gives a REE deposit with a high proportion of Nd and a higher proportion of HREE (Eu–Lu including Y) than most other carbonatites. Since Nd and HREE are currently the most sought REE for commercial applications, the conditions that give rise to this REE profile are particularly important to understand. Multiple apatite crystallisation stages have been differentiated texturally and geochemically at Songwe and fluorapatite is divided into five different types (Ap-0–4). While Ap-0 and Ap-1 are typical of apatite found in fenite and calcite-carbonatite, Ap-2, -3 and -4 are texturally atypical of apatite from carbonatite and are progressively HREE-enriched in later paragenetic stages. Ap-3 and Ap-4 exhibit anhedral, stringer-like textures and their REE distributions display an Y anomaly. These features attest to formation in a hydrothermal environment and fluid inclusion homogenisation temperatures indicate crystallisation occurred between 200–350 °C. Ap-3 crystallisation is succeeded by a light (L)REE mineral assemblage of synchysite-(Ce), strontianite and baryte. Finally, late-stage Ap-4 is associated with minor xenotime-(Y) mineralisation and HREE-enriched fluorite. Fluid inclusions in the fluorite constrain the minimum HREE mineralisation temperature to approximately 160 °C. A model is suggested where sub-solidus, carbonatite-derived, (carbo)-hydrothermal fluids remobilise and fractionate the REE. Chloride or fluoride complexes retain LREE in solution while rapid precipitation of apatite, owing to its low solubility, leads to destabilisation of HREE complexes and substitution into the apatite structure. The LREE are retained in solution, subsequently forming synchysite-(Ce). This model will be applicable to help guide exploration in other carbonatite complexes.

1. Introduction

Carbonatites (igneous rocks containing >50% carbonate minerals; Le Maître et al., 2002) are host to some of the largest REE resources (Chakhmouradian and Wall, 2012; Wall, 2014; Verplanck et al., 2016). However the REE-minerals currently extracted from carbonatites (REE-fluorocarbonates, monazite) are typically LREE-rich (La–Sm) and HREE-poor (Eu–Lu + Y; Wall, 2014). With the exception of Nd, they are, therefore, deficient in the majority of the REE considered 'critical', i.e. of high economic importance, but at risk of supply disruption (European Commission, 2014; Gunn, 2014). Only a few examples of carbonatite-related HREE enrichment are known (e.g. Kangankunde, Malawi; Khibiny, Russia; Deadhorse Creek, Canada; Huanglongpu and Huayangchuan, China; Lofdal, Namibia; Pivot Creek, New Zealand; and Bear Lodge, USA; Wall and Mariano, 1996; Zaitsev et al., 1998; Potter and Mitchell, 2005; Xu et al., 2007; Wall et al., 2008; Kynicky et al., 2012; Cooper et al., 2015; Andersen et al., 2016). With the exception of Lofdal, these are typically minor occurrences forming in late-stage fluid-rich environments.

In this study the composition and texture of REE-bearing minerals at the Songwe Hill carbonatite, Malawi, were investigated with the objective of understanding if there is any mineral phase, or stage in the carbonatite evolution, in which HREE enrichment may occur. Particular attention was paid to the relationship between apatite and REE phases because low-tenor HREE enrichment occurs in late-stage apatite at the Tundulu, Kangankunde and Juquiá carbonatites (Ngwenya, 1994; Wall and Mariano, 1996; Broom-Fendley et al., 2016a; Walter et al., 1995).

Abbreviations: L, liquid; V, vapour; TREO, total rare earth oxides.

[*] Corresponding author at: Camborne School of Mines, University of Exeter, Penryn Campus, Penryn, Cornwall TR10 9FE, UK.

E-mail address: s.l.broom-fendley@ex.ac.uk (S. Broom-Fendley).

[1] Present address: IGS (International Geoscience Services) Ltd., Geoscience Innovation Hub, British Geological Survey, Environmental Science Centre, Keyworth, Nottingham NG12 5GG, UK.

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Furthermore, the REE have been identified as a potential co- or by-product of phosphate production (Mariano and Mariano, 2012; Ihlen et al., 2014).

Fluorapatite ($Ca_5(PO_4)_3F$), is ubiquitous in carbonatites and is typically a liquidus phase, but can occur through early magmatic to late hydrothermal stages (Eby, 1975; Kapustin, 1980; Hogarth, 1989). It readily accommodates the REE in its structure (Pan and Fleet, 2002; Hughes and Rakovan, 2015). Consequently, the timing of apatite crystallisation during carbonatite evolution can strongly affect the whole-rock REE distribution of a carbonatite and the likelihood of REE deposit formation (Zaitsev et al. 2015). Apatite habits can vary with the conditions of formation (e.g. Wyllie et al., 1962), and compositional variation in apatite has been demonstrated to track the magmatic and hydrothermal evolution of alkaline rocks (Zirner et al., 2015; Ladenburger et al., 2016). Similarly, apatite can elucidate the relationship between carbonatites and associated alkaline rocks (Le Bas and Handley, 1979; Stoppa and Liu, 1995; Wang et al., 2014), trace carbonatite evolution (Walter et al., 1995), and provide information on the process of REE mineralisation (Campbell and Henderson, 1997; Broom-Fendley et al., 2016a).

Considering the above characteristics, a secondary objective of this study is to elucidate the composition of late-stage carbonatite-derived fluids and understand mechanisms for REE transport and fractionation. To this end, trace element analyses of apatite, fluorite and other REE-bearing minerals, are presented, as well as a preliminary fluid-inclusion study.

2. The Songwe Hill carbonatite

The Songwe Hill carbonatite is located in south-eastern Malawi, near the Mozambique border, and is part of the Chilwa Alkaline Province (Fig. 1). This province is an essentially intrusive suite of Early Cretaceous alkaline rocks intruded into Precambrian basement (Garson, 1965; Woolley, 2001). Songwe is the fourth largest of the carbonatites in the province and exploration work by Mkango Resources Ltd. has established a (NI 43-101 compliant) mineral resource estimate, comprising an indicated and inferred component of 13.2 million tonnes (grading 1.62% Total Rare Earth Oxide (TREO)) and 18.6 million tonnes (grading 1.38% TREO) respectively, using a cut-off grade of 1% TREO (Croll et al., 2014).

The geology of the Songwe Hill carbonatite is described in detail in Croll et al. (2014) and Broom-Fendley (2015) and only a brief overview is presented here. There is evidence for a coarse-grained calcite carbonatite (C1) at depth; however, most exposed rocks at Songwe comprise two, fine-grained, carbonatites (Fig. 1C), which incorporate varying proportions of brecciated fenite. The earlier stage is a light grey, calcite carbonatite (C2) and the latter is darker and more Fe-rich, termed ferroan calcite carbonatite (C3). REE concentrations are higher in the later-stages of the intrusion, with total REE concentrations in C2 and C3 carbonatite averaging approximately 15,000 and 30,000 ppm, respectively (Broom-Fendley, 2015). The carbonatite is cross-cut by numerous, laterally discontinuous, late-stage veins varying in width between 1 cm and approximately 1 m. These veins include REE-rich apatite-fluorite veins and, lastly, Fe-Mn-veins caused by low temperature alteration. The intrusion is surrounded by a fenitized and commonly brecciated aureole, extending for an unknown distance from the intrusion.

3. Methodology

Samples were obtained from diamond drill-core drilled by Mkango Resources in 2011 and 2012. Specimens with high whole-rock P_2O_5 concentrations were selected to ensure the presence of apatite. Petrography was carried out using cold-cathodoluminescence (CL) and SEM (using the same techniques as described in Broom-Fendley et al., 2016a) before samples were analysed for trace elements using electron probe micro-analyser (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

EPMA analyses were undertaken at the British Geological Survey (BGS) and Natural History Museum (NHM), London, using a FEI-Quanta 600 scanning electron microscope (SEM) and Cameca SX100 electron microprobe, respectively. The BGS-SEM was operated using the same method detailed in Walters et al. (2013) and Broom-Fendley et al. (2016a). The operating conditions for the NHM EPMA were 20 kV and 20 nA with a beam size of 5–10 μm. Peak counting times were 20 s for Na, Ca, Mn, P, La, Ce, Cl; 30 s for F, Si, Fe, Pr, Nd, Gd, S; 40 s for Sm, Dy, and 60 s for Y when analysing for apatite and 20 s for Na, Mg, Al, Ca, Mn, P, La, Ce, Cl; 30 s for F, Si, Fe, Pr, Nd, Eu, Gd, S; 40 s for Sm, Dy; 60 s for Y; and 120 s for Th when analysing for REE minerals. Background-counting times were half the peak value. X-ray counts were converted to wt% oxide using the Cameca PAP correction program. Empirical interference corrections were performed for La, Ce and the HREE following Williams (1996). Correction factors were calculated by measuring the interferences observed on individual REE reference standards. A variety of natural and synthetic primary reference materials were used with an internal apatite standard for quality control.

Trace elements were analysed, using LA ICP-MS, at the BGS and at Aberystwyth University in Wales. Ablation at the BGS utilized the same methodology as described in Broom-Fendley et al. (2016a). The laser system at Aberystwyth is based on a Coherent/Lambda Physik Compex Pro excimer ArF laser, working at 193 nm, coupled to a Coherent/Lambda Physik GeoLas Pro ablation system. The spot size was 20 μm with a repetition rate of 5 Hz and a corresponding fluence of 10 J cm^{-2}. Ablated material was analysed using a Thermo-Finnigan Element 2 high resolution ICP-MS, obtaining 10 spectra over 24 s. Analyses were calibrated using SRM 610 as an external standard and SRM 612 as a check standard.

Microthermometric analyses were carried out at the BGS and at McGill University, Canada, using a Linkam THM600 and a TS1500 stage, respectively. Instrument calibration utilized synthetic fluid inclusion standards at −56.6, 0 and 374 °C. Estimated analytical error is ±0.2 °C for low (<50 °C) and ±2 °C for higher (>75 °C) temperatures.

4. Paragenesis of apatite and other REE-bearing minerals

REE minerals at Songwe Hill include REE-fluorocarbonates, florencite-(Ce), and minor xenotime-(Y). Importantly, the REE also occur as minor and trace elements in fluorapatite, calcite and fluorite. Compositional data and textural observations for apatite, synchysite-(Ce), florencite-(Ce), fluorite and xenotime-(Y) are presented in paragenetic order in the following subsections, with the interpreted paragenetic sequence summarised in Fig. 2. The composition and texture of apatite is highly variable and is divided into five groups (Ap-0–4; Table 1).

4.1. Ap-0 (fenite)

Ap-0 occurs in potassic fenite, outside of the main Songwe carbonatite. It is characterised by large (typically >0.1 mm), partially fragmented anhedral grains, in association with altered K-feldspar and minor zircon. Under CL Ap-0 luminesces purple–mauve, and is compositionally homogeneous in BSE images (Table 1).

All apatite at Songwe is fluorapatite. Ap-0 has the highest SiO_2 and SO_3 concentration of all the analysed apatite types, but lower U, Th and Na (Tables 2 and 3; Fig. 3). It is strongly enriched in the LREE with a near-linear REE distribution decreasing towards the HREE, and a small negative Eu-anomaly (Fig. 4).

4.2. Ap-1, Ap-2, (C1—early igneous carbonatite)

Ovoid apatite occurs in early (C1) calcite carbonatite and is subdivided into Ap-1 and Ap-2, respectively representing cores and