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Trace-element modeling of the magmatic evolution of rare-earth-rich carbonatite from the Miaoya deposit, Central China

Cheng Xu^{a,*}, Jindrich Kynicky ^b, Anton R. Chakhmouradian ^c, Ian H. Campbell ^d, Charlotte M. Allen ^d

^a Laboratory of Orogenic Belts and Crustal Evolution, Peking University, Beijing 100871, China

b Department of Geology and Pedology, Mendel University, Brno, Czech Republic

^c Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada

^d Research School of Earth Sciences, Australian National University, Canberra, Australia

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Carbonatites are known to contain the highest concentrations of rare-earth elements (REE) among all igneous rocks. The REE distribution of carbonatites is commonly believed to be controlled by that of the rockforming Ca minerals (i.e., calcite, dolomite, and ankerite) and apatite because of their high modal content and tolerance for the substitution of Ca by light REE (LREE). Contrary to this conjecture, calcite from the Miaoya carbonatite (China), analyzed in situ by laser-ablation inductively-coupled-plasma mass-spectrometry, is characterized by low REE contents (100–260 ppm) and relatively flat chondrite-normalized REE distribution patterns [average $(La/Yb)_{CN} = 1.6$]. The carbonatite contains abundant REE-rich minerals, including monazite and fluorapatite, both precipitated earlier than the REE-poor calcite, and REEfluorocarbonates that postdated the calcite. Hydrothermal REE-bearing fluorite and barite veins are not observed at Miaoya. The textural and analytical evidence indicates that the initially high concentrations of REE and P in the carbonatitic magma facilitated early precipitation of REE-rich phosphates. Subsequent crystallization of REE-poor calcite led to enrichment of the residual liquid in REE, particularly LREE. This implies that REE are generally incompatible with respect to calcite and the calcite/melt partition coefficients for heavy REE (HREE) are significantly greater than those for LREE. Precipitation of REE-fluorocarbonates late in the evolutionary history resulted in depletion of the residual liquid in LREE, as manifested by the development of HREE-enriched late-stage calcite $[(La/Yb)_{CN} \approx 0.7]$ in syenites associated with the carbonatite. The observed variations of REE distribution between calcite and whole rocks are interpreted to arise from multistage fractional crystallization (phosphates⇒calcite⇒REE-fluorocarbonates) from an initially REE-rich carbonatitic liquid.

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1. Introduction

The utility of rare-earth elements (REE) as petrogenetic tracers in igneous processes has long been recognized. A large amount of experimental data on hydrothermal REE transport and partitioning is available (e.g., [Wood, 1990; Haas et al., 1995; Migdisov et al., 2008](#page--1-0)). In conjunction with voluminous empirical data (e.g., [Morogan, 1989;](#page--1-0) [Williams-Jones et al., 2000; Wall and Zaitsev, 2004; Bühn, 2008\)](#page--1-0), this experimental evidence has led to an improved understanding of the behavior of REE during water–rock interaction. However, the effects of crystal fractionation involving multiple phases separating at different stages during magma evolution have not been studied in adequate detail for carbonatites. Carbonatites are known to contain the highest concentrations of REE (500 to >10 000 ppm) among all igneous rocks,

⁎ Corresponding author. E-mail address: xucheng1999@hotmail.com (C. Xu). and are a major source of economic REE mineralization. However, carbonatite-related REE deposits usually have very limited reserves, and only a few economically important deposits have been documented since the discovery of the world-class Mountain Pass deposit in California ([Castor, 2008\)](#page--1-0). In most carbonatites, REE are primarily dispersed in rock-forming and accessory Ca minerals such as calcite, dolomite, apatite and silicates (e.g., allanite; [Hornig-Kjarsgaard, 1998](#page--1-0)). Rare-earth minerals (particularly, carbonates and phosphates) are commonly enriched in magnesiocarbonatite and ferrocarbonatite dikes that may be either igneous or hydrothermal rocks [\(Le Bas,](#page--1-0) [1989; Wall and Mariano, 1996; Ruberti et al., 2008](#page--1-0)). The Miaoya carbonatite stocks in China consist predominantly of calcite and contain abundant REE minerals (up to 5 vol.%), making this deposit an economic REE resource [\(Qian and Li, 1996](#page--1-0)). Importantly, the Miaoya carbonatite is not associated with obvious hydrothermal REE mineralization, which distinguishes it from most other REE deposits (e.g., [Samson et al., 2004; Smith, 2007; Xu et al., 2008\)](#page--1-0). The main objective of the present work is to establish genetic relations between calcite and

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major REE hosts in the Miaoya carbonatite and to assess the parameters that control the distribution of REE in minerals precipitating from carbonatitic liquids.

2. Geological setting

The Miaoya REE deposit is located in the southwestern margin of the Wudang Terrane at the southern margin of the Qinling orogenic belt (Fig. 1). The Qinling belt, which separates the North China block from the South China block, is divided into two parts (North and South Qinling) along the Shangdan suture (Fig. 1). The North Qinling belt is regarded as a Mid-Paleozoic orogen with widespread Paleozoic island-arc type magmatism and metamorphism ([Sun et al., 2002](#page--1-0)). The South Qinling belt is interpreted as a Late-Paleozoic to Early-Mesozoic orogen characterized by abundant Triassic granitic magmatism and metamorphism ([Mattauer et al., 1985; Sun et al., 2000](#page--1-0)). There is a general consensus that the North Qinling belt was an active continental margin, whereas the South Qinling structure was a passive margin forming the northernmost part of the South China block [\(Lu](#page--1-0) [et al., 2006\)](#page--1-0). Detailed descriptions of the geological framework and tectonic evolution of the Qinling region are given in [Meng and Zhang](#page--1-0) [\(2000\), Ratschbacher et al. \(2003\) and Chen et al. \(2009\)](#page--1-0).

Fig. 1. Schematic geological map of the Miaoya REE deposit (modified after [Li, 1980; Meng and Zhang, 2000\)](#page--1-0).

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