Lithos 308–309 (2018) 65–82

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos

The origin of secondary heavy rare earth element enrichment in carbonatites: Constraints from the evolution of the Huanglongpu district, China

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ARTICLE INFO

Article history:
Received 27 October 2017
Accepted 25 February 2018
Available online 04 March 2018

Keywords:
Rare earth elements
Carbonatite
Hydrothermal
Sulphate
Brine

ABSTRACT

The silico-carbonatite dykes of the Huanglongpu area, Lesser Qinling, China, are unusual in that they are quartz-bearing, Mo-mineralised and enriched in the heavy rare earth elements (HREE) relative to typical carbonatites. The textures of REE minerals indicate crystallisation of monazite-(Ce), bastnäsite-(Ce), parisite-(Ce) and aeschynite-(Ce) as magmatic phases. Burbankite was also potentially an early crystallising phase. Monazite-(Ce) was subsequently altered to produce a second generation of apatite, which was in turn replaced and overgrown by britholite-(Ce), accompanied by the formation of allanite-(Ce). Bastnäsite and parisite where replaced by synchysite-(Ce) and röntgenite-(Ce). Aeschynite-(Ce) was altered to uranopyrochlore and then pyrochlore with uraninite inclusions. The mineralogical evolution reflects the evolution from magmatic carbonatite, to more silica-rich conditions during early hydrothermal processes, to fully hydrothermal conditions accompanied by the formation of sulphate minerals. Each alteration stage resulted in the preferential leaching of the LREE and enrichment in the HREE. Mass balance considerations indicate hydrothermal fluids must have contributed HREE to the mineralisation. The evolution of the fluorcarbonate mineral assemblage requires an increase in $a_{Ca^{2+}}$ and $a_{CO_3^{2-}}$ in the metasomatic fluid (where a is activity), and breakdown of HREE-enriched calcite may have been the HREE source. Leaching in the presence of strong, LREE-selective ligands (Cl^-) may account for the depletion in late stage minerals in the LREE, but cannot account for subsequent preferential HREE addition. Fluid inclusion data indicate the presence of sulphate-rich brines during alteration, and hence sulphate complexation may have been important for preferential HREE transport. Alongside HREE-enriched magmatic sources, and enrichment during magmatic processes, late stage alteration with non-LREE-selective ligands may be critical in forming HREE-enriched carbonatites.

1. Introduction

The rare earth elements (REE) (here defined as the lanthanides plus Y), have long been a focus of research because of their utility as tracers for geochemical processes from magma source and differentiation, through to hydrothermal system evolution (e.g. Chakhmouradian, 2006; Haas et al., 1995; Henderson, 1984; Migdisov et al., 2009). In recent years they have also become a focus of intense economic interest because of the restriction in supply caused by a focus of production in China, coupled with increasing use in renewable energy and high technology applications (Chakhmouradian and Wall, 2012). Rare earth element resources are dominated by concentrations, either from magmatic or hydrothermal processes, associated with alkaline igneous rocks, notably carbonatites. A significant issue with primary resources is that carbonatite concentrations tend to be preferentially enriched in the light REE (La to Nd), which, with the exception of Nd, are less economically important than the heavy REE (Eu to Lu) (Chakhmouradian and Wall, 2012). Middle to HREE enriched carbonatites do occur however, and are of great interest both because of their economic potential, and because of the need to understand the processes leading to this enrichment (e.g. Xu et al., 2007). Hydrothermal processes have been shown to fractionate the REE via differential solubility during leaching of primary phases, controls on relative solubility exerted by

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https://doi.org/10.1016/j.lithos.2018.02.027
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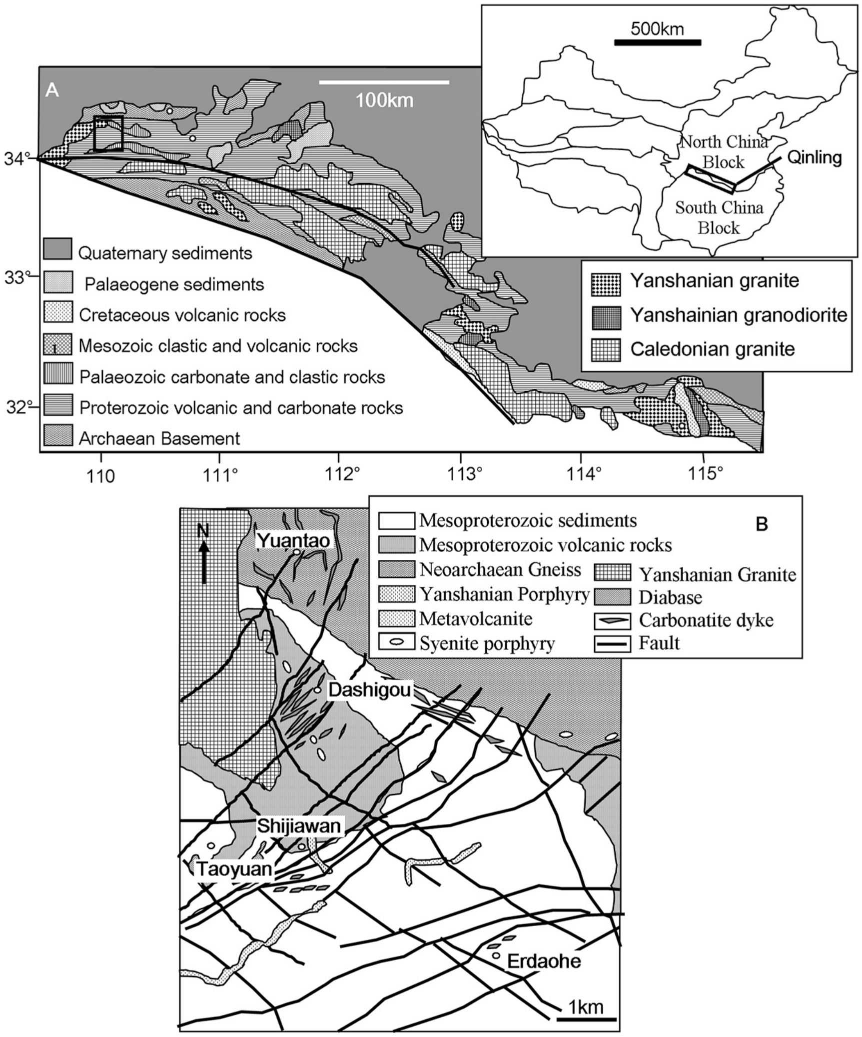

Fig. 1. (A) Geological map of the eastern Qinling mountains showing the location of the Huanglongpu area. Inset shows the overall location within China in relation to major crustal blocks. (B) Geological map of the Huanglongpu Mo-district (highlighted in bold in A). Maps adapted from Xu et al. (2010). Samples labelled HLP are from the Dashigou site, samples labelled YT are from Yuantao.

the variation in the stability of aqueous complex ions with different ligands (Haas et al., 1995; Migdisov et al., 2009; Wood, 1990), variation in the relative solubility of secondary phases, and all of these coupled with dynamic flow and reaction pathways (Williams-Jones et al., 2013). In this study we have investigated the paragenetic and chemical evolution of rare earth minerals in the Huanglongpu carbonatites, Qinling Mountains, China (Fig. 1; Xu et al., 2007, 2010; Song et al., 2015). These carbonatites are exceptional because of their association with economic molybdenite mineralisation, a relatively silica-rich geochemistry and hence an association with quartz, and a relative enrichment in the HREE compared to typical carbonatites (Kynicky et al., 2012). The exceptional geochemistry of the dykes, and the preservation of a wide range of reaction textures, make this an ideal site to assess the role of post-magmatic processes in the genesis of HREE-enriched carbonatites globally. Heavy rare earth enrichment has been reported from a number of carbonatites, typically associated with late stage hydrothermal phenomena (e.g. Tundulu - Ngwenya, 1993; Songwe - Swinden and Hall, 2012; Bear Mountain - Moore et al., 2017; Lofdal - Bodeving et al., 2017). Bulk rock analyses of the Huanglongpu carbonatites show that their REE patterns are transitional between more typical carbonatites and the HREE-enriched hydrothermal deposits (Fig. 2). Thus the Huanglongpu district may provide an exceptionally well exposed site, suitable for characterisation of hydrothermal enrichment process, with wider implications for HREE-enrichment in carbonatites globally.

2. Geological setting

The Huanglongpu district is composed of four carbonatite-related orefields with a total ore reserve of >180 Kt of Mo. Almost all spatially

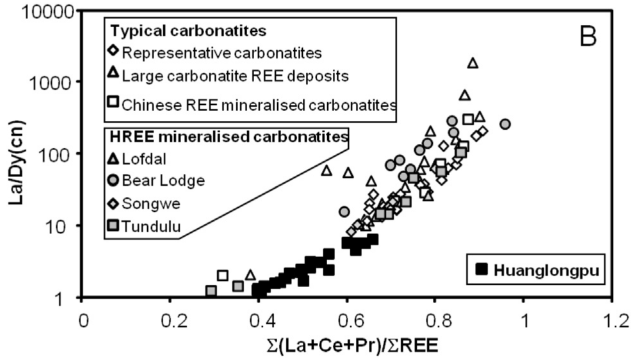

Fig. 2. Comparison of ratios characterising the REE pattern for the Huanglongpu carbonatites with Chinese REE mineralised carbonatites (Kynicky et al., 2012), typical carbonatites (Hornig-Kjarsgaard, 1998), and carbonatites with reported high HREE contents (Bodeving et al., 2017; Moore et al., 2017; Ngwenya, 1993; Swinden and Hall, 2012) Data from Huanglongpu from Xu et al. (2010), Kynicky et al. (2012) and Song et al. (2015). Chondrite values from Sun and McDonough (1989) here and throughout.