Fingerprinting REE mineralization and hydrothermal remobilization history of the carbonatite-alkaline complexes, Central China: Constraints from in situ elemental and isotopic analyses of phosphate minerals

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Abstract
Carbonatites and related alkaline rocks host most REE resources. Phosphate minerals, e.g., apatite and monazite, commonly occur as the main REE-carriers in carbonatite systems, and have been used for tracing magmatic and mineralization processes. Many carbonatite intrusions undergo metamorphic and/or metasomatic modification after emplacement; however, the effects of such secondary events are controversial. In this study, the Miaoya and Shaxiongdong carbonatite-alkaline complexes, in the South Qinling Belt of Central China, are selected to unravel their magmatic and hydrothermal remobilization histories. Both the complexes are accompanied by Nb-REE mineralization and contain apatite and monazite-(Ce) as the major REE carriers.

Apatite grains from the two complexes commonly show typical replacement textures related to fluid metasomatism, due to coupled dissolution-reprecipitation. The altered apatite domains, which contain abundant monazite-(Ce) inclusions or are locally surrounded by fine-grained monazite-(Ce), have average REE concentrations lower than primary apatite. These monazite-(Ce) inclusions and fine-grained monazite-(Ce) grains are proposed to have formed by the leaching REE from primary apatite grains during fluid metasomatism. A second type of monazite-(Ce), not spatially associated with apatite, shows porous textures and zoning under BSE imaging. Spot analyses of these monazite-(Ce) grains have variable U-Th-Pb ages of 210–410 Ma and show a peak age of 230 Ma, which is significantly younger than the emplacement age (440–430 Ma) but is roughly synchronous with a regionally metamorphic event related to the collision between the North China Craton and Yangtze Block along the Mianlue suture. However, in situ LA-MC-ICP-MS analyses of those grains show that they have initial Nd values same as those of magmatic apatite and whole rock. We suggest these monazite-(Ce) grains crystallized from the early Silurian carbonatites and have been partially or fully modified during a Triassic metamorphic event, partially resetting U-Pb ages over a wide range. Mass-balance calculations, based on mass proportions and the REE contents of monazite-(Ce) and apatite, demonstrate that the quantity of metasomatized early Silurian monazite-(Ce) is far higher than the proportion of monazite-(Ce) resulting from the metasomatic alteration of the apatite. Therefore, Triassic metamorphic events largely reset the U-Th-Pb isotopic system of the primary monazite-(Ce) and apatite but only had limited or local effects on REE remobilization in the carbonatite-alkaline complexes in the South Qinling Belt. Such scenarios may be widely applicable for other carbonatite and hydrothermal systems.

Keywords: Carbonatite-alkaline complex, phosphate minerals, REE mineralization, in situ isotopic analyses, metasomatic alteration; Experimental Halogens in Honor of James Webster

Introduction
Global demand for rare earth elements (REE) has been continuously increasing during the past decades because of their critical roles in modern industries (Weng et al. 2015; Goodenough et al. 2017; Zhou et al. 2017). These elements are mainly sourced from carbonatites and related alkaline complexes (Chakhmouradian and Wall 2012; Goodenough et al. 2017; Zhou et al. 2017), and hence