Nucleation of Th-rich cerianite on halloysite surface in a regolith-hosted rare earth elements deposit in South China

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Abstract

The ion-adsorption rare earth element (REE) deposit, a valuable type of REE deposit, has been thought to be derived from the release and enrichment of REE during granite weathering. Understanding the REE occurrence in regolith-hosted deposits is crucial for more efficient extraction. We investigated a weathering granite profile of a regolith-hosted REE deposit located in South China. X-ray diffraction (XRD) and X-ray absorption near edge structure (XANES) analysis of the clay fractions reveal that the highest Ce(IV) content located in intensely weathered layers and cerianite nanoparticles (CeNPs) can be observed, besides invisible adsorbed REEs. Interestingly, most of the CeNPs scatter on halloysite basal surface and exhibit preferred orientation. Detailed analysis demonstrates that the diagonal plane of cerianite matches with the exposed basal surfaces (Si-O tetrahedron) of halloysite. Such a lattice match may contribute to the nucleation and growth of CeNPs after oxidation of the adsorbed Ce(III), which results in great REE enrichment by clays. The findings provide new insight into the mechanism of Ce precipitation and REE mineralization during granite weathering.

Keywords: Nucleation, halloysite, lattice match, cerianite, ion-adsorption rare earth element deposit, South China

Introduction

Rare earth elements (REEs) are not only critical metals widely used in the development of various functional materials but are also regarded as important geochemical indicators due to their unique properties (Chakhmouradian and Wall 2012). Among the 14 REE members, Ce has attracted the most attention because of its high redox sensibility. In natural settings, Ce commonly presents as a less soluble tetravalent state [Ce(IV)] in oxidizing conditions and behaves differently from other REEs, which makes it enriched or depleted relative to other REE members (Akagi and Masuda 1998; Braun et al. 1990; Piepgras and Jacobsen 1992). In general, Ce anomaly [Ce/Ce* = Ce/((La0.8×Pr0.2)1/2)] can be used to trace the redox conditions of sedimentary and diagenetic environments (Mukhopadhyay et al. 2014; Murakami et al. 2001). Its behaviors in weathering process reflect the geochemical cycle of REE, including enrichment in specific layers and migration from parent rocks to rivers, groundwater, and finally, oceans (Leybourne and Johannesson 2008; Singh 2009; Su et al. 2017). Strong Ce enrichment in specific layers of weathered granite profiles even leads to the formation of ion-adsorption REE deposits, which have been widely discovered and exploited in South China (Li et al. 2017). Based on the comprehensive investigation, three main occurrences of the REEs, which were released from weathered primary REE-bearing minerals, have been reported (Janots et al. 2015; Laveuf and Cornu 2009; Li et al. 2017). Besides the dissolved REEs in pore water, part of the released REEs were adsorbed by clay and Fe-Mn oxides, which are mainly present as exchangeable states. The others, especially Ce(IV), precipitated as secondary minerals. Among these various states of REEs, the formation of cerianite nanoparticles (CeNP) represents the oxidation of Ce(III) and usually accounts for commonly observed Ce anomalies. Manganese oxides have been found to play important roles in Ce(III) oxidation and Ce(IV) precipitation in weathering processes (Janots et al. 2015; Santos et al. 2019). However, halloysite and kaolinite are the main components in regolith layers where cerianite particles on halloysite surfaces have been observed rather than any other minerals (Braun et al. 1990; Huang et al. 2021). However, little attention has been paid to the kinetic mechanism for the crystallization of cerianite, especially the selective growth on halloysite.

Halloysite, first described by Berthier (1826), is a dioctahedral 1:1 clay mineral of the kaolin group, which differs from kaolinite in the intercalated water, widely observed in soils and weathered profiles (Joussen et al. 2005; Lu et al. 2016). In general, halloysite exhibits a tubular morphology due to the mismatch between tetrahedral and octahedral sheets (Singh 1996). As the Si-O tetrahedral sheet is larger (though slightly) than the Al-O octahedral sheet, the Si-O tetrahedral surface is always the external surface (Singh 1996). Although halloysite and kaolinite generally act as the carrier of exchangeable REE and secondary cerianite particles (Bao and Zhao 2008; Borst et al. 2020; Li and Zhou 2020; Li et al. 2017), little attention has...