The role of clay minerals in formation of the regolith-hosted heavy rare earth element deposits

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ABSTRACT

Rare earth elements (REEs) have become increasingly important to our modern society due to their strategical significance and numerous high technological applications. Regolith-hosted heavy rare earth element (HREE) deposits in South China are currently the main source of the HREEs, but the ore-forming processes are poorly understood. In these deposits, the REEs are postulated to accumulate in regolith through adsorption on clay minerals. In the Zudong deposit, the world’s largest regolith-hosted HREE deposit, clay minerals are dominated by short, stubby, nanometer-scale halloysite tubes (either 10 or 7 Å) and microcrystalline kaolinite in the saprolite and lower pedolith and micrometer-sized vermicular kaolinite in the humic layer and upper pedolith. A critical transformation of the clay minerals in the upper pedolith is coalescence and unrolling of halloysite to form vermicular kaolinite. Microcrystalline kaolinite also transformed to large, well-crystalline vermicular kaolinite. This transformation could result in significant changes in different physicochemical properties of the clay assemblages. Halloysite-abundant clay assemblages in the deep regolith have specific surface area and porosity significantly higher than the kaolinite-dominant clay assemblages in the shallow soils. The crystallinity of clay minerals also increased, exemplified by decrease in Fe contents of the kaolinite group minerals (from ~1.2 wt% in the lower saprolite to ~0.35 wt% in the upper pedolith), thereby indicative of less availability of various types of adsorption sites. Hence, halloysite-abundant clay minerals of high adsorption capacity in deep regolith could efficiently retain the REEs released from weathering of the parent granite. Reduction in adsorption capacity during the clay transformation in shallow depth partially leads to REE desorption, and the released REEs would be subsequently transported to and adsorbed at deeper part of the soil profile. Hence, the clay-adsorbed REE concentration in the lower pedolith and saprolite (~2500 ppm on average) is much higher than the uppermost soils (~400 ppm on average). Therefore, weathering environments that favor the release of the REEs in the shallow soils but preservation of halloysite in the deep regolith can continuously adsorb REEs in the clay minerals to form economically valuable deposits.

Keywords: Rare earth elements (REEs), REE adsorption, halloysite, kaolinite, regolith-hosted REE deposits, weathering

INTRODUCTION

In facing a continuously growing demand for the rare earth elements (REEs) in various high-technological applications in our modern society, REE resources have become a popular exploration target in the world, especially for the more scarce but important heavy REEs (HREEs). Currently, regolith-hosted HREE deposits are the dominant source of global HREE production (Simandl 2014). These deposits are characterized by low grades (0.05–0.2 wt% rare earth oxide; REO) and individually small tonnages (<10 kt REO resources), except the super-large Zudong deposit (Xie et al. 2016; Li et al. 2017). They formed through mobilization, circulation, and accumulation of the REEs in regolith, mostly developed from granites and associated volcanic rocks (Sanematsu and Watanabe 2016; Li et al. 2017). Such deposits occur mostly in South China and other subtropical and tropical localities, including Southeast Asia, Madagascar, Malawi, and Brazil (Berger et al. 2014; Sanematsu and Watanabe 2016; Li et al. 2017). Accumulation of the REEs in these deposits is postulated to the REE adsorption on various clay minerals as weakly bound outer sphere complexes (Yamaguchi et al. 2018). This explains the feasibility of low-cost extraction through chemical leaching by dilute electrolyte solutions (Moldoveanu and Papangelakis 2016).

Albeit the importance of clay minerals in accumulating the REEs, most previous studies dealt with bulk mineralogy and geochemistry of these deposits (e.g., Wu et al. 1990; Bao and Zhao 2008; Sanematsu et al. 2013, 2015; Berger et al. 2014; Padrones et al. 2017). Some recent studies have considered and examined size fractionation of the REEs (Cheshire 2011; Cheshire et al. 2018; Elliott et al. 2018). However, detailed investigations on the clay-sized particles are still lacking. It has been demonstrated that the REEs concentrate in the lower pedolith (B horizon) and upper saprolite (C horizon). The interface between the pedolith and