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Ion-adsorption REEs in regolith of the Liberty Hill pluton, South Carolina, USA: An effect of hydrothermal alteration

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ABSTRACT

Ion-adsorbed rare earth element (REE) deposits supply the majority of world heavy REE production and substantial light REE production, but relatively little is known of their occurrence outside Southeast Asia. We examined the distribution and forms of REEs on a North American pluton located in the highly weathered and slowly eroding South Carolina Piedmont. The Hercynian Liberty Hill pluton experiences a modern climate that includes ~ 1500 mm annual rainfall and a mean annual temperature of 17 °C. The pluton is medium- to coarse-grained biotite-amphibole granite with minor biotite granite facies. REE-bearing phases are diverse and include monazite, zircon, titanite, allanite, apatite and bastnäsite. Weathered profiles were sampled up to 7 m-deep across the ~400 km^2 pluton. In one profile, ion-adsorbed REEs plus yttrium (REE + Y) ranged up to 581 mg/kg and accounted for up to 77% of total REE + Y in saprolite. In other profiles, ion-adsorbed REE + Y ranged 12–194 mg/kg and only accounted for 3–37% of totals. The profile most enriched in ion-adsorbed REEs was located along the mapped boundary of two granite facies and contained trioctahedral smectite in the saprolite, evidence suggestive of hydrothermal alteration of biotite at that location. Post-emplacement deuteric alteration can generate easily weathered REE phases, particularly fluorocarbonates. In the case of Liberty Hill, hydrothermal alteration may have converted less soluble to more soluble REE minerals. Additionally, regolith P content was inversely correlated with the fraction ion-adsorbed REEs, and weathering related secondary REE-phosphates were found in some regolith profiles. Both patterns illustrate how low P content aids in the accumulation of ion-adsorbed REEs. The localized occurrence at Liberty Hill sheds light on conditions and processes that generate ion-adsorbed REEs.

1. Introduction

Rare earth elements (REEs) are crucial raw materials with a broad variety of high technology manufacturing applications (Kynicky et al., 2012; Van Gosen et al., 2014). Of the deposit types which supply REEs, ion-adsorption deposits are of particular importance because they can be considerably enriched in the less abundant and more valuable heavy REEs (HREEs), and they currently supply virtually all of the HREEs for global consumption (Yang et al., 2013). Recently, there have been efforts to improve the knowledge of all types of potential REE resources in the United States (Bern et al., 2016; Emsbo et al., 2015; Foley and Ayuso, 2013; Long et al., 2010), including ion-adsorption deposit potential (Foley and Ayuso, 2015; Foley et al., 2014, 2015).

A model for ion-adsorption REE deposits has emerged (Sanematsu and Watanabe, 2016; Wu et al., 1990). The model involves igneous, generally granitic, rocks that have undergone extensive weathering. Warm, wet climates promote more rapid weathering and settings with such current or past climates are therefore prospective. Erosion can strip away the products of weathering and therefore erosion-limited settings, where weathering rates greatly exceed erosion rates, are prospective. Deposit genesis involves the decomposition of REE-bearing minerals in the surface weathering environment, release of REEs to solution, and retention as hydrated cations on negatively charged sites on the surfaces of clay minerals, an outer-sphere surface complex. Release of REEs to solution is promoted by less resistant and often alteration derived, pre-weathering host phases like fluorocarbonates and silicates, compared to common phosphates like monazite (Bao and Zhao, 2008; Ishihara et al., 2008; Sanematsu et al., 2013). Low P content in parent rock appears to be key for development (Sanematsu et al., 2015). The REEs migrate vertically and laterally in weathered regolith during deposit genesis, fractionating relative to each other and generating zones of depletion and enrichment. Zones of maximum enrichment are commonly 3–10 m-deep (Chi and Tian, 2008; Sanematsu et al., 2013). The resource extraction methods are straightforward and use a salt solution, usually ammonium sulfate, in an ion-exchange process to liberate REEs from the weathered material (Chi and Tian, 2008; Moldoveanu and Papangelakis, 2012). The ion-adsorbed form of the REEs and exchange-process extraction distinguish ion-adsorption deposits from other weathering derived, lateritic REE mineralization

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(e.g., Berger et al., 2014). Ease of extraction and poor consolidation of the weathered ore make development relatively inexpensive. Low costs are important because ore grade is also low. Ion-adsorption REEs are currently only mined in southeast China, where grades range from 500 to 6500 ppm REE, 60–90% of which are in ion-adsorbed form (Chi and Tian, 2008; Sanematsu and Watanabe, 2016). Ion-adsorption REE deposits and significant occurrences have been identified in Thailand, Northern Vietnam, Brazil, Malawi, and Madagascar (Mentani et al., 2010; Moldoveanu and Papangelakis, 2012; Sanematsu et al., 2013; Sanematsu and Watanabe, 2016).

Here we examine the abundance of ion-adsorption REEs in regolith (soil and underlying saprolite) derived from the Liberty Hill pluton of South Carolina. The pluton is exposed in the Piedmont region of North America where relatively warm and wet climatic conditions have combined with relatively slow erosion rates to yield thick accumulations of weathered material at the surface. Elemental and mineralogical properties of the parent granite and its weathering products were measured and the data are interpreted to understand how weathering and alteration processes influenced the accumulation of ion-adsorption REEs. The results shed light on the potential for ion-adsorption REE deposits in North America and how relevant processes may have occurred in other settings.

2. Study area and methods

2.1. Study area description

The majority of the Liberty Hill pluton is medium – coarse-grained biotite-amphibole granite with minor fine and coarse-grained biotite granite facies (Speer et al., 1989). Small dikes and stocks that make up a fine-grained central facies occur within the medium–coarse-grained facies (Fig. 1). The pluton covers an outcrop area of over ~360 km^2, extending across Kershaw, Lancaster, and Fairfield counties in South Carolina. The Liberty Hill pluton is Hercynian in age and intrudes greenschist-grade metasedimentary rocks of the Carolina Slate belt. Fullagar and Butler (1979) reported a Rb-Sr isotopic age of 293 ± 15 Ma. More recent dating by ion microprobe Shrimp-RG on zircon indicates an age of 305 Ma (Foley et al., 2015).

The current climate is subtropical with a mean annual temperature of 17 °C and mean annual precipitation of 1150 mm based upon weather stations surrounding the pluton (National Climatic Data Center, 2015). Upland weathering profiles in the Piedmont are commonly 10–20 m thick and have estimated residence times of between 1 and 5 Ma, though most may be at the younger end of that range (Pavich, 1989). During the late 1800s through the early 1900s, deforestation and subsequent poor erosion control and agricultural practices combined with heavy rainfall to cause average erosion estimated at 25–31 cm across the part of the Piedmont containing the Liberty Hill pluton (Trimble, 1974).

2.2. Sample collection

Unweathered granite was collected from exposures at four quarries, two from the fine-grained facies and two from the coarse-grained facies (Fig. 1). Regolith (soil + saprolite) profiles were sampled at four locations, each at the top of a hill or ridge crest to avoid contributions of eroded material from upslope. At the locations sampled, the soils have been mapped as eroded Kanhapludults of the Pacolet (LH2 and LH4) and Madison (LH3 and LH9) series (Soil Survey Staff, 2015). Soil profile LH2 is located above the contact zone between fine and coarse-grained granite, LH4 occurs above the fine-grained facies and LH3 and LH9 overlie coarse-grained granite. The transition to saprolite typically occurs at 0.9–1.7-m depth for these series. Regolith profiles were collected by

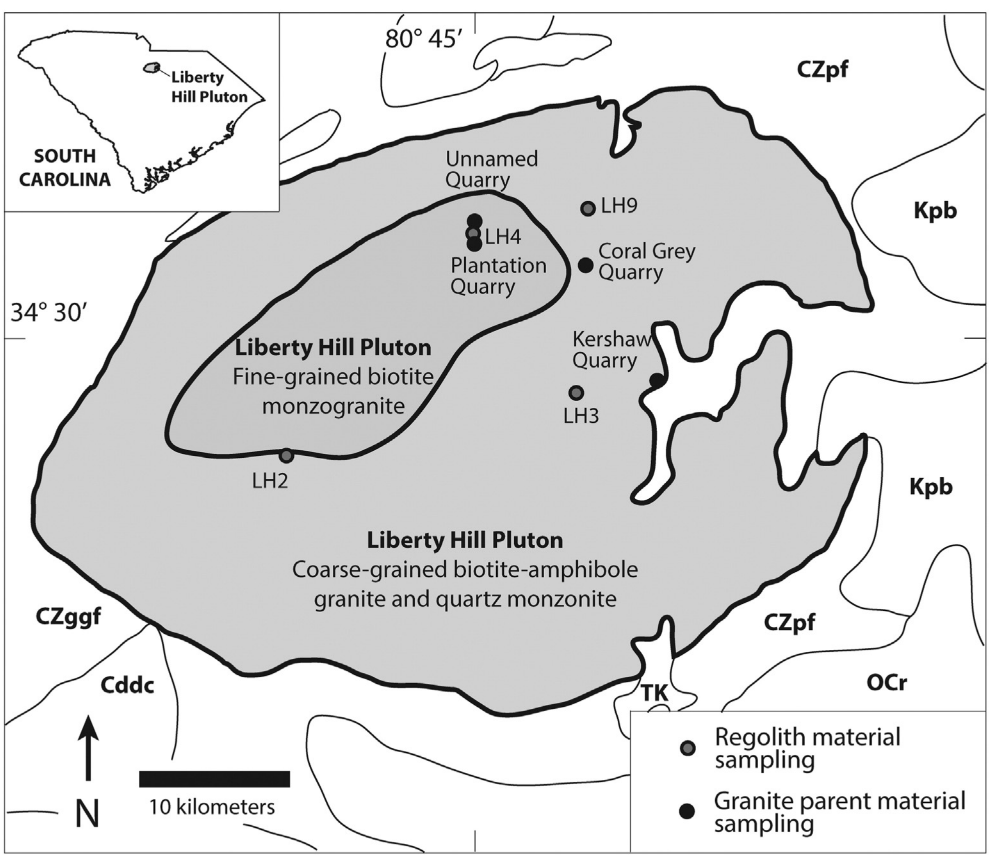

Fig. 1. Map of Liberty Hill pluton and sampling sites. Surrounding geologic units are Cddc, Dutchman's Creek pluton; CZpf, Persimmon Fork Formation; CZggf, Great Falls metagranite; Kpb, Peedee Formation; OCr, Richtex Formation.
Map modified from Speer et al. (1989).