

REE enrichment in granite-derived regolith deposits of the Southeastern United States: Prospective source rocks and accumulation processes



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Recommended citation: Foley, N. and Ayuso, R., 2015. REE enrichment in granite-derived regolith deposits of the Southeastern United States: Prospective source rocks and accumulation processes. In: Simandl, G.J. and Neetz, M., (Eds.), Symposium on Strategic and Critical Materials Proceedings, November 13-14, 2015, Victoria, British Columbia, British Columbia Ministry of Energy and Mines, British Columbia Geological Survey Paper 2015-3, pp. 131-138.

Summary

The Southeastern United States contains numerous anorogenic, or A-type, granites, which constitute promising source rocks for REE-enriched ion adsorption clay deposits due to their inherently high concentrations of REE. These granites have undergone a long history of chemical weathering, resulting in thick granite-derived regoliths, akin to those of South China, which supply virtually all heavy REE and Y, and a significant portion of light REE to global markets. Detailed comparisons of granite regolith profiles formed on the Stewartville and Striped Rock plutons, and the Robertson River batholith (Virginia) indicate that REE are mobile and can attain grades comparable to those of deposits currently mined in China. A REE-enriched parent, either A-type or I-type (highly fractionated igneous type) granite, is thought to be critical for generating the high concentrations of REE in regolith profiles. One prominent feature we recognize in many granites and mineralized regoliths is the tetrad behaviour displayed in REE chondrite-normalized patterns. Tetrad patterns in granite and regolith result from processes that promote the redistribution, enrichment, and fractionation of REE, such as late- to post-magmatic alteration of granite and silicate hydrolysis in the regolith. Thus, REE patterns showing tetrad effects may be a key for discriminating highly prospective source rocks and regoliths with potential for REE ion adsorption clay deposits.

1. Introduction

Currently mined only in South China (Kynicky et al., 2013), rare earth element (REE) ion-adsorption clay deposits are of global economic importance because they supply virtually all heavy (Gd-Lu) REE and a significant portion of light (La-Eu) REE to global markets. Nonetheless, considerable ambiguity remains about the source rocks, genesis, and global distribution of this deposit type. Herein we present the results of ongoing studies to investigate the role of parent rock in the formation of REE ion adsorption deposits in the southeast United States. Our objective is to understand the genesis of REE-enriched regolith profiles and establish the potential for economic REE

ion-adsorption clay deposits. Although all weathered materials may contain some exchangeable REE, one of our aims is to identify the role of source rock composition and mineralogy in generating high concentrations of REE in a regolith. Our initial work (e.g., Foley, et al., 2013, 2014, 2015) focused on anorogenic granite as a promising source rock for ion adsorption type REE deposits because they contain inherently high concentrations of REE (e.g., Whalen et al., 1987).

The main features of the deposit type (Bao and Zhou, 2008) include: the presence of igneous suites, generally granitic rocks; long periods of intense weathering with little subsequent erosion; and evidence for enrichment of REE in the regolith. REE mobilization processes are thought to include late-magmatic-to-deuteric (hydrothermal) alteration and deep lateritic weathering (Bao and Zhou, 2008, Ishihara et al., 2008). Ore consists of REE ions or hydroxides attached to interlayer and edge sites in clay minerals, and forms when REE are released from host igneous phases and adsorbed to newly formed clay minerals generated by weathering of aluminosilicate minerals. Mined deposits in China reportedly have grades in the range of 500 to over 3000 ppm REE, contain 3-5 times the REE concentration of the source rock and contain mainly either light REE or heavy REE (Bao and Zhou, 2008). Differential mobility of REE within soil profiles is thought to contribute to formation of heavy-REE- vs. light-REE-enriched deposits (Bao and Zhou, 2008). Protoliths for the Chinese deposits were originally considered as calc-alkaline to alkaline granites, with peralkaline syenite and granite as likely parents for ore with mainly heavy-REE and Y (Wu et al., 1996, and references therein). More recent work by Wang et al. (2015) indicates that both REE-enriched anorogenic (A-type) granites and highly fractionated igneous (I-type) granites are prospective source rocks in South China.

2. Granites and granite-derived regoliths, Southeastern United States

The Southeastern United States contains three major belts of weathered igneous rocks. The westernmost belt consists of

Neoproterozoic anorogenic plutons and related rocks that have highly silicic compositions, high contents of Ga, F, Nb, Sn, Ta, Y, and Zr, and high total REE (Tollo et al., 2004). Granite discrimination diagrams classify these rocks as high-K calc-alkaline granites, having compositions that range from slightly metaluminous to peraluminous and peralkaline. These granites were emplaced along the eastern flank of the Blue Ridge province during regional crustal extension related to opening of the Iapetus Ocean and breakup of the supercontinent Rodinia (Tollo et al., 2004). In Virginia, the plutons formed mainly during an early period of extension, between 765 and 680 Ma (Tollo et al., 2004). Plutons and prospective regolith sites (Fig. 1) were selected based on geologic attributes, such as rock type, whole-rock chemistry, topographic setting, and accessibility. Studies were conducted on the Stewartsville (SHRIMP U-Pb zircon age of 680 ± 5.7 Ma, unpublished data) and Striped Rock (SHRIMP U-Pb zircon age of 735.4 ± 5.2 Ma, unpublished data) plutons, and two younger plutons (SHRIMP U-Pb zircon ages of 703.6 ± 13.4 Ma for the Amissville granite, and 697.2 ± 6.8 Ma for the Battle Mountain granite, unpublished data) of the Robertson River batholith (Tollo and Aleinikoff, 1996).

The Stewartsville pluton (Fig. 1) is a medium- to coarse-grained biotite granite that forms a narrow lobate to irregular belt southeast of Roanoke, Virginia (Henika, 2011). It is one of a number of medium-grey, poorly foliated to massive, biotite granitoid bodies of similar age that occur throughout central Virginia (Henika, 2011). The granite is equigranular and contains quartz, sericitized and albitized, perthitic, pale red and white feldspars, sodic plagioclase, and mafic clots and stringers. Feldspars contain inclusions of synchysite-(Nd) and fergusonite. Mafic clots are primarily composed of

biotite and stilpnomelane and, less typically, include magnetite, remnant cores of green and green-brown hornblende, and accessory minerals including apatite, epidote, garnet, Nb-rutile, fergusonite, monazite, titanite, xenotime, gadolinite, and zircon. Abundant allanite and fluorite are diagnostic of the Stewartsville granite (Henika, 2011).

The Striped Rock pluton (Fig. 1) is slightly foliated to equigranular and composed of medium- to coarse-grained hornblende-biotite granite, with minor amounts of fine-grained aplite and dikes (Essex, 1993). The main body of the pluton is lens-shaped and is exposed over an area of approximately 65 km², with small outliers to the northeast making it one of the largest single Neoproterozoic granite bodies in Virginia. The granite is composed mainly of white, grey, and pink alkali feldspar, anhedral and interstitial quartz, and plagioclase. Alkali feldspar commonly has rapikivi textures and albitized rims. Anhedral clots of green biotite are the most common mafic phase and, in the centre of the pluton, the green biotite is intergrown with sodic amphibole (ferro-pargasite; Essex, 1993). Aplites contain porphyritic quartz, alkali feldspar, and plagioclase and, as a late-stage alteration product, muscovite. Accessory phases in all rock types include allanite and fluorite, zircon, epidote, ilmenite, fine-grained apatite, and rare anhedral to subhedral titanite. Fine-grained biotite and epidote also form fracture fillings in and around quartz and feldspar. Allanite is typically metamict and zoned, with epidote rims. Purple fluorite occurs mainly as fracture fillings in the medium- to coarse-grained granite, and as anhedral grains and inclusions in plagioclase and biotite in the aplite.

The Robertson River batholith (Tollo and Aleinikoff, 1996) was emplaced in two pulses, at 735–722 Ma and 706–702 Ma. Most of the batholith is composed of metaluminous granite, with peralkaline rocks of the Battle Mountain complex (Fig. 1) making up the younger magmatic phase (Tollo and Aleinikoff, 1996). Granite of the Battle Mountain complex contains mainly feldspar and quartz with mafic clots of biotite, sodic clinopyroxene (aegirine) and amphibole (riebeckite), stilpnomelane, and abundant fluorite (Tollo et al., 2004). The rocks have high concentrations of Zr (~1000 ppm), contained in zircon and chevkinite (Belkin, 2015), and high concentrations of REE plus yttrium (>1000 ppm; Tollo and Aleinikoff, 1996). Other REE-bearing phases include fluorocarbonate minerals, mainly bastnäsite-(Ce), with minor parisite-(Ce), and synchysite-(Ce); chevkinite-(Ce), allanite-(Ce), gadolinite-(Y), and a variety of Nb phases (aeschnite-euxenite, fergusonite, and samarskite) (Belkin, 2015).

3. Regolith formation

Many naturally exposed granite outcrops in the Piedmont region of Virginia are intensely weathered, with overlying regolith consisting of saprolite extending to depths of tens of metres overlain by B-horizon type soils, and the region is highly vegetated. The regoliths may be thin and discontinuous or metres thick and laterally extensive. Regolith is sparsely distributed across the Battle Mountain pluton, whereas the

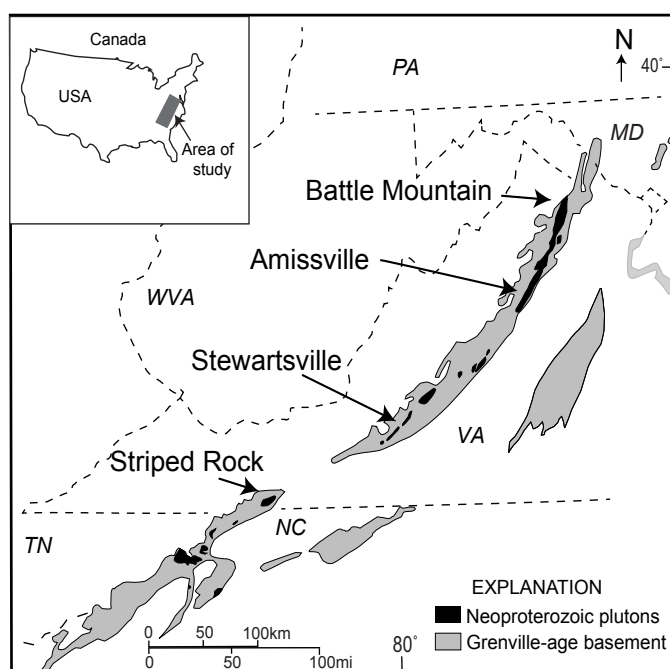


Fig. 1. General location of the granitic plutons and granite-derived regoliths reported on here. Modified from Tollo et al. (2004).

Striped Rock pluton is one of the most deeply weathered of the anorogenic plutons. Regolith formed by weathering of the Stewartsville pluton is well developed in near-vertical exposures that crop out near the Roanoke River in southwest Virginia. The Stewartsville exposures consist of >30 metre high by >60 metre long weathered sections that extend from bedrock up through regolith materials (Fig. 2). The sections include units of nearly fresh rock, highly weathered saprolite, indurated gravels and sands, and poorly delineated layers of subsoil and topsoil. Granite at the base of the profile is iron stained and weathered on exposed surfaces and along cracks. Partially weathered sections of the profiles display a range of rock textures throughout rather than systematic changes from base to surface. In the lower parts, cobble- and boulder-sized relics of spheroidally weathered granite retaining distinctive primary textures are surrounded by nearly disaggregated granite that crumbles to sand- and gravel-sized fragments when sampled. Soil layers overlying the saprolite are mainly of B-horizon-type and contain a higher proportion of clay (mixed chlorite and kaolinite) than the saprolite. A thin veneer of A-horizon-type soil overlies the Stewartsville profile.

4. REE and Pb-Nd isotope geochemistry

Whole rock REE patterns for the granites (Fig. 3a) show steep chondrite-normalized patterns that are light-REE-enriched at



Fig. 2. Granite-derived regolith field site, Stewartsville pluton, Virginia, showing a profile with bedrock at base, which is overlain by a 30-metre high exposure of partly weathered granite knobs, saprolite, disaggregated granite gravels and sands, and soils. The uppermost metre is mainly B-horizon type soil.

200 to 800x chondrite and with heavy-REE at ~20 to 100x chondrite. The range in REE patterns shows a wide variability in total REE concentrations among plutons within the batholith (compare Amissville and Battle Mountain) and within a single pluton (e.g., Stewartsville). All the granites show a negative Eu anomaly and most lack a Ce anomaly. REE data for bedrock, saprolite, and soils at the Stewartsville site (Fig. 3c) show an increase from 300-650 ppm REE in bedrock at the base of the profile to over 2880 ppm REE in clay-rich soils. A negative Eu anomaly in the granite is retained in weathered alluvium, and the uppermost soil samples show a pronounced negative Ce anomaly, likely due to downward migration of Ce and cerianite precipitation elsewhere in the weathering profile. Normalized to average values for bedrock at the base of the profile, the soils and saprolite show increases in light and middle-REE (La-Dy) relative to bedrock (Fig. 3d). The heavy REE (Dy-Lu) show a subtle expression of tetrad behaviour in the M-type rounding seen in third and fourth tetrads (Fig. 3d). These results compare favourably with light REE-enriched deposits at Heling (Figs. 3e-f), in contrast to heavy REE-enriched deposits such as those at Xinzui (Figs. 3g-h). Sequential leaching of regolith samples from Stewartsville included a weak acid-ion exchange process (Na-acetate at pH~5) to extract ions adsorbed to clay (Fig. 3b), and aqua regia and four-acid leaches to assess the proportion of refractory REE-bearing minerals (e.g., monazite, zircon) remaining in the regolith. The fraction of readily extractable REE in the bedrock-soil profile varied from 30 to 70%, with an average yield of 900 ppm REE from saprolite and soils.

Characterization of Pb and Nd isotopes of parent rocks, soils, and potential anthropogenic inputs can provide critical data for quantifying in-situ vs. transported REE in soils (Harlavan et al., 2009; Ohlander et al., 2000). Nd isotopes in igneous rocks are commonly distributed in rock-forming minerals and accessory minerals, and in alteration products that differ in Sm/Nd ratios. At the Stewartsville site, values of $^{143}\text{Nd}/^{144}\text{Nd}$ for regolith samples vary from 0.512037 to 0.512415, compared to a bedrock value of 0.512424. Nd isotope compositions show limited correlation with Nd, Sm, and Sm/Nd ratios (soils: 0.242-0.260; bedrock: 0.180-0.271). The moderate scatter in Nd isotope ratios and Sm/Nd values in the surficial materials, compared to bedrock, is consistent with mineral weathering. In comparison, Sm/Nd values of mild acid leachates range from 0.233 to 0.261. This suggests that one or more weathering minerals have bulk Sm/Nd comparable to bedrock. Such minerals would be important hosts of REE in the profile. Pb in regoliths results from a combination of Pb from feldspar and other igneous minerals and Pb from anthropogenic sources such as fertilizers, other clay-based agricultural amendments, and past use of leaded gas. Pb isotope signatures can be used to discriminate natural versus anthropogenic Pb in soils (Ayuso et al., 2008) and, by inference, indicate local anthropogenic addition of REE to a profile from clay-based agricultural amendments. In the Stewartsville profile, changes in Pb isotopes from bedrock to surface soils correlate with total REE and reflect progressive and sequential weathering of igneous

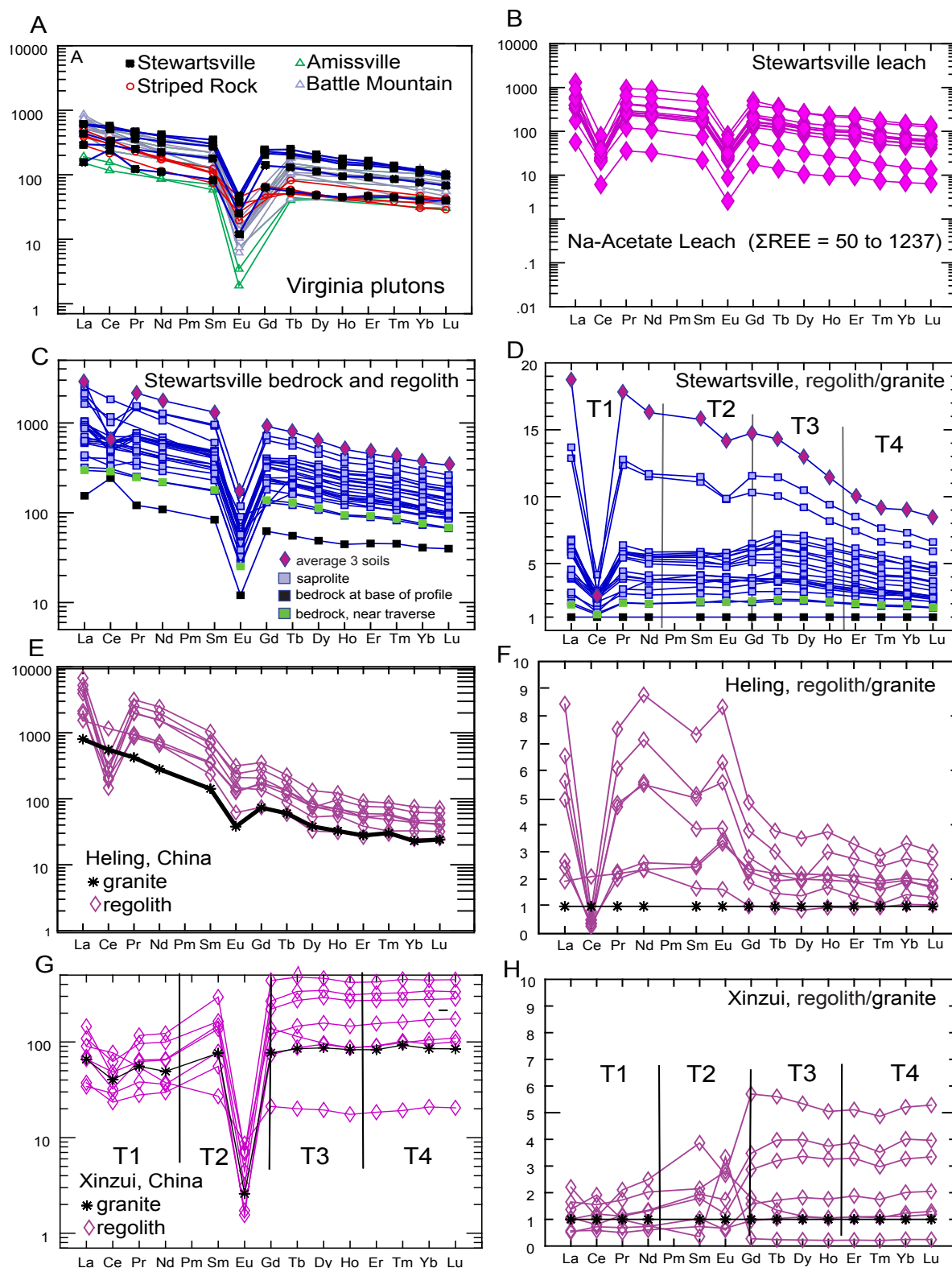


Fig. 3. a) REE patterns for four Neoproterozoic anorogenic granites showing whole rock concentrations ranging from ~200 to nearly 1000 ppm REE. b) Selected sequential leach results for regolith samples from a Stewartville profile. REE patterns for c) Stewartville granite and granite-derived regolith showing increases in REE concentrations in saprolite and overlying soils, and d) regolith samples from a bedrock-soil profile over the Stewartville granite, normalized to average REE values for 2 bedrock samples near the site. Vertical lines show tetrad subdivisions (T1, T2, T3, T4). See text for details. Analyses from ActLabs, Canada. e) and f) Granite-regolith patterns for light REE enriched deposits at Heling, China ion adsorption clay deposit; g) and h) patterns for heavy REE deposit at Xinxui, China (data from Bao and Zhou, 2008). Chondrite-normalization values from Sun and McDonough (1989). Note scale change for pattern pairs c) - d), versus g) - h).

allanite, biotite, and feldspars, thus establishing that the profiles likely contain no anthropogenic addition of REE.

5. Mineral residence and REE enrichment in regolith

Allanite is the predominant source mineral for light-middle-REE in most of these granites; zircon is the most abundant mineral that selectively incorporates heavy-REE. Apatite, garnet, titanite, and fluorite in the rocks generally have REE contents that are less than 0.5 weight percent or below limits of detection (0.1-0.2 wt.% by element: electron microprobe analysis). Monazite, xenotime, fergusonite, chevkinite, gadolinite, and other phosphate and niobate minerals are volumetrically minor. REE-fluorocarbonate minerals are unevenly distributed and volumetrically minor in all plutons, except where they occur as late phases in peralkaline rocks, such as at Battle Mountain. The granite-derived regolith studied in detail at Stewartsville contains a diverse suite of REE-bearing minerals, including refractory igneous minerals (e.g. zircon, xenotime, monazite) and remnants of relatively soluble igneous phases (e.g. allanite, titanate, apatite), a wide variety of secondary and authigenic REE-bearing minerals (e.g., cerianite, monazite-(Ce), Ca-REE fluorocarbonate minerals) as replacements and cements, and REE adsorbed to neoformed clay minerals.

Allanite is generally abundant in all the granites and forms euhedral to subhedral, brown crystals that commonly attain lengths of up to 3 mm, contain greater than 18 wt.% REE, and are zoned in Th contents. For example, unweathered allanite from Stewartsville has Sm/Nd values of 0.140 to 0.160, 23-27 wt.% REE, and up to 2 wt.% Th. Allanite weathers readily in granites on exposed surfaces and is typically completely altered to orange and white clays and iron-oxide (Fig. 4a). In the Stewartsville profile, REE released from allanite are distributed within clay mineral sheets (Fig. 4b) and as oxide and fluorocarbonate fill in veins and fractures that cut altered grains. Secondary REE minerals are also found at grain boundaries,

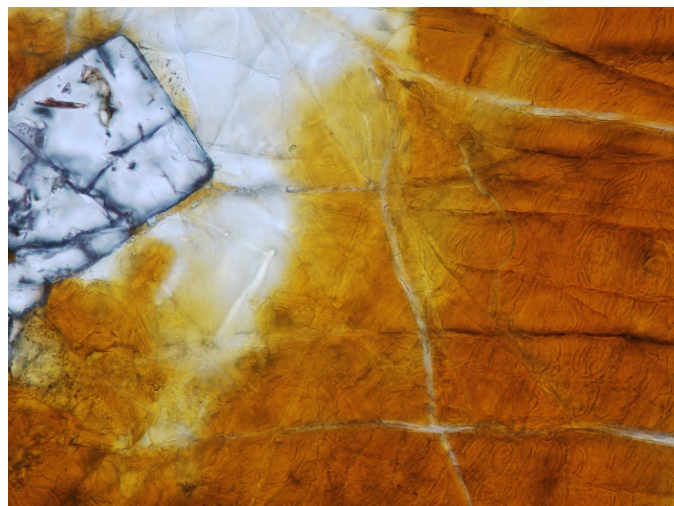


Fig. 4. a) Altered core of deeply weathered allanite from Stewartsville regolith profile showing white kaolinite, yellow-orange Fe-clay, and zircon. Field of view is 500 µm.

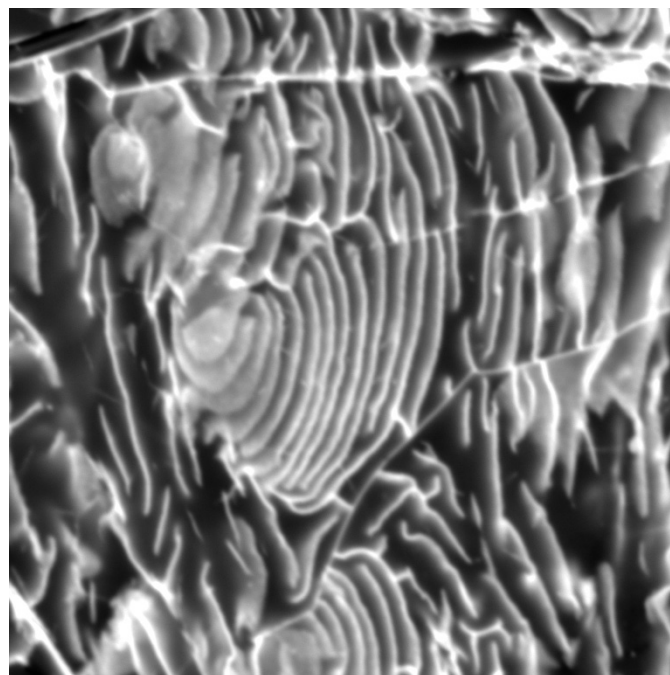


Fig. 4. b) SEM back-scatter electron image showing area of Fe-Al clays (dark layers) defined by REE oxide edges (bright areas are REE: La, Nd, Sm, Gd, Dy) in weathered allanite from saprolite; Stewartsville pluton. Field of view is 20 µm.

in crosscutting stringers and anastomosing veinlets, and as cements in weathered saprolite. Cements typically consist of varying mixtures of Mn-oxide or Mn-clays, kaolinite, and goethite intermixed with spheroidal cerianite and a monazite-(Ce).

Zircon in most of these plutons shows complex and highly variable features, including variations in color, size, and compositional zoning. For example, in the Stewartsville and Striped Rock plutons, some zircon populations have features typical of magmatic zircon, such as Hf-zonation, low Th and U, REE contents of less than 2500 ppm, and patterns with La at 1x-100x chondrite and Lu at ~10,000x chondrite. Another population has complex interiors with dark cores enriched in REE up to 1.8% REE (light REE at 10,000x chondrite, 2800 ppm Th, and 4800 ppm U). Zircon rims from peralkaline rocks of the Battle Mountain complex form amoeboid and altered masses that have mean values of ~1.3 wt.% REE plus Y (Belkin, 2015); in contrast, Hf-zoned cores have patterns typical of magmatic zircon with La at 0.1-100x chondrite and Lu at 1000-10,000x chondrite. Zircon from the Amissville pluton is spongy and fragmented with up to 1.6 wt.% REE. The patterns show La at 1-1000x chondrite and Lu at 1000-10,000x chondrite. Zircon is the most abundant residual igneous accessory phase in most of the saprolites and soils. Zircon separates from weathered profiles at Stewartsville show removal of light-middle REE from the dark cores, likely due to metamictization.

At Stewartsville and many other granite-derived regoliths of the central Appalachians, we consider that enrichment of REE in the regolith is predominantly a result of hydrolysis of igneous

minerals (feldspars, allanite, apatite, biotite) and removal of the alkali elements. Progressive weathering of allanite, biotite, feldspars, hornblende, apatite, and titanite results in the occurrence of secondary Fe-oxides (goethite, hematite) and Al-clays (illites, kaolinite, halloysite) throughout the regolith. The redistribution of REE as either adsorbed ions or secondary minerals is likely controlled by local microchemical domains in the regolith defined by solubility factors inherent in the aqueous phase, such as pH, redox state, and available complexing agents. Silicate weathering is acid-consuming and if it proceeds unbuffered (for example, by acidic meteoric waters), pH will move to neutral values where the relative stability of REE-carbonate or phosphate complexes may result in formation of monazite or fluorocarbonate minerals (Wood, 1990, and references therein). At Stewartsville, the enrichment of REE in the regolith is predominantly a result of light-middle-enriched allanite weathering, with subsequent fixing of released REE as ions or hydroxyl ions on clays, or as poorly crystalline secondary oxide, niobate, fluorocarbonate, and phosphate minerals.

6. Comparison with granite source rocks of China

Large igneous suites of the Southeastern United States generally match the compositional range of granitic rocks associated with the South China REE deposits. Chinese granites that host REE ion adsorption deposits also include both highly fractionated and anorogenic granites; for example, at Zhaibei and Xihuashan, Jiangxi Province, South China. Weathering of the highly peraluminous A-type Zhaibei granite led to formation of light-middle REE ion adsorption deposits (Wang et al., 2015). The Zhaibei granite has chondrite-normalized REE patterns exhibiting strong enrichment in light-REE with steep positive slopes (average $La_N/Yb_N = 32$), negative Eu anomalies, and whole rock REE concentrations of <600 ppm REE. REE are distributed among a variety of minerals, including titanite (~7500 ppm REE), allanite, thorite (~4.5 % by wt. Y), zircon, monazite, apatite, and REE fluorocarbonate minerals. In contrast, the Xihuashan granite has light REE at 40x chondrite and heavy REE at ~100x chondrite, a strong negative Eu anomaly, whole rock concentrations of ~100 ppm REE, and $La_N/Yb_N < 1$. The rare earth minerals include xenotime, monazite, fergusonite, samarskite, gadolinite, aeschynite, euxenite and parisite-(Y). Weathering of the high-silica A-type granite at Xihuashan resulted in regolith containing ion adsorption deposits enriched in heavy REE (Xiao et al., 2009). Regoliths formed on the metaluminous-peraluminous granites of the southeastern US share many of the attributes of the Zhaibei granite and regolith, whereas peralkaline granites of the southeastern US (e.g., Battle Mountain, Amissville) share mineralogical similarities that are more comparable to the Xihuashan granite.

Petrographic and mineralogical evidence from a number of studies (e.g., Whalen et al., 1987) indicates an important role for late diagenetic to hydrothermal processes in REE enrichment in A-type granites. The common development of a fluid

phase rich in F, CO₂ and H₂O late in the evolution of A-type and highly fractionated granites can lead to hydrolysis-type reactions capable of converting, for example, monazite to bastnäsite and xenotime to synchysite-(Y) (Johan and Johan, 2005). Furthermore, the low concentrations of phosphate in most A-type granite melts (e.g., Bonin, 2007) may limit initial monazite formation, leaving light-to-middle REE available for incorporation in less refractory minerals such as allanite and soluble REE fluorocarbonates. Thus, hydrothermal alteration and mineralization have a significant influence on the diverse character of ion adsorption type REE deposits because they catalyse conversion of more refractory igneous phases to less refractory REE-rich minerals and provide possible pathways for generating granites with high concentrations of REE in minerals that weather readily in surface environments.

We suggest that the notable development of tetrad behaviour in REE patterns of granites and granite-derived regoliths, such as those at Zudong and Guanxi, China (Fig. 5), represent an important attribute of highly prospective source rocks for ion adsorption clay deposits, particularly those of the heavy REE type. Tetrad behaviour controls REE distributions in geological samples such that REE representing quarter, half, three-quarter, and completely filled 4f shells have increased stability (e.g., McLennan, 1994). Tetrad effects in REE patterns may highlight the occurrence of processes such as high degrees of fractional crystallization, hydrothermal alteration, and mineralization (Jahn et al., 2001). Expressions of tetrad behaviour are well documented for granite-related rare metal deposits (see, for example, Monecke et al., 2002) and in rare metal granites of South China (e.g., Zhao et al., 2002). We note that tetrad expressions are retained in regoliths associated with many South China REE ion adsorption deposits (Fig. 5). The tetrad effect is especially pronounced for heavy REE ion adsorption deposits at Zudong and Xinzui (Figs. 3e, 5) and light-middle REE deposits at Guanxi and Heling (Figs. 3g, 5). The concave-down M-type patterns in the third (T3) and fourth (T4) tetrads (Figs. 3, 5), suggest mobility in the middle and heavy REE. The Zhaibei granites, which host light REE ion adsorption deposits, lack the tetrad behaviour exhibited by many Chinese source granites. In contrast, subtle tetrad effects in T3 and T4 do appear in the granite and regolith that host the heavy REE ion adsorption deposits at Xihuashan (data from Xiao et al., 2009). REE patterns for most anorogenic granites of the Southeastern United States also lack obvious tetrad behaviour. However, some regolith samples from Battle Mountain and Stewartsville display subtle expressions of T3 and T4 (for example, Fig. 3d). Belkin (2015) noted that many accessory phases in the peralkaline rocks of Battle Mountain and Amissville are altered and show complex zoning, overgrowths, and multiple generations, leading him to suggest that late-stage, Na, Fe, and F-rich fluids carrying REE, Y, Nb, and Zr moved through the rock during early cooling. Likewise, garnet, fluorite, zircon, allanite, and niobate minerals in much of the Stewartsville granite show embayments, altered cores, overgrowths, and veining, suggesting multiple generations of hydrothermal and

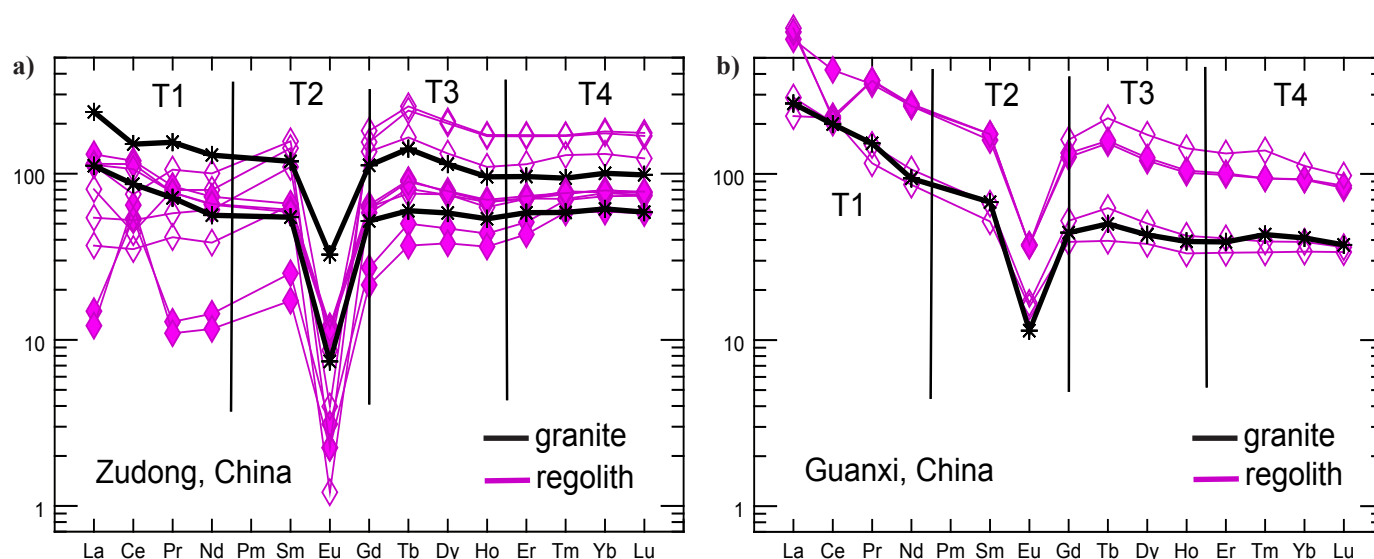


Fig. 5. Chondrite-normalized REE patterns for 2 Chinese granites (black) and associated regolith materials (pink) showing subtle tetrad behavior in T3, T4. **a)** Zudong heavy REE ion adsorption clay deposits (Longnan, China) and **b)** Guanxi regolith deposits enriched in light and light-middle REE. Data from Ishihara et al. (2008), Bao and Zhao (2008), and Murakami and Ishihara (2008).

deuteric alteration, both early and late in the petrogenesis.

7. Conclusions

Our studies demonstrate significant potential in the Southeastern United States for REE ion adsorption clay deposits of a type containing light-middle REE and yttrium, and an-as-yet unknown potential for high-value heavy REE deposits.

- Large igneous suites of the Southeastern United States generally match the compositional ranges of granitic rocks associated with South China REE ion adsorption clay deposits. Source rocks that result in regolith deposits highly enriched in REE in the Southeastern United States include high-silica anorogenic granitic suites with high total REE and low P. Granites that show tetrad behaviour in REE patterns may be highly prospective source rocks for REE ion adsorption clay deposits.
- The importance of weathering of a REE-enriched parent (A-type or highly fractionated I-type granite) is in the potential for generating high concentrations of mobile REE in the developing regolith. The Stewartville example highlights the importance of allanite weathering in generating a light-middle-REE-enriched regolith. However, weathering of other REE-bearing minerals, such as garnet, metamict zircon, REE-fluorocarbonates (for example, bastnäsite, parisite, synchysite), chevkinite, gadolinite, and niobates (aeschnite-euxenite, fergusonite, and samarskite) may be key to generating a heavy REE enriched regolith.
- It remains to be fully established if regoliths containing high enough concentrations of readily extractable and high-value REE occur in adequate volumes to be considered a future resource in the US. Further studies are underway to refine the full range of potential source rocks for REE-bearing clay deposits and to determine,

in particular, the most prospective source rocks for high-value REE-bearing clay deposits.

Acknowledgments

We thank M. Carter, A. Merschat, and C.S. Southworth for valuable discussions on geology field sites. Excellent laboratory support was provided by J. Jackson (XRD, mineral separations), R. Indela and S. Robinson (USGS Reston-Radiogenic Isotope Lab), J. Vazquez (USGS-Stanford SHRIMP), H. Belkin (USGS-Reston Microprobe) and L. Hayden (USGS-Menlo Park Microprobe). Constructive reviews of an early version by reviewers and the Editors resulted in a much improved paper.

References cited

- Ayuso, R., Foley, N., and Lipfert, G., 2008. Lead isotopes as monitors of anthropogenic and natural sources affecting the surficial environment. In: DeVivo, B., Belkin, H., and Lima, A., (Eds.), *Environmental Geochemistry: Site Characterization, Data Analysis and Case Histories*. Elsevier, Chapter 12, 291-318.
- Bao, Z.W., and Zhao, Z.H., 2008. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in South China. *Ore Geology Reviews*, 33, 519-535.
- Belkin, H.E., 2015. REE, Y, Zr, and Nb mineralogy of the Neoproterozoic rift-related Robertson River igneous suite, Northern Virginia, USA [abs]. AGU-GAC-MAC-CGU Joint Assembly, Abstracts volume, p. 297.
- Bonin, B., 2007. A-type granites and related rocks: Evolution of the concept, problems, and prospects. *Lithos*, 97, 1-29.
- Essex, R.M., 1993. Age and petrogenesis of the Striped Rock pluton, Virginia. Unpublished M.S. thesis, Virginia Tech, Blacksburg, Virginia, 98 p.
- Foley, N. K., and Ayuso, R.A., 2013. REE mobility in high-alumina altered metavolcanic deposits, South Carolina, USA. *Journal of Geochemical Exploration*, 133, 50-67.
- Foley, N.K., Ayuso, R.A., Bern, C.R., Hubbard, B., and Vazquez, J., 2014. REE distribution and mobility in regolith formed on granite bedrock, Southeast United States. *Acta Geologica Sinica*, 88(supp. 2), 428-430.
- Foley, N.K., Ayuso, R.A., Hubbard, B., Bern, C., and Shah, A., 2015. Geochemical and mineralogical characteristics of REE in

- granite-derived regolith of the Southeastern United States. 13th SGA Biennial Meeting, Mineral Resources in a Sustainable World. Proceedings, 2, 725-728.
- Harlavan, Y., Erel, Y., and Blum, J.D., 2009. The coupled release of REE and Pb to the soil labile pool with time by weathering of accessory phases, Wind River, WY. *Geochimica et Cosmochimica Acta*, 73, 320-336.
- Henika, W.S., 2011. Geologic map of the Hardy quadrangle, Virginia. Virginia Division of Geology and Mineral Resources Open File Report 2011-3, 1:24,000 scale.
- Ishihara, S., Renmin, H., Hoshino, M., and Murakami, H., 2008. REE abundance and REE minerals in granitic rocks in the Nanling Range, Jiangxi Province, Southern China, and generation of the REE-rich weathered crust deposits. *Resource Geology*, 58, 355-372.
- Jahn, B.M., Wu, F.Y., Capdevila, R., Martineau, F., Zhao, Z.H., and Wang, Y.X., 2001. Highly evolved juvenile granites with tetrad REE patterns: the Woduhe and Baerzhe granites from the Great Xing'an Mountain in NE China. *Lithos*, 59, 171-198.
- Johan, Z., and Johan, V., 2005. Accessory minerals of the Cínovec (Zinnwald) granite cupola, Czech Republic: indicators of petrogenetic evolution. *Mineralogy and Petrology*, 83, 113-150.
- Kynicky, J., Smith, M.P., and Xu, Cheng, 2013. Diversity of rare earth deposits: The key example of China. *Elements*, 8, 361-367.
- McLennan, S.M., 1994. Rare earth element geochemistry and the "tetrad" effect. *Geochimica et Cosmochimica Acta*, 58, 2025-2033.
- Monecke, T., Kempe, U., Monecke, J., Sala, M., and Wolf, D., 2002. Tetrad effects in rare earth distribution patterns: A method of quantification with application to rock and mineral samples from granite-related rare metal deposits. *Geochimica et Cosmochimica Acta*, 66, 1185-1196.
- Murakami, H., and Ishihara, S., 2008. REE Mineralization of weathered crust and clay sediment on granitic rocks in the Sanyo Belt, SW Japan and the Southern Jiangxi Province, China. *Resource Geology*, 58, 373-401.
- Ohlander, B., Ingri, J., Land, M., and Schoberg, H., 2000. Change of Sm/Nd isotope composition during weathering of till. *Geochimica et Cosmochimica Acta*, 64, 813-820.
- Sun, S., and McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders, A.D., and Norry, M.J. (Eds.), *Magmatism in the Ocean Basins*. Special Publication, Geological Society of London 42, 313-345.
- Tollo, R.P., and Aleinikoff, J.N., 1996. Petrology and U-Pb geochronology of the Robertson River Igneous Suite, Blue Ridge province, Virginia: evidence for multistage magmatism associated with an early episode of Laurentian rifting. *American Journal of Science*, 296, 1045-1090.
- Tollo, R.P., Aleinikoff, J.N., Bartholomew, M.J., and Rankin, D.W., 2004. Neoproterozoic A-type granitoids of the central and southern Appalachians. *Precambrian Research*, 128, 3-38.
- Wang, L., Xu, C., Zhao, Z., Song, W., and Kynicky, J., 2015. Petrological and geochemical characteristics of Zhaibei granites in Nanling region, Southeast China: Implications for REE mineralization. *Ore Geology Reviews*, 64, 569-582.
- Whalen, J.B., Currie, K.L., and Chappell, B.W., 1987. A-type granites: geochemical characteristics, distribution and petrogenesis. *Contributions to Mineralogy and Petrology*, 95, 407-419.
- Wood, Scott, 1990. The aqueous geochemistry of the rare earth elements and yttrium, 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chemical Geology*, 82, 159-186.
- Wu, C., Yuan, Z., and Bai, G., 1996. Rare earth deposits in China. In: Jones, A.P., Wall, F., and Williams, C.T., (Eds.), *Rare Earth Minerals, Chemistry, Origin, and Ore Deposits*. Mineralogical Society Series 7, 281-310.
- Xiao, J., Wang, Y., Hong, Y.L., and Zhou, Y.Z., 2009. Geochemical characteristics of Xihuashan tungsten granite and its relationship to tungsten metallogenesis. *Journal of the East China Institute of Technology*, 32, 23-31.
- Zhao, Z.H., Xiong, X., Han, X.D., Wang, Y., Wang, Q., Bao, Z.W., and Jahn, B.M., 2002. Controls on the REE tetrad effect in granites: Evidence from the Qianlishan and Baerzhe Granites, China. *Geochemical Journal*, 36, 527-543.