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The role of fluids in the formation of rare earth element deposits

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Abstract

Fluids play an important role in the formation of many rare earth element (REE) deposits. Groundwater and hydrothermal fluids can transport these elements and with changes in fluid composition or properties, the REEs can be removed from solution by adsorption or precipitation of REE-rich minerals. Currently, REEs are primarily produced from two types of ore deposits, ion adsorption clay deposits (located in southern China) and carbonatites. Ion adsorption clay deposits in southern China form by lateritic weathering of underlying granites. Groundwater is responsible for the mobilization, transport, and deposition of the REEs in forming these ore deposits. Carbonatites are a relatively rare type of igneous rock that contain the highest concentrations of REEs of any igneous rocks. Ore-grade REE enrichment in carbonatites can result from crystallization of REE mineral phases directly from the magma or by hydrothermal processes. One carbonatite-related REE ore deposit, the Mount Weld deposit (Australia), was formed by lateritic weathering of the underlying carbonatite.

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1. Abstract

Rare earth elements (REEs) are not as rare in nature as their name implies, but economic deposits are not common and few deposits have been large REE producers. In the past 20 years, demand for REEs has increased dramatically because of their applications including chemical catalysts, metal alloys, glass polishing, and permanent magnets. Because of their unique properties, REEs are essential for use in high tech devices including smart phones, digital cameras, computer hard disks, fluorescent and light-emitting-diode (LED) lights, flat screen televisions, computer monitors, and electronic displays.

The REE group is composed of 15 elements that range in atomic number from 57 (lanthanum) to 71 (lutetium), and yttrium (atomic number 39) is commonly regarded as a REE because of its chemical and physical similarities

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and affinities. Scandium (atomic number 21) is chemically similar to, and thus sometimes included with, the REEs, but it does not occur in economic concentrations in the same geological settings as the other REEs and will not be discussed further. Rare earth element deposits are generally enriched in either light REEs (LREEs; La-Gd) or heavy REEs (HREEs; Tb-Lu).

The present global production of REEs comes from only a few sources. Two ore-deposit types account for the vast majority of world's REE production. A few carbonatite-related deposits provide the world's LREEs, and numerous small ion adsorption clay deposits in southern China provide the world's production of HREEs. Carbonatites are a relatively rare type of igneous rock composed of greater than 50 vol.% primary carbonate minerals, dominantly calcite and/or dolomite, and contain the highest concentrations of REEs of any igneous rocks. Chondrite-normalized REE patterns for carbonatites display extreme LREE enrichment, no Eu anomaly and a steep pattern with a negative slope. Ore-grade enrichment of REEs in carbonatites can occur by primary magmatic crystallization of REE-rich mineral phases or by late-stage fluid mobilization and consequential REE-phase crystallization. In one deposit currently being mined, Mount Weld, the REE ore-grade enrichment is due to lateritic weathering of an underlying carbonatite. The second deposit type, ion adsorption clay deposits in southern China, form by tropical weathering of granites where the REEs are released to solution from minerals within the granite and a significant fraction are adsorbed on to clays in the weathered zone. Chondrite-normalized REE patterns of these deposits vary due to a number of factors that will be discussed in the following sections. Compared to other REE deposits, these deposits are relatively low grade but are economic to mine because they can be enriched in the more valuable HREEs and are relatively inexpensive to mine.

Fluids can play a significant role in ore-grade enrichment of REEs in both carbonatite and ion adsorption clay deposits. This paper will review the fluid-driven processes involved in REE deposit genesis. Similar to many metals, the behavior of REEs in aqueous solutions can be described as a competition between the formation of stable aqueous complexes and the tendency of REEs to partition to solid phases either by adsorption or (co)precipitation. Solution chemistry plays an important role with the dominant inorganic ligands being carbonate, phosphate, sulfate, hydroxide, chloride, and fluoride. Other factors that may affect partitioning between solid and aqueous phases include: pH, temperature, redox conditions, and the composition of solid phases.

2. Discussion

2.1. *Hydrothermal fluid-derived REE enrichment in carbonatites*

Carbonatites and certain alkaline igneous suites of rocks are enriched in REEs, some of which have been mined or are in the advanced exploration stage. Ore-grade REE enrichment due to orthomagmatic/hydrothermal fluids is evident in a variety of these locations. The requirements for achieving ore-grade REE enrichment are an adequate endowment of REEs in the initial magma and evolution of the magma such that the REEs are concentrated. In general, these magmas evolve by fractional crystallization and the gravitational separation of early formed crystals^{1,2}. Carbonatite and other alkaline magmas may contain a variety of volatile components that include CO₂, H₂O, Cl, F, and S. As crystallization progresses, these components become enriched in the residual magma along with various incompatible elements and can exsolve into a separate fluid phase. Fluid inclusions and fenite alteration (alkali metasomatism) provide clear evidence for the separation of a volatile-rich fluid phase. Depending on the composition of the magma and its evolution, primary REE-bearing minerals can crystallize directly from the magma, as is the case for bastnäsite at the Mountain Pass deposit, or the REEs can remain in the magma behaving as incompatible elements and partition into the fluid phase. REE minerals crystallizing from these late-stage fluids tend to be fluorocarbonates (bastnäsite, parisite, and synchysite, Fig. 1A) and phosphates (monazite and apatite, Fig. 1B). The fluorocarbonates are generally described as very fine-grained (1-100 µm), forming syntaxial intergrowths as bundles, clusters, or aggregates of radiating needles. The crystals may form in miarolitic cavities or at the expense of primary minerals. The origin of these REE mineral phases is commonly attributed to the late-stage magmatic-hydrothermal phase of carbonatite evolution. The REEs may behave as incompatible elements that partitioned into this phase during carbonatite evolution, or they could have been remobilized from earlier formed mineral phases.

The initial magma composition and petrogenetic evolutionary path both control the composition of the crystallizing phases, and thus the composition of the residual melt. The exsolution of a fluid phase from the melt depends not only on the melt composition, but also on pressure and temperature variations. Fluid inclusion

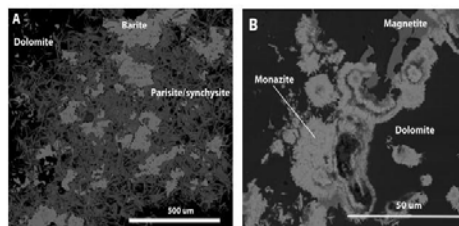


Fig. 1. SEM backscattered electron images of REE phases in in the Elk Creek carbonatite. (A) REE fluorocarbonates; (B) Monazite infilling.

studies provide general characteristics of fluid phases exsolved from carbonatite melts and document the presence of H_2O , CO_2 , alkalis, and ligands, including F^- , OH^- , Cl^- , SO_4^{2-} , CO_3^{2-} , and PO_4^{2-} . These ligands play a key role in the disposition of REEs in magmatic and aqueous systems. Mineral saturation controls the removal of REEs from the aqueous phase and is controlled by changes in pressure, temperature, pH, and chemical composition.

2.2. Ore-grade REE enrichment in weathered deposits

Lateritic weathering is an important process in the formation of some REE deposits including the ion adsorption clay deposits in south China and the Mount Weld deposit in Australia. Factors controlling the degree of lateritization include climate, topography, length of time exposed in a stable environment, and bedrock composition. Optimal conditions for the formation of substantial lateritic zones include a topography that allows the entrapment of newly formed residual minerals and a tectonically stable region where denudation rates are low and the weathering profiles are preserved. Lateritization is driven by the interaction between infiltrating groundwater and the bedrock it contacts. Physical properties, such as cleavage and porosity, are important because they control the amount of mineral surfaces available for interaction. Aqueous properties, such as temperature, acidity, redox potential, and dissolved constituents affect the type of chemical reactions that will occur and their rate. The mineralogy of the rock being weathered not only plays a role in the rate of weathering, but also influences the composition of the aqueous phase, which in turn can control the degree to which REEs are released to the downward moving fluid and the formation of secondary phases. In general, Ca, Mg, K, and Na partition to the aqueous phase and are then leached from the system. In contrast, Fe is quite reactive, as can be Al, and these elements end up in secondary phases, including goethite, hematite, gibbsite, and various clay minerals.

The ion-adsorption type REE deposits in south China (Jiangxi, Guangdong, Fujian, Zhejiang, Hunan, Guangxi, and Yunnan provinces) are generally 6 to 10 m thick, but can reach 30 m, and form above granites. The thickest part of the profiles tends to be at the top of hills and ridges, and the thickness decreases downslope³. This area is characterized as a temperate climate region that receives an average annual rainfall of 1500-2000 mm and has an annual temperature of 18°-21°C⁴. The denudation rate is low because it is a stable tectonic area and the topography is relatively gentle. The underlying granites that form the REE deposits are generally biotite and muscovite granites characterized by metaluminous to weakly peraluminous compositions and low P_2O_5 contents⁵. These granites can either be LREE or HREE enriched, and the chondrite-normalized REE patterns of the resulting weathered zone generally reflects the character of the underlying granite³. The HREE-rich granites are highly differentiated ($\text{SiO}_2 > \sim 75\%$) muscovite granites³. In the granites, the REEs initially were primarily hosted in accessory mineral phases including allanite, titanite, monazite, zircon, and xenotime. A deuteric alteration event altered the magmatic allanite and titanite to secondary REE mineral phases, which subsequently host the REEs in the deposits^{3,5}.

Downward percolating groundwater near the surface is slightly acidic and breaks down susceptible REE-bearing mineral phases partitioning the REEs into the aqueous phase. Ce can be oxidized in the shallow environment and precipitate either with Mn or as cerianite (CeO_2). REEs move down gradient in groundwater as dissolved constituents or associated with colloidal particles. A fraction of REEs leave the system laterally. One key to higher

REEs concentrations in the product is when the groundwater flow has restricted lateral movement. Removal of REEs from solution occurs by sorption and precipitation driven by solution chemistry and solid phase composition (pH, ligand concentrations, mineral saturation, redox conditions, temperature, solid phase chemistry and composition). In general, as the groundwater moves downward, the pH increases due to mixing or water-rock interactions, and the REEs partition onto solid phases, adsorbing onto clay particles including kaolinite and halloysite or forming secondary REE mineral phases. This “ore zone” has grades ranging from 140 to 6,500 ppm (typically ~800 ppm)⁵. These deposits are relatively inexpensive to mine either by shallow pits or in situ leaching.

The Mount Weld REE deposit in western Australia is hosted in a lateritic sequence that reflects supergene enrichment of the underlying carbonatite complex. The laterite sequence consists of a supergene enrichment zone as thick as 90 m, which is located above a 3- to 30-m-thick residual zone that overlays the unweathered carbonatite. The underlying calcite carbonatite is composed of calcite with minor magnetite, apatite, olivine, biotite, and pyrochlore. Rare earth element-rich minerals include calcite, apatite, and possibly pyrochlore⁶. The chondrite-normalized REE pattern of the carbonatite (Fig. 2) is typical of an average carbonatite, with LREE enrichment, no Eu anomaly, and HREE depletion. In the laterite, secondary monazite is the dominant REE-bearing phase in the laterite ore and typically is fine grained and can occur as pseudomorphs after apatite and rhabdophane. In addition, cerianite and crandallite subgroup minerals can be host phases for REEs. Gangue minerals include goethite and hematite, with minor calcite, cryptomelane, dolomite, hollandite, kaolinite, maghemite, montmorillonite, magnetite, pyrochlore, ilmenite, and rutile, and traces of quartz, barite, anatase, and vermiculite^{7,8}.

The chondrite normalized REE pattern of the laterite displays extreme LREE enrichment compared to the underlying carbonatite (Fig. 2). Oxygenated groundwater in the near-surface environment can be slightly acidic. This water interacts with primary minerals, such as calcite, dolomite, and apatite, to mobilize Ca and Mg and liberate REEs. Other elements, such as Al, Fe, P, K, and Na, are also released from these and other phases. In this environment, dissolved ligands likely available to complex REEs include phosphate, carbonate, fluoride, and chloride. Note that lateritic mineralization on a carbonatite substrate does not require the presence of early crystallized, discrete REE-rich minerals, like in a granitic terrain, because a substantial fraction of the REEs can be hosted by rock-forming minerals. Phosphate, from the breakdown of apatite, and REEs form monazite in the laterite.

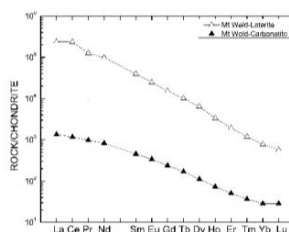


Fig. 2. Chondrite-normalized rare earth element diagram for laterite and carbonatite samples from the Mount Weld deposit.

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