THE ROLE OF EARTH SCIENCE FOR THE SUPPLY OF RARE EARTH ELEMENTS

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Abstract

Earth Science can play an important role in various stages of rare earth elements production, including target defining, geochemical prospecting, evaluation of mineral resource and reserve, beneficiation, etc. This is because of the limited experience in the exploration and exploitation of REE by exploration and mining companies outside China, compared to the other metal commodities. In particular, some of the heavy rare earth elements demanded by the industry are new targets for the companies. However, ongoing vast researches on the occurrence, behaviour, concentration and extraction of REE will be able to ease the criticality of REE in near future.

Introduction

The Behaviour of rare earth elements (REE) in melts and fluids have been widely applied in earth science as tracer of magmas genesis and evolution, index of oxidation state of magmas and fluids, geochronology (Sm-Nd radiometric dating), etc. Despite the wide recognition of the behaviour of REE in magmas and fluids, it has not been well understood how REE are transported, fractionated and concentrated to form economic-grade rare earth deposits. For example, why only a few carbonatites such as Mountain Pass and Bayan Obo possess ore-grade rare earth concentration[1], which ligand (fluorine, chlorine, etc.) is most important for the transportation of REE in magmas and fluids[2], are still debated. Now vast researches on the occurrence, behaviour, concentration of REE are ongoing, and wide spectrum of knowledge is accumulating.

Recent development of rare earth products used in high-technology and/or new materials (NdFeB magnets, semiconductor, ceramic knives, fuel cell, etc.) has demanded not only the light rare earth elements (LREE; La-Eu) but also some of the heavy rare earth elements (HREE; Gd-Lu + Y) such as Dy, Tb and Y. Those HREE have not been well explored in the history, except for xenotime in placer sands along continental coasts and ion-adsorption type deposits in southern China. Thus, new exploration and exploitation projects of HREE meet a lot of challenges. Earth science can contribute to such projects to overcome difficulties in providing exploration strategy, knowledge of mineralogy and mineral chemistry, as well as ore mineral beneficiation. This paper presents some examples that scientific researches contributed to the REE (especially HREE) exploration projects.

Project targeting

World resource database

Until the progress of many REE exploration projects in recent years, there was no dataset that show the resource potential of the individual REE such as Nd, Pr, Dy and Tb that are used for the production of NdFeB magnets. A preliminary attempt was made in 2006 to evaluate the resource of such specific elements to reveal potential regions on the basis of the available datasets that compiled whole rare earth resources of individual deposits in the world[3]. The result shows that Brazil has the greatest potential of Nd and Pr, and three regions, Canada, southern Africa and Saudi Arabia, have good potential of Dy and Tb (Figure 1). Such new data were used for targeting exploration regions for HREE.

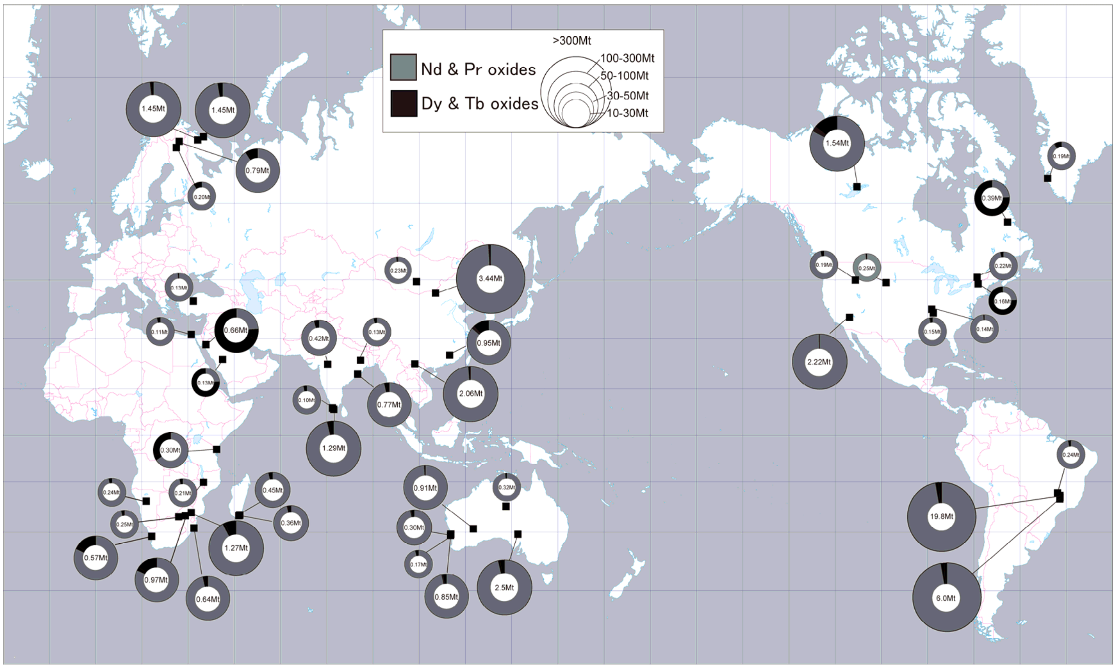

Figure 1: Calculated Nd, Pr, Dy and Tb resources based on the data available before 2006. The amounts of Nd and Pr, and Dy and Tb are combined together, respectively.

Favourable lithology and environment

The present production of HREE is dominated from ion-adsorption deposits in southern China. This-type deposits are formed in weathering profiles of granite and felsic volcanic rocks. Rare earth elements absorbed on clay minerals formed by weathering are easily leached with diluted ammonium sulphate solutions. For this reason, the weathering profiles containing more than 500 ppm ion-exchangeable REE with commercially significant sizes (area and thickness) are considered as ores[4]. Recent studies show that HREE are concentrated in fractionated ilmenite-series granites[5], and rare earth elements are present as secondary fluorocarbonates in addition to refractory apatite and allanite in the host granites of the ion-adsorption deposit areas[6, 7]. Thus, favourable conditions to form HREE-enriched ion-adsorption deposits are 1) tectonically stable and tropical to semi-tropical climate regions to preserve thick weathering profiles, and 2) regions of fractionated ilmenite-series granitoids, which underwent deuteric alteration to form fluorocarbonates to supply ion-exchangeable REE to the profiles. The exploration strategy based on these results leads to the discovery of ion-adsorption type mineralization in Southeast Asia such as Vietnam and Thailand [7, 8].

It has been well known that HREE are typically concentrated in peralkaline rock complexes, in particular, in the most fractionated parts of the complexes with other HFSE such as Zr and Nb. Accumulated mineralogical and geochemical knowledge by scientific researches[9,10] immediately leads to the exploration projects in the regions (northeast Canada, Greenland, and southern Africa) where peralkaline rock complexes are common. These projects are supported by continuous geochemical and mineralogical studies at Strange Lake[11], Thor Lake[12,13], etc., which provide indispensable information for mineral concentration and REE extraction.

Geochemical prospecting

Recent spread of portable XRF analyser in geochemical prospecting has enabled us to detect low grade REE mineralization. Comparison of the chemical data obtained by portable XRF with the results by ICPMS in the laboratory shows that La and Ce is detectable as low as 150 ppm and Y as low as 30 ppm for the ion-adsorption clay samples (Figure 2). These results show that portable XRF analyser is effective in the survey of ion-adsorption and other type REE deposits, in particular, HREE exploration, because Y detection limit is lower than La and Ce. This method was applied to delineate Y anomalies in a fluorite prospect in South Africa[14] (Figure 3).

Mineralogy and mineral chemistry

A number of rare earth minerals are present in alkaline rock complexes and pegmatites, and detailed mineralogical works are indispensable for the recovery of these minerals. Some of the minerals contain minor amounts of REE and if these minerals contain important elements (Dy, Tb), they become a target for exploration and exploitation. It has been known that zirconium silicates are occasionally concentrated in HREE[15], although, these minerals have not been regarded as a resource source until recently, due to scarcity of geochemical data and lack of the established beneficiation methods. Recent advance in trace element quantitative analysis by LA-ICPMS has made it easier to determine rare earth concentration in such minerals[16, 17].

The Jabal Tawlah deposit in Saudi Arabia is reported to be HREE-concentrated microgranite with Nb and Zr in the Proterozoic sedimentary rocks. The granite forms a small sill-like body with 330m extension and a maximum thickness of 50m, and 6.4Mt of ore is estimated[18]. The microgranite is heavily fractionated and is composed of quartz, albite and microcline with accessory zircon, Nb oxides and REE minerals. Total REE content including Y is about 1.2wt% as oxides. Major ore minerals are columbite, fergusonite, Ca-Y-F minerals, and xenotime. A mineralogical study shows that Ca-Y-F minerals are composed of waimirite-(Y) (YF_3) and a Ca-Y-F undetermined phase (Figure 4). Waimirite[19] is a mineral approved by IMA in December 2013, and nearly half of REE in the deposit is present in these new and undetermined phases, sharing the other half with xenotime. The deposit is regarded to be the highest Dy grade deposit in the world.

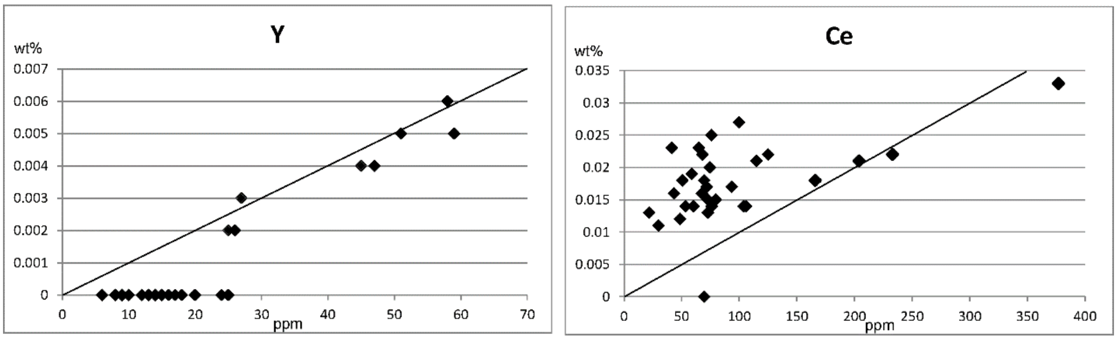

Figure 2: Comparison of analytical results by portable XRF and ICPMS for the samples of ion-adsorption clay in Conception, Chile. Vertical and horizontal axes are the results by XRF and ICPMS, respectively.

Figure 3: Y concentration (ppm) in termite mounds in the Blockspruit prospect in South Africa, measured by portable XRF analyser[14].

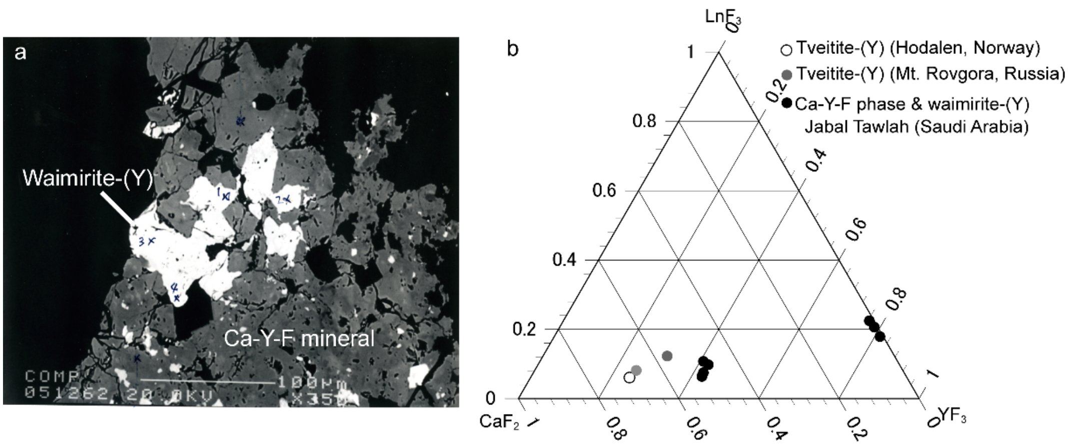

Figure 4: SEM image of Ca-Y-F phase and waimirite-(Y) (a) and chemical compositions of these minerals determined by EPMA. The compositions of tveitite-(Y) from Norway and Russia are also shown.

One of the target minerals for HREE extraction is eudialyte that contains a few to 10 wt% of REE. Because eudialyte is relatively enriched in HREE and occur abundantly in peralkaline complexes, several projects aim to produce REE from eudialyte. However, the REE content in eudialyte is variable even in the same unit of an intrusion and precise chemical analysis is necessary. An example is the Ilímaussaq peralkaline complex in Greenland, discovery place of eudialyte, which is divided into lower kakortokite and upper lujavrite. The REE compositions of eudialyite determined by LA-ICPMS show that eudialytes in the kakortokite and lujavrite contain 2.2-2.3wt% and 4.1-4.9wt% REE, respectively[20].

A whole rock analytical method using LA-ICPMS newly developed is to use a glass bead ablation method similar to XRF techniques[17]. This method has several advantages: 1) higher sensitivity than that achieved by the XRF method, 2) obviation of erroneous measurements due to incomplete dissolution of heavy minerals, and 3) simple and rapid sample preparation procedures for the analysis of both major and trace elements. The precisions of this method are better than 10% for Y, La, Pr and 20% for the other REE, and the method can provide REE compositional data of rocks faster than conventional ICPMS analysis.

Extraction

The extraction techniques of REE from conventional minerals (bastnäsite, monazite, xenotime) and ion-adsorption clay were well established[21,22]. However, to establish economically feasible REE extraction methods for other unconventional minerals are challenging.

Apatite

It has been known that apatite contain minor amounts of REE[23], and REE by-production has been explored in the process of phosphoric acid production. The methods using hydrochloric or nitric acid can extract more than 80% of REE, but when sulphuric acid is used, recovery of REE is low because majority of REE is incorporated into gypsum residue[24]. Various attempts are being conducted for the extraction of REE from apatite, including a hydrochloric acid method[25].

Zircon

Zircon is a refractory mineral and generally contains less than 1wt% of REE, however, many varieties of zircon containing a large amount of REE, Th, U, Nb and Ta have been reported from peralkaline rocks and granites[13]. A REE extraction experiment indicates that more than 90% of REE can be leached out from REE-bearing metamict zircon with 1M-HCL solution at temperature of 150°C[26].

Conclusion

Earth Science can play an important role for the supply of REE, by providing exploration strategy, target determination, geochemical prospecting, evaluation of resource and reserve, and beneficiation. This is because the exploration and mining experience is still immature for the mining sectors outside China. However, abrupt increase of REE demand, in particular, some specific elements such as Dy and Tb, urged industrialised countries to secure raw REE materials. Vast scientific researches are ongoing to clarify the occurrence, behaviour, concentration of REE in rocks, minerals, and solutions, which will be able to ease the criticality of REE in near future.

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