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Rare earth minerals and resources in the world

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Abstract

About 200 rare earth (RE) minerals are distributed in a wide variety of mineral classes, such as halides, carbonates, oxides, phosphates, silicates, etc. Due to the large ionic radii and trivalent oxidation state, RE ions in the minerals have large coordination numbers (c.n.) 6–10 by anions (O, F, OH). Light rare earth elements (LREEs) tend to occupy the larger sites of 8–10 c.n. and concentrate in carbonates and phosphates. On the other hand, heavy rare earth elements (HREEs) and Y occupy 6–8 c.n. sites and are abundant in oxides and a part of phosphates. Only a few mineral species, such as bastnaesite (Ce,La)(CO_3)F, monazite (Ce,La)PO_4, xenotime YPO_4, and RE-bearing clay have been recovered for commercial production. Bayan Obo, China is the biggest RE deposit in the world. One of probable hypotheses for ore geneses is that the deposit might be formed by hydrothermal replacement of carbonate rocks of sedimentary origin. The hydrothermal fluid may be derived from an alkaline–carbonatite intrusive series. Following Bayan Obo, more than 550 carbonatite/alkaline complex rocks constitute the majority of the world RE resources. The distribution is restricted to interior and marginal regions of continents, especially Precambrian cratons and shields, or related to large-scale rift structures. Main concentrated areas of the complexes are East African rift zones, northern Scandinavia-Kola peninsula, eastern Canada and southern Brazil. Representative sedimentary deposits of REE are placer- and conglomerate-types. The major potential countries are Australia, India, Brazil, and Malaysia. Weathered residual deposits have been formed under tropical and sub-tropical climates. Bauxite and laterite nickel deposit are the representative. Ion adsorption clay without radioactive elements is known in southern China. Weathering processes concentrate REE in a particular clay mineral-layer in the weathered crusts whose source were originally REE-rich rocks like granite and carbonatite. The production is increasing in recent years. However, the process of chemical extraction has brought environmental problems.

Keywords: Rare earth minerals; Rare earth resources; Bayan Obo ore deposit; Carbonatite; Ion adsorption clay

1. Introduction

It is said that rare earths are not rare in natural occurrence. It is true for light rare earth elements (LREEs). However, heavy rare earth elements (HREEs) are less common. Furthermore, RE resources are unevenly distributed in the world. The world mine production in 2003 is concentrated in several countries: China, India, CIS, Malaysia, and Sri Lanka [1]. Especially, China occupies more than 90% of the production. The other productive countries are USA, Australia, Canada, South Africa, Brazil, and others. Recent industrial demands for HREE would bring exhaustion of the resources in near future. Exploitation of RE resources also involves environmental problems. One of problems is due to radioactive elements associated with REE in the minerals.

Here, overview of RE minerals and the resources would be useful for the development from now on. In this paper, we first present the mineralogical features of RE minerals. Secondly, the ore deposit types and the world distribution of RE resources are presented with remarks for future developing.

2. Classification of rare earth minerals and their crystal-chemical features

So far, a total of about 200 distinct species of RE minerals have been described. And crystal structures of about the

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Table 1
Classification of rare earth minerals

Mineral class	Mineral examples and chemical formulae
Halides	Fluocerite-(F), CeF_3
Carbonates	
With fluoride	Bastnaesite, $(Ce,La)(CO_3)F$
Without fluoride	Ancylite, $(Ce,Sr,Ca)(CO_3)(OH,H_2O)$
Borates	Braistschite, $(Ca,Na_2)_7CeB_{22}O_{43}\cdot 7H_2O$
Oxides and hydrates	
AO_2-type	Cerianite, $(Ce^{4+},Th^{4+})O_2$
ABO_3-type	Perovskite group, $(Ca,Ce,Na,Sr)(Ti,Nb,Ta)O_3$
ABO_4-type	Fergusonite–Formanite, $Y(Nb,Ta)O_4$–$Y(Ta,Nb)O_4$
$AB_2(O,OH)_6$-type	Euxenite group, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$
$A_2B_2O_6(O,OH,F)$-type	Pyrochlore group, $(Na,RE,K,U)_2(Nb,Ta,Ti)_2(O,OH,F)$
Others	Hibonite, $(Ca,Ce)(Al,Ti,Mg)_{12}O_{19}$
Phosphates, arsenates and vanadates	Apatite, $(Ca,RE,Sr,Na,K)_3Ca_2(PO_4)_3(F,OH)$
	Monazite, $(Ce,La)PO_4$
	Xenotime, YPO_4
Silicates (The following groups are based on the linkage manner of tetrahedral anionic group.)	
Isolated group	Cerite, $(Ce,La,Ca)_9(Fe^{3+},Mg)(SiO_4)_6[SiO_3(OH)](OH)_3$
	Garnet, $(Ca,Fe,Mg,Mn,Y)_3(Al,Cr,Fe,Mn,Ti,V,Zr)_2(Si,Al)_3O_{12}$
	Sphene, $CaTiSiO_4$
Diortho group	Allanite, $Ca(Ce,Y,Ca)Al(Al,Fe)(Fe,Al)(SiO_4)_3(OH)$
Chain group	Stillwellite, $CeBSiO_5$
Ring group	Eudialyte, $(Na,Ca,Ce)_6(Zr,Fe)_2Si_7(O,OH,Cl)_{22}$
Sheet group	Gadolinite, $(Y,Ce)_2Fe^{2+}Be_2Si_2O_{10}$
Framework group	Kainosite, $Ca_2(Y,RE)_2(Si_4O_{12})CO_3\cdot H_2O$
Others	Iimoriite, $Y_2(SiO_4)(CO_3)$

half have been reported. Miyawaki and Nakai [2,3] stated that minerals, whose chemical formulae indicate significant contents of rare earths, are defined as RE minerals, even if their contents appear unessential to the minerals. They have reviewed all the reported structures in “Crystal Structures of Rare Earth Minerals”, which is useful for database and a textbook on RE minerals. Here, we grouped RE minerals into conventional ways, such as halides, carbonates, oxides, phosphates, silicates, etc. in Table 1 with the chemical formulae. This classification indicates that RE minerals distribute in a wide variety of mineral classes and structural types. In Table 1, it is noticed that the important RE minerals, bastnaesite, monazite, and xenotime are expressed by simple chemical formulae.

According to Shannon and Prewitt [4], the effective ionic radii of La^{3+}–Eu^{3+} (LREEs) for the coordination number 8 by oxygen atoms are 1.18–1.07 Å and those of Y^{3+} and Gd^{3+}–Lu^{3+} (HREEs) are 1.015 and 1.07–0.97Å. It is noticed that there is a small difference between the radii of LREE and HREE groups. The difference influences the crystal structures and/or the coordination number of the sites for rare earths. We investigated the relationship between RE–(O, F) bond distances and coordination numbers for RE sites in reported structures of RE minerals. Fig. 1 summarizes relative abundance and coordination numbers of LREEs and HREEs for each mineral class. It is obvious that LREEs occupy the sites of larger coordination numbers of 7–11. Most of LREEs are in the numbers of 8–10. The bond distances are in the range of 2.43–2.68 Å. On the other hand, HREEs are abundant in the numbers from 6 to 8 and the distances range from 2.24 to 2.49 Å. The coordination number 8 is predominantly preferred by HREEs. As for mineral class, LREEs are rich in carbonates and phosphates, and HREEs are rich in oxides, such as titanates, niobates, and tantalates. REEs in phosphates are concentrated in the coordination number 8 and 9. REEs in silicates comparatively disperse in the whole coordination numbers. This tendency may reflect a variety of structure types of silicates. From the view point of RE resources, LREEs are expected in carbonates and phosphates, and HREEs in oxides and a part of phosphates. Silicates include both REEs. However, the extraction of rare earths

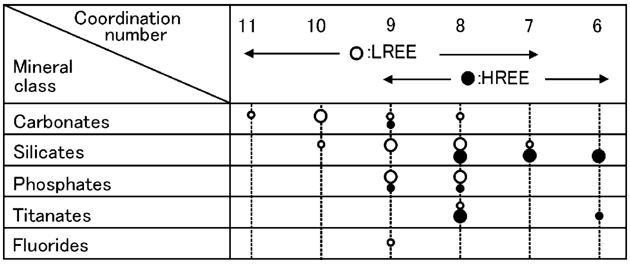

Fig. 1. The coordination numbers and abundance of LREEs and HREEs in the structural sites for RE mineral classes; (○) and (●) show LREEs and HREEs, respectively. The size of circles shows rough abundance of REE for each mineral class.

Table 2
Classification of rare earth ore deposits

Deposit-type	Mines
(1) Igneous	
Hydrothermal	Bayan Obo (China)
Carbonatites	Mt. Pass (USA), Weshan, Maoniuping (China), Mount Weld (Austraria), Araxa, Catalao (Brazil)
Alkaline rocks	Khibiny, Lovozeiro (Russia), Posos de Caldas
Alkaline granites	(Brazil), Strange Lake (Canada)
(2) Sedimentary	
Placer	Kerala (India), Western Australia, Queesland State (Australia), Richards Bay (south Africa)
Conglomerate	Elliot Lake (Canada)
(3) Secondary	
Weathered residual of granite (ion-adsorption clay)	Longnan, Xunwu (China)

from the minerals needs high energy (or high costs) because of the strong chemical bonds in the structure.

The above ionic radii of rare earths are similar to those of especially Na^+(1.16 Å), Ca^{2+}(1.12 Å), Th^{4+}(1.06 Å), and U^{4+}(1.00 Å). Therefore, these elements are frequently associated with rare earths in the crystals. The substitutions between rare earths and the heterovalent ions are commonly taken place in the mineral structures. Several types of isomorphous substitutions of rare earth ions for the heterovalent ions are observed mainly in oxides and silicates. The commonest substitution in oxides, such as titanates, niobates, and tantalates, is the coupled substitution of $Ca^{2+} + (Nb,\ Ta)^{5+} \leftrightarrow RE^{3+} + Ti^{4+}$. This substitution is frequently balanced by another substitution of $O^{2-} \leftrightarrow (OH,\ F)^-$. The usual substitution of $2Ca^{2+} \leftrightarrow RE^{3+} + Na^+$ is present in perovskite. Apatite in phosphates also takes the same substitution. The substitution accompanied with Th^{4+} is expressed by $Ca^{2+} + Th^{4+} \leftrightarrow 2RE^{3+}$. A unique substitution, $Ca^{2+} + (Al,\ Fe^{3+}) \leftrightarrow RE^{3+} + Fe^{2+}$, takes place in allanite of diortho group of silicates. In garnet structure, $Ca^{2+} + Si^{4+} \leftrightarrow RE^{3+} + (Al,\ Fe^{3+})$ is a feasible substitution and results in synthetic YAG and YIG.

3. The ore deposit types of rare earths and the world distribution

The classification of the deposit types is indicated in Table 2 based on Kamitani [5]. The major deposits are classified genetically into igneous, sedimentary, and secondary types. The world distribution corresponding to the classification is shown in Fig. 2.

Bayan Obo, China is the biggest RE deposit in the world. The deposit was formed by hydrothermal replacement of the carbonate rocks of sedimentary origin, but the hydrothermal fluids may be derived from an alkaline–carbonatite intrusive series [6–9].

Carbonatite/alkaline rocks constitute the majority of the world RE resources following Bayan Obo. More than 550 carbonatite/alkaline complexes are distributed in the world [10]. The distribution is restricted to interior and marginal regions of continents, especially Precambrian cratons and shields, or related to large-scale rift structures. Main concentrated areas of the complexes are the East African rift zones, northern Scandinavia-Kola peninsula, eastern Canada, and southern Brazil. The carbonatites are

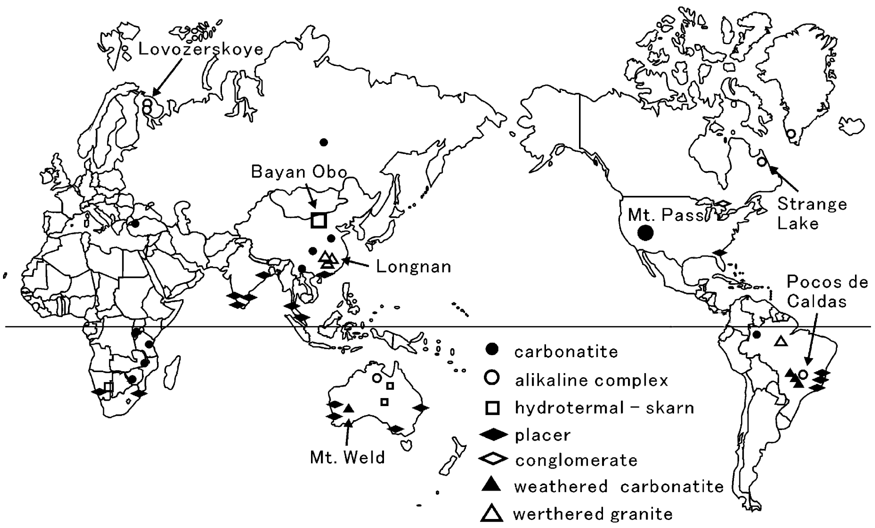

Fig. 2. Distribution of RE deposits in the world.

generally associated with ultramafic and/or alkaline rocks, and in so many cases occur as isolated dykes, cylindrical intrusives and volcanic cones. The ages of complexes vary from Archean to Recent time, and each group of the complexes is closely related to their regional structural events. In East Africa, many carbonatites and alkaline rocks are arranged along the East African rifts and the related structurally weak zones. The Oldoinyo Lengai carbonatite, Tanzania that is famous for the eruption in 1960, consists mainly of tuffs, agglomerates, and lava flows of Na-rich carbonatites with ijolite, nepheline syenites, and phonolite flows [11]. Carbonatites representing deeper substances are recognized in the northern Scandinavia-Kola peninsula, eastern Canada, southern Brazil, etc. They are mostly associated with alkaline and mafic to ultramafic rock suites, such as ijolite, melteigite, jacupirangite, pyroxenite, and peridotite. Mountain Pass, USA has the high-grade and large-sized carbonatite-type deposits. The occurrence of the RE minerals is considered primary igneous. The other deposits of hydrothermal and supergene origin in carbonatites also represent a large RE resource and occur at, for example, Araxa and Catalao I, Brazil and Mount Weld, Australia. A small amount of REE-bearing minerals are accompanied by granite, alkaline granite, and alkaline suite rocks. However, these are not economical for RE resources. In pegmatite- and skarn-stages, some RE minerals have formed but almost all of the deposits are also sub-economic. Carbonatite/alkaline complexes contain a considerable amount of niobium, titanium, REE, copper, molybdenum, and phosphorus.

Representative sedimentary deposits of REE are placer- and conglomerate-types. The detrital minerals originate from a wide variety of primary source rocks ranging from simple quartz veins to complexes of igneous and/or metamorphic origin. Economic concentrations occur where source rocks have produced sufficient quantities of valuable minerals and where geography and climate have provided suitable conditions for deposition. The placer deposits are widely distributed in the world. The major producing countries are Australia, India, Brazil, and Malaysia. Monazite and xenotime are the main RE minerals. They are associated with titanium minerals and zircon. From a conglomerate-type deposit RE products enriched in Y-group have been recovered after uranium ore dressing in Elliot Lake, Blind river area, Canada.

Weathered residual deposits have been formed under tropical and sub-tropical climates. Weathering processes concentrate REE in a particular mineral-layer in the weathered crusts whose source were originally REE-rich rocks like carbonatite and granite. Bauxite and laterite nickel deposits are the representatives. A new type of RE deposits is reported from Jiangxi province and its peripheral areas, South China [12–14], where granitoids containing comparatively much REE are perfectly weathered and almost the RE have been concentrated in clay layer in the weathered crusts. Chinese geologists are regarded as new type deposit "ion adsorption-type" (e.g. [12]).

4. Major RE deposits

4.1. Bayan Obo deposit, China

Bayan Obo Fe–REE–Nb deposit is located 135 km northwest of Baotou in Inner Mongol Autonomous Province. RE minerals closely associated with the iron ores have been recovered from the iron ore dressing plant. The reported total reserves are at least 1.5 billion metric t of iron (average grade 35%), at least 48 million t of RE oxides (REO) (average grade 6%), and about 1 million t of niobium (average grade 0.13%) [6]. Recent statistics shows 89 million t of REO in China [1]. The principal RE minerals are bastnaesite and monazite and accompanied with a various kind of RE–Nb minerals, such as aeschynite, felgusonite, and columbite.

The rift system developed in the northern margin of the Sino-Korean massif during the Early-Middle Proteozoic era made a favourite tectonic setting for the depositions of Bayan Obo Group and the ore deposits. The host dolomites extend 18 km from east to west and approximately 2 km in width. There are three main ore zones: the Main Ore Body, the East Ore Body, and the West Ore Body. The Main and the East ore bodies are being actively exploited at present. The Main ore bodies consist of tabular and/or lenticular bodies of REO-bearing magnetite and hematite iron ores. The average REO content in the Main Ore Body and the East Ore Body are 6 and 5%, respectively. There have been many discussions on the genesis of Bayan Obo deposit so far. One of considerable ore geneses is as follows. The original iron (hematite) ore bodies were formed syngenetically before REE–Nb mineralization. The hydrothermal fluid with an alkaline–carbonatite chemistry was derived from the upper mantle, and printed the REE–Nb mineralization over the original iron bodies [7]. In addition to Bayan Obo, many REE carbonatites are distributed in China. Wushan and Maoniuping deposits produce LREE.

4.2. Mountain Pass carbonatite deposit, USA

Mountain Pass deposit is the second largest RE deposit following Bayan Obo. The carbonatite deposit is located near the border between the southern part of California and Nevada where Precambrian metamorphic rocks are widely distributed. Syenite, shonkinite, granite, and many carbonatites intruded into the metamorphic basement. The Sulphide Queen carbonatite body is the main deposit with 1000 m long and 250 m wide, and mainly composed of dolomite and calcite accompanied with barite and a considerable amount of bastnaesite. The potassium-rich igneous rocks and intrusive carbonate rocks were formed approximately 1400 Ma [15]. The proved REO reserves are approximately 28 million t and the grade is 5–10% REO. The recent mine production, however, has been abruptly decreased into 5000 t/y due to several problems.

4.3. Mount Weld carbonatite deposit, Australia

According to home pages of Lynas Co. Ltd., Mount Weld carbonatite intrusive pipe is approximately 3 km in diameter located 35 km south of Laverton, WA, USA. The surface is strongly weathered. Nb–Ta, P, and REE are concentrated but considerable less radioactive elements of Th and U. The richest part of REE is the Central Lanthanide Deposit (CLD) where estimated reserve is 7.7 Mt at 12% for 917,000 t REO. Bastnaesite is the main mineral of REE.

4.4. Placer deposits in Australia

Heavy minerals sand placer deposits containing RE minerals are widely distributed along the Australian coast. They fall geographically and mineralogically into three distinct categories: the rutile–zircon–ilmenite deposits of the east coast, the ilmenite deposits of the south-west coast, and the ilmenite–zircon–rutile deposits of the Eneabba region of the west coast. The deposits of the east coast have been formed by wave, wind-brown, and their combination. The west coast, on the other hand, composed mainly of paleobeach placers and then the principal deposits are located at inland and 10–100 m above sea level. REE sands are monazite and xenotime.

4.5. Ion adsorption clay

The ion adsorption clay deposits of REE distribute over an extensive area of southern China, especially in Nanling area. The numerous small deposits occur as a result of lateritic weathering of granites that extensively intruded during Yanshanian, Variscan-Indosinian, and Caledonian movements. In particular, granitic rocks of Yinshen age (195–130 million years ago) are the most common host rocks for ion-adsorption deposits. Under warm and moist weather in subtropical zone, these granites have been suffered strong chemical and biological weathering, in which REEs were adsorbed mainly on the surface of clay minerals as ion state, then forming ion adsorption type REE deposits. This type of deposits satisfies at least two major general requirements for their formation. First, there must be a sufficient quantity of RE-bearing host rock. Second, the weathering or lateritic processes must be preserved for a long period without erosion.

The weathering crusts are divided into four layers based on mineral assemblages [16]. (A) An upper layer of colluvium and soil: 0–2 m thick, (B) a strongly weathered layer enriched in REE: 5–10 m thick with kaolinite, quartz and mica, (C) a semi-weathered layer: 3–5 m thick with kaolinite and sericite, (D) a weakly weathered layer with the same mineral compositions as the host rock. RE-ions were adsorbed by kaolinite and halloysite. The most abundant RE, which is enriched three–four times of the host occurs in the strongly weathered layer (B). Although ion-adsorption rare earth deposits are substantially low grade (0.05–0.2%), the mining and processing is easy. The deposits are mined by open-pit methods and no milling and/or ore dressing is required. The REOs can be produced by a very simple procedure. Some chemical acids are used for leaching of RE. The other advantage of the ion-adsorption type ores is the very low content of radioactive elements [17].

5. Concluding remarks

Recent demands for HREEs are increasing in high-tech industries. Extraction of HREEs from bastnaesite and monazite, even if xenotime causes the excessive production of LREEs and the harmful accumulation of radioactive elements. One way to cope with the situation is to extract HREEs from ion-adsorption clay. This type of clay is produced only in the southern China. It is recommended to the other countries to investigate lateritic clay formed by weathering of granites. Otherwise R&D for mineral separation, smelting, and the recovery should be promoted including disposal of radioactive wastes. The protection of the environment is always a serious task for exploitation of natural resources.

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References

[1] J.B. Hedrick, Mineral Commodity Summaries, January 2004, U. S. Geological Survey (2004) 132–133.
[2] R. Miyawaki, I. Nakai, Rare Earths 11 (1987) 133.
[3] R. Miyawaki, I. Nakai, in: E. Gshneidner Jr. (Ed.), Handbook on the Physics and Chemistry of Rare Earths, vol. 16, Elsevier Science Publishers B.V., 1993, pp. 249–518.
[4] R.D. Shannon, C.T. Previtt, Acta Crystallogr. B 25 (1969) 925–945.
[5] M. Kamitani, Proceedings of International Conference on Rare Earth Minerals and Minerals for Electronic Uses, 1991, pp. 181–191.
[6] L.J. Drew, Q. Meng, W. Sun, Lithos 26 (1990) 42–65.
[7] R. Cao, S. Zhu, J. Wang, Chin. Sci. Chin. (Ser. B) 38 (1995) 1003–1014.
[8] G. Bai, Z. Yuan, Z. Zhang, L. Zheng, Demonstration of Geological Features and Genesis of the Bayan Obo Ore Deposit, Geological Publishing House, 1996, p. 107.
[9] Y. Kanazawa, T. Nakajima, T. Takagi, Mining Geol. 49 (1999) 203–216.
[10] M. Kamitani, H. Hirano, Bull. Geol. Survey Jpn. 41 (1990) 631–640.
[11] J.B. Dawson, in: O.F. Tuttle, J. Gittins (Eds.), Carbonatites, John Wiley and Sons Ltd., New York, 1966, pp. 155–168.
[12] Z. Yang, Sci. Geol. Sinica 1 (1987) 70–80.
[13] Z. Den, J. Guillin Coll. Geol. (1988) 39–48.
[14] C. Wu, D. Huang, Z. Guo, Acta Geol. Sinica 4 (1989) 349–362.
[15] M.A. Lanphere, J. Geol. 72 (1964) 381–399.
[16] S. Peng, Proceedings of International Conference on Rare Earth Minerals and Minerals for Electronic Uses, 1991, pp. 33–42.
[17] A.L. Clark, S. Zheng, Proceedings of International Conference on Rare Earth Minerals and Minerals for Electronic Uses, 1991, pp. 577–601.