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MINERALOGICAL ASPECTS OF RARE EARTH ELEMENTS

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ABSTRACT

Rare earth elements or rare earth metals are a group elements including the fifteen lanthanides (Z=57 to Z=71). Scandium (Z=21) and yttrium (Z=39) are considered rare earths by IUPAC since they tend to occur in the same ore deposits as the lanthanides and have similar chemical properties. The present article describes mineralogical properties of yttrium and the lanthanides. A total of two hundred and seventy seven (277) minerals are known, the most common being monazites and bastnäzites. The rare earth metals have many important industrial applications.

KEY WORDS: **Rare earth elements, lanthanides, yttrium, mineralogical aspects**

RESUMO

Os elementos denominados de terras raras ou metais de terras raras consistem de um grupo de elementos incluindo os quinze lantanídeos (Z=57 a Z=71). O escândio (Z=21) e o ítrio (Z=39) são considerados terras raras pela IUPAC, já que ocorrem nos mesmos depósitos de minérios e possuem propriedades químicas semelhantes. O presente artigo trata das propriedades mineralógicas do ítrio e dos lantanídeos.

Um total de duzentos e setenta e sete (277) espécies minerais são conhecidas, sendo as mais importantes as monazitas e bastnäzitas. Os metais de terra raras têm muitas aplicações industriais importantes.

PALAVRAS CHAVE: **Terras raras, lantanídeos, ítrio, aspectos mineralógicos**

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INTRODUCTION

This article represents a continuation o four work dealing with the mineralogy of the elements of the Periodic Table. We have already published a series of papers dealing with mineralogical aspects of Ag, Cu, Au, Pb, Pt, Li, H and U[1-7].

Rare earth elements or rare earth metals are defined by IUPAC as a collection of seventeen chemical elements in the Periodic Table, specifically, scandium (Z=21), yttrium (Z=39) and the fifteen lanthanides, Z=57 to Z=71, (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

Scandium and yttrium are considered rare earths since they trend to occur in ore deposits with the lanthanides and have similar chemical properties. Geochemically speaking, scandium (Z=21) is not considered a member of this class[8] and we will not consider its mineralogy in this article.

The term "rare earth" comes from rare earth minerals. In old usage, the name was given to the mixture of oxide minerals was earth mixture. [9-12]

In 1787 Lt. Carl Axel Arrhenius discovered a black mineral in a quarry in the village of Ytterby in Sweden. The mineral was originally called ytterbite and was renamed gadolinite in 1800, after John Gadolin, a professor at Turku University in Finland. It was Gadolin that first isolated yttrium from the mineral.

A few years later, in 1803, Jacob Berzelius and Wilhelm Hisinger obtained cerium from bastnäzite, a mineral from Bastnäs near Riddarhyttan, Sweden. Eventually, a more careful separation and characterization of the earths from the mineral yielded Sc, Y, La and the fourteen lanthanide metals. [13,14,22-26]

Three of the rare earth elements (Tb, Er and Yb) derive their name from the village of Ytterby. The others are named for scientists who studied or discovered them, Roman, Greek or Scandinavian mythology or places (Holmia is the Latin name of Stockholm, Lutetia for Paris).

The rare earth elements are not rare. Their absolute abundances in the lithosphere are relatively high. Cerium is the 25th most abundant element in the Earth's crust (~56ppm) and even the scarcest, thulium (~0.29ppm) is as common as bismuth ($\sim 2x10^{-2}$ wt%) and more common than As, Cd, Hg and Se that are not considered rare. [13,14,22-26]

Significant deposits of rare earth minerals are located in Scandinavia, India, Russia, Brazil, South Africa, Australia, United States and China. At the present time, China is responsible for most of the world production of rare earth metals,

Promethium occurs in Nature only in trace amounts in uranium ores ($4x10^{-5}$ g/kg) as a spontaneous fission fragment of ^{238}U. Milligram quantities of $^{147}Pm^{+3}$ can be isolated by ion exchange techniques from fission products of nuclear reactors where ^{147}Pm ($beta^{-}$, 2.64y) is formed. [24]

Some properties of the rare earth elements are summarized in Table 1.[13,22-26]

The rare earth themselves, i.e., the minerals, are usually mixed oxides of the metals and are difficult to separate because of their chemical similarity. The rare earth metals never occur free in nature and have similar chemical properties because their atomic structures are similar. The most common valence is +3 and they all form stable oxides, carbides, borides and halides. They also form organic salts with chelates. [22-26]

These elements are important geochemical markers, are used to identify rocks and have high geochemical immobility. Even with prolonged geological times,

Table 1. Some Properties of the Rare Earth Elements. [13,14,22-26]

Properties	Y	La	Ce	Pr	Nd	Pm	Sm	Eu
Atomic mass (g/mol)	88,90585(2)	138,90547(7)	140,116(1)	140,90765(2)	144,242(3)	140,90765(2)	150,36(2)	151,964(1)
Electronic configuration	$[Kr]4d^15s^2$	$[Xe]5d^16s^2$	$[Xe]4f^26s^2$	$[Xe]4f^36s^2$	$[Xe]4f^46s^2$	$[Xe]4f^56s^2$	$[Xe]4f^66s^2$	$[Xe]4f^76s^2$
Density (g/cm^3)	4.47	6.15	6.77	6.77	7.01	7.3	7.52	5.24
Melting point (°C)	1526	920	798	931	1016	931	1072	822
Boiling poing (°C)	3338	3457	3426	3512	3068	3512	1791	1597
Heat of vaporization (kJ/mol)	363	414	414	296.8	273	-	166.4	143.5
Heat of fusion (kJ/mol)	11.4	6.2	5.46	6.89	7.14	86.7	8.63	9.21
Ionic Radius (Å)	0.9	1.061	1.034	1.013	0.995	0.979	0.964	0.947
Crystal structure	hexagonal	hexagonal	cubic face centered	hexagonal	hexagonal	Hexagonal	trigonal	cubic face centered
Discoverer	J.Gadolin	C. G.Mosander	W. von Hisinger and J.J.Berzelius	C.A. von Welsbach	C.A. von Welsbach	J.A. Marinky, L.E. Glendenin and C.D. Coryell	P.E.L. de Boisbaudran	E. A. Demarçay
Discovery year	1794	1839	1803	1885	1885	1945	1879	1901

Properties	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic mass (g/mol)	157,25(3)	158,92535(2)	162,500(1)	164,93032(2)	167,259(3)	168,93421(2)	173,054(5)	174,9668(1)
Electronic configuration	$[Xe]4f^75d^16s2$	$[Xe]4f^96s2$	$[Xe]4f^{10}6s2$	$[Xe]4f^{11}6s2$	$[Xe]4f^{12}6s2$	$[Xe]4f^{13}6s2$	$[Xe]4f^{14}6s2$	$[Xe]4f^{14}5d^16s2$
Density (g/cm^3)	7.895	8.23	8.55	8.8	9.07	9.32	6.9	9.84
Melting point (°C)	1312	1357	1412	1470	1522	1545	824	1663
Boiling poing (°C)	3266	3023	2562	2695	2863	1947	1194	3395
Heat of vaporization (kJ/mol)	359.4	330.9	230	241	261	191	128.9	355.9
Heat of fusion (kJ/mol)	10.05	10.8	11.06	12.2	19.9	16.84	7.66	
Ionic Radius (Å)	0.938	0.923	0.912	0.901	0.881	0.869	0.858	0.848
Crystal structure	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	cubic face centered	hexagonal
Discoverer	J.C.G. de Marignac	C.G. Mosander	P.E.L. de Boisbaudran	M.Delafontaine and J.L. Soret	C.G. Mosander	P.T. Cleve	J.C.G. de Marignac	C.A. von Welsbach and G. Urbain

geochemical separation of the lanthanides was slow. There exists only a broad separation between light and heavy rare earths, commonly known as the cerium and yttrium earths. [9-12]

The more common minerals that contain yttrium and the heavier elements are gadolinite, euxenite, samarskite, xenotime, fergusonite, yttrotantalite, yttrotungstite, yttrofluorite, thalenite and yttrialite. Some of the heavy lanthanides are responsible for the typical yellow fluorescence of zircon.

Common minerals that contain cerium and the lighter lanthanides include monazite, bastnäzite, allanite, loparite, parasite, ancylite, cerite, chevkinite, lnthanite, stillwellite, fluorecite, britholite and cerianite. During the years, the principal ores of cerium and the lighter rare earths have been monazite from marine sands from Brazil, Egypt, India and Australia and rocks from South Africa, bastnäzite from California and China and loparite from Russia. 22-26

Among the anhydrous rare earth phosphates, the tetragonal mineral xenotime incorporates preferentially yttrium and yttrium earths, whereas monoclinic monazite incorporates cerium and the cerium earths. Because of their smaller size, yttrium and yttrium earths have a greater solubility in the rock forming mineral of the Earth's mantle and show less enrichment in the Earth's crust as compared to cerium and cerium earths, relative to chondritic abundance. Large orebodies of the cerium earths are known and are actively exploited around the world, while the yttrium orebodies are rarer, less concentrated and smaller. At the present most of the yttrium supply comes from the ion adsorption clay ores of Southern China.

Efficient separation techniques of the rare earth metals were developed mostly after 1960.They include ion exchange, solvent extraction, fractional crystallization and electrolytic reduction. Rare earth minerals are difficult to mine and the extraction of the metals is laborious because of their similar properties. For this reason, the rare earth metals are relatively expensive.

The rare earth elements exhibit complex spectra and the mixed oxides, when heated, produce an intensive white light similar to sun light. One application of this property are the cored carbon arcs.

Mixed rare earths are reduced to metals (misch metal) and the corresponding alloys are used in metallurgy. Alloys of cerium and mixed rare earths are used in lighter flints and rare earths have applications as catalysts in the petroleum industry. Garnets of yttrium and aluminum (YAG) have been employed as artificial diamonds in jewelry.

Rare earth ions are used in luminescent materials and optoelectronics, the most common being the Nd:YAG laser. Phosphors with rare earth dopants are common in cathode ray tube technology and television sets. Erbium doped fiber amplifiers are used in optical fiber communication systems. Batteries, magnets and superconductors contain rare earths. Samarium-cobalt and neodymium-iron-boron are examples of high flux rare earth magnets. Yttrium iron garnet (YIG) has been used as tunable microwave resonator and rare earth oxides are mixed with tungsten to improve high temperature welding. [22-26]

MINERALS CONTAINING RARE EARTH ELEMENTS

The International Mineralogical Association (IMA) had validated up to 2008 a total of two hundred and seventy two (272) species of minerals containing rare earth elements.[15] Five more species were validated by the IMA after 2008.

The mineralogical species with the corresponding rare earth element are listed as follows:

Abenakiite-(Ce); adamsite-(Y); aeschynite-(Ce); aeschynite-(Nd); aeschynite-(Y); agardite-(Ce); agardite-(La); agardite-(Y); allanite-(Ce); ancylite-(Ce); allanite-(Y); ancylite-(La); arsenoflorencite-(Ce); ashcroftine-(Y); astrocyanite-(Ce); bario-olgite; bastnäsite-(Ce); bastnäsite-(La); bastnäsite-(Y); belovite-(Ce); belovite-(La); bijvoetite-(Y); biraite-(Ce); bobtraillite; braitschite-(Ce); brannerite; britholite-(Ce); britholite-(Y); brockite; burbankite; byelorussite-(Ce); calcioancylite-(Ce); calcioancylite-(Nd); calcioburbankite; calciosamarskite; calkinsite-(Ce); cappelenite-(Y); carbocernaite; caysichite-(Y); cerianite-(Ce); ceriopyrochlore-(Ce); cerite-(Ce); cerite-(La); cervandonite-(Ce); chernovite-(Y); chevkinite-(Ce); chukhrovite-(Ce); chukhrovite-(Nd); chukhrovite-(Y); churchite-(Nd); churchite-(Y); ciprianiite; cordylite-(Ce); coskrenite-(Ce); crichtonite; daqingshanite-(Ce); darapiozite; davidite-(Ce); davidite-(La); davidite-(Y); decrespignyte-(Y); deloneite-(Ce); dessauite-(Y); dingdaohengite-(Ce); dissakisite-(Ce); dissakisite-(La); diversilite-(Ce); dollaseite-(Ce); donnayite-(Y); dusmatovite; euxenite-(Y); ewaldite; fergusonite-beta-(Ce); fergusonite-beta-(Nd); fergusonite-beta-(Y); fergusonite-(Ce); fergusonite-(Y); ferriallanite-(Ce); ferronordite-(Ce);

ferronordite-(La); fersmite; florencite-(Ce); florencite-(La); florencite-(Nd); fluocerite-(Ce); fluocerite-(La); fluorbritholite-(Ce); fluorcalciobritholite; fluorcaphite; flurthalénite-(Y); formanite-(Y); françoisite-(Ce); françoisite-(Nd); gadolinite-(Ce); gadolinite-(Y); gagarinite-(Y); galgenbergite-(Ce); gasparite-(Ce); gatelite-(Ce); georgbarsanovite; gerenite-(Y); goudeyite; gramaccioliite-(Y); gysinite-(Nd); häleniusite-(La); hellandite-(Ce); hellandite-(Y); hibonite; hingganite-(Ce); hingganite-(Y); hingganite-(Yb); hiortdahlite II; horváthite-(Y); huanghoite-(Ce); hundholmenite-(Y); hyalotekite; hydroxylbastnäesite-(Ce); hydroxylbastnäesite-(La); ikranite; iimoriite-(Y); ilmajokite; iraqite-(La); ishikawaite; isolueshite; iwashiroite-(Y); joaquinite-(Ce); johnsenite-(Ce); kainosite-(Y); kamotoite-(Y); kamphaugite-(Y); kapitsaite-(Y); karnasurtite-(Ce); keiviite-(Y); keiviite-(Yb); kentbrooksite; khanneshite; khristovite-(Ce); kimuraite-(Y); kobeite-(Y); kazoite-(La); kozoite-(Nd); kuannersuite-(Ce); kukharenkoite-(Ce); kukharenkoite-(La); kuliokite-(Y); landauite; lanthanite-(Ce); lanthanite-(La); lanthanite-(Nd); laplandite-(Ce); lepersonnite-(Gd); levinsonite-(Y); lokkaite-(Y); loparite-(Ce); loranskite-(Y); loveringite; lucasite-(Ce); lukechangite-(Ce); manganiandrosite-(Ce); manganiandrosite-(La); manganonordite-(Ce); maoniunpingite-(Ce); mckelveyte-(Y); melanocerite-(Ce); merrillite; michelelsenite; minasgeraisite-(Y); mineevite-(Y); miserite; monazite-(Ce); monazite-(La); monazite-(Nd); monazite-(Sm); monteregianite-(Y); mosandrite; moskvinite-(Y); mottanaite-(Ce); moydite-(Y); murataite-(Y); nacareniobsite-(Ce); nioboaeschynite-(Ce); nordite-(Ce); nordite-(La); okanoganite-(Y); olgite; orthojoaquinite-(Ce); orthojoaquinite-(La); paraniite-(Y);

paratooite-(La); parisite-(Ce); peprossiite-(Ce); percleveite-(Ce); perrierite-(Ce); petersenite-(Ce); petersite-(Y); phosinaite-(Ce); piergorite-(Ce); pisekite-(Y); plumboagardite; polyakovite-(Ce); polycrase-(Y); pyatenkoite-(Y); qaquarssukite-(Ce); reederite-(Y); remondite-(Ce); remondite-(La); retzian-(Ce); retzian-(La); rhabdophane-(Ce); rhabdophane-(La); rhabdophane-(Nd); rinkite; röntgenite-(Ce); rowlandite-(Y); sahamalite-(Ce); samarskite-(Y); samarskite-(Yb); saryarkite-(Y); sazhinite-(Ce); sazhinite-(La); sazykinaite-(Y); schuilingite-(Nd); seidite-(Ce); semenovite-(Ce); shabaite-(Nd); shomiokite-(Y); stavelotite-(La); steenstrupine-(Ce); stillwellite-(Ce); stornesite-(Y); strontiochevkinite; synchysite-(Ce); synchysite-(Nd); synchysite-(Y); tadzhikite-(Ce); tantalaeschynite-(Y); tanteuxenite-(Y); tengerite-(Y); thalénite-(Y); thomasclarkite-(Y); thobastnäsite; thorosteenstrupine; thortveitite; tienshanite; tombarthite-(Y); törnebohmite-(Ce); törnebohmite-(La); tritomite(Ce); tritomite(Y); tundrite-(Ce); tundrite-(Nd); vanadoandrosite-(Ce); västmanlandite-(Ce); vicanite-(Ce); vigezzite; vitusite-(Ce); vyuntspakhkite-(Y); wakefieldite-(Ce); wakefiedite-(Y); xenotime-(Y); xenotime-(Yb); yakovenchukite-(Y); yttrialite-(Y); yttrobetafite-(Y); yttrocrasite-(Y); yttropyrochlore-(Y); yttrotantalite-(Y); yttrotungstite-(Ce); yttrotungstite-(Y); zajacite-(Ce); zirsilite-(Ce) and zugshunstite-(Ce).

The following minerals containing rare earth elements, validated by the International Mineralogical Association (IMA) after 2008 are the following: nioboaeschynite-(Y)[16]; uedaite-(Ce)[17]; wakefieldite-(La)[18]; bussyite-(Ce)[19]; and stetindite[20].

Minerals such as aqualite contain rare earth elements in their empirical formula $(Fe_{0.23}Mn_{0.12}]\Sigma_{13.18}(Ca_{5.79}REE_{0.19})\Sigma_{5.98}$ $(Zr_{2.92}Ti_{0.08})\Sigma_{3}(Si_{25.57}Ti_{0.21}Al_{0.19}Nb_{0.03})\Sigma_{26}$ $[O_{66.46}(OH)_{5.54}]\Sigma_{72.0}$ $[(OH)_{2.77}Cl_{1.23}]\Sigma_{4.0}$ on a basis of 29(Si, Zr, Ti, Al, N), but they are not present in the ideal formula $((H_3O)_8(Na,K,Sr)_5Ca_6Zr_3Si_{26}O_{66}(OH)_9Cl)$[21].

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