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AN INTRODUCTION TO THE GEOCHEMISTRY OF GADOLINIUM

by

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INTRODUCTION

Gadolinium is one of the fifteen elements 1/ of atomic numbers 57 to 71 that are generally considered to comprise the rare-earth group of elements. Table 1 gives some of the properties of these elements, and of yttrium for comparison, and figure 1 illustrates graphically the abundance of these elements in the earth's crust.

The figures given in table 1 for abundance are of a low degree of reliability although they probably are of the right order of magnitude. They are based on the analysis by Minami 2/ of three shales.

Gadolinium has seven naturally occurring isotopes 3/ whose relative abundances are as follows: Gd^{152} 0.20 percent, Gd^{154} 2.15 percent, Gd^{155} 14.78 percent, Gd^{156} 20.59 percent, Gd^{157} 15.71 percent, Gd^{158} 24.78 percent, Gd^{160} 21.79 percent.

1/ The element yttrium also is often included in the rare-earth group, which it closely resembles in chemical properties and with which it is always associated in natural occurrence.

2/ Minami, E., Gehalte an seltenen Erden in europaischen und japanischen Tonschiefern: Gesell. Wiss. Gottingen, Nachr., Math.-phys. Kl., Fachgruppe IV, 1, no. 14, pp. 155-170, 1935.

3/ Seaborg, G. T., and Perlman, I., Table of isotopes: Rev. modern physics 20, pp. 585-667, 1948.

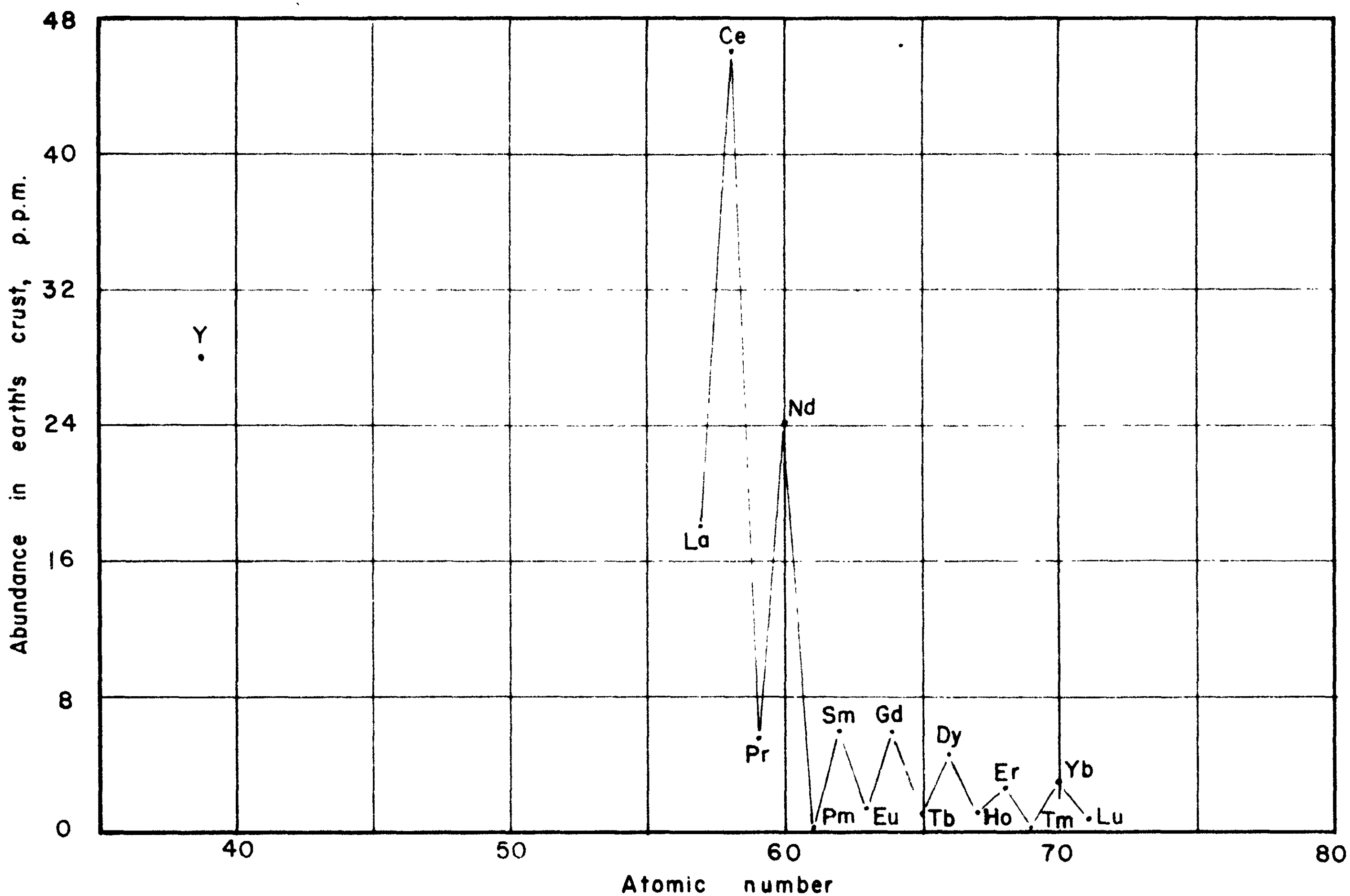

Figure I. — Abundance of rare earths in earth's crust

Table 1.--Atomic properties and abundance of rare-earth elements and yttrium

Element	Symbol	Atomic no.	Atomic wt.	Ionic radius (a)	Abundance in earth's crust in parts per million (b)
Lanthanum	La	57	138.92	1.22	18
Cerium	Ce	58	140.13	1.18	46
Praseodymium	Pr	59	140.92	1.16	5.5
Neodymium	Nd	60	144.27	1.15	24
Promethium	Pm	61	147.	--	0
Samarium	Sm	62	150.43	1.13	6
Europium	Eu	63	152.0	1.13	1
Gadolinium	Gd	64	156.9	1.11	6
Terbium	Tb	65	159.2	1.09	0.9
Dysprosium	Dy	66	162.46	1.07	4.5
Holmium	Ho	67	164.94	1.05	1
Erbium	Er	68	167.2	1.04	2.5
Thulium	Tm	69	169.4	1.04	0.2
Ytterbium	Yb	70	173.04	1.00	3
Lutetium	Lu	71	174.99	0.99	0.8
Yttrium	Y	39	88.92	1.06	28

(a) For trivalent ions
(b) To convert to weight percent, move the decimal point four places to the left

GENERAL GEOCHEMISTRY OF THE RARE EARTHS

The rare earths are strongly lithophilic elements which characteristically occur in igneous silicate rocks. Because of their high charge (+3) and large ionic radii, they do not replace magnesium or iron during the early stages of crystallization. They can and do replace calcium (ionic radius 1.06) in plagioclase, but only to a slight extent, and most of the rare-earth elements are concentrated in the residual magma as crystallization proceeds. They are therefore especially abundant in granitic and syenitic rocks, particularly in the pegmatite phases. As a group, therefore, these elements are unusually concentrated in a few types of rocks.

Over 60 minerals are known in which the rare earths are major constituents. Most of these are mineralogical curiosities, and many occur only in nepheline syenite pegmatites. A list of these minerals is given in table 2. Of these, monazite, $(Ce,La,Pr,Nd)PO_4$, is the present source of all rare earths now produced. Others that may be important sources are xenotime, YPO_4, and bastnaesite, $(Ce,La)FCO_3$.

Table 2.--Minerals containing major amounts of rare earths

Name	Composition	Maximum content of rare-earth oxides + Y_2O_3 (Wt. %)	Type of occurrence*
Abukumalite	Complex silicophosphate of Ca and Y	52.4	A
Aeschynite, see eschynite			
Allanite	$(Ca,Ce)_2(Al,Fe,Mg)_3Si_3O_{12}(OH)$	29.1	A,B,E
Ambatoarinite	Probably is ancylite		
Ampangabeite	Columbate-tantalate	8.2	A
Ancylite	$Sr_3Ce_4(CO_3)_7(OH)\cdot 3H_2O$	48.0	B
Bastnaesite	$(Ce,La)FCO_3$	76.8	A
Bazzite	Silicate of rare earths and scandium	no anal.	A
Beckelite	$Ca_3(Ce,La,Pr,Nd)_4Si_3O_{15}$	62.5	B

Befanamite, see thortveitite

Betafite	$(U,Ca)(Cb,Ta,Ti)_3O_9 \cdot nH_2O$?	6.0	A

Blömstrandine-priorite-eschynite, see eschynite

Brannerite	$(U,Ca,Fe,Y,Th)_3Ti_5O_{16}$?	3.9	C,A
Britholite	Silicate-phosphate of rare earths	60.5	B
Buszite	Silicate of rare earths	no anal.	A
Cappelenite	$(Ba,Y)_2SiBO_6$	57.7	B
Caryocerite	Borosilicate of Ce and Y	38.1	B
Cenosite	$2CaO \cdot (Ce,Y)_2O_3 \cdot CO_2 \cdot 4SiO_2 \cdot H_2O$	38.7	contact zone?
Cerite	Ce_2SiO_5 Complex Ce silicate	71.1	A

Chevkinite = tscheffkinite

Churchite	Hydrous phosphate of Ce and Ca	51.9	E
Cordylite	$BaCe_2F(CO_3)_3$	49.4	B
Delorenzite	$(Y,U,Fe^2)(Ti,Sn)_3O_8$?	14.6	A
Erdmannite	Hydrous silicate of Ca, Ce,Al,Fe	36.3	?
Erikite	Phosphate-silicate of rare earths	40.5	B
Eschwegite	Near euxenite	27.3	C?
Eschynite	$(Ce,Ca,Fe?,Th)(Ti,Cb)_2O_6$	31.4	B
Euxenite-polycrase series	$(Y,Ca,Ce,U,Th)(Cb,Ta,Ti)_2O_6$	29.7	A
Fergusonite-formanite series	$(Y,Er,Ce,Fe)(Cb,Ta,Ti)O_4$	41.3	A
Florencite	$CeAl_3(PO_4)_2(OH)_6$	28.0	C

Fluocerite	$(Ce,La)F_3$	70.5	A
Fluorite, see yttrocalcite			
Gadolinite	$Be_2FeY_4Si_2O_{13}$	54.3	A
Hellandite	$Ca_2(Fe,Al,Mn)_6Si_4O_{19}\cdot 3H_2O$	40.1	A
Hjelmite	$(Y,Fe,U)(Cb,Ta,Sn)_2O_6$?	6.3	A
Ishikawaite	$(U,Fe,Y)(Cb,Ta)O_4$?	8.4	A
Johnstrupite	Complex silicate of Na, Ca,Ce, and Ti	14.6	B
Kainosite = cenosite			
Khlopinite	$(Y,U,Th)_3(Cb,Ta,Ti,Fe)_7O_{20}$	17.7	A
Lanthanite	$La_2(CO_3)_2\cdot 9H_2O$	54.7	D
Lessingite	Silicate of rare earths	62.2	C
Loparite	$(Na,Ca,Ce)_2(Ti,Cb)_2O_6$	36.6	B
Loranskite	$(Y,Ce,Ca)(Ta,Zr)O_4$?	13.0	A
Lovchorrite, see rinkite			
Lyndochite, see euxenite			
Melanocerite	Borosilicate of rare earths	54.1	B
Monazite	$(Ce,La,Pr,Nd)PO_4$	**68.7**	**A,E**
Mosandrite	Complex silicate of Na,Ca, Ce, and Ti	26.6	B
Nagatelite, a phosphate-bearing variety of allanite			
Nordite	Silicate of Na,Sr,Ce	20.2	B
Nuevite	Contains Y,Fe,Cb,Ta,Ti		
Nuolaite, see wiikite			
Orthite = allanite			
Parisite	$CaCe_2F_2(CO_3)_3$?	60.4	A

Pisekite	Complex columbate-tantalate of rare earths	no anal.	A
Polycrase, see euxenite			
Polymignite	$(Ca,Y,Fe,Zr)(Cb,Ta,Ti)O_4$	26.7	B
Priorite, see eschynite			
Retzian	Basic arsenate of rare earths and Mn	10.3	D
Rhabdophanite	$(Ce,Y)PO_4 \cdot H_2O$?	65.8	D
Rinkite	Complex silicate of Na,Ca,Ce, and Ti	22.2	B
Rinkolite	Complex silicate of Na, Ca,Ce, and Zr	18.0	B
Rowlandite	Yttrium silicate	62.1	A
Samarskite	$(Y,Er,U,Ca)(Cb,Ta)_2O_6$	21.8	A
Scheteligite	$(Ca,Y,Sb,Mn)_2(Ti,Ta,Cb)_2(O,OH)_7$	6.0	A
Steenstrupine	Complex silicate of rare earths, Th,Na,K,Fe,Mn, Mg,P,Be,Al, and Ta, with (OH) and F	37.7	B
Stiepelmannite = florencite			
Synchisite	$CaCeF(CO_3)_2$	52.2	B
Tengerite	$CaY_3(CO_3)_4(OH)_3 \cdot 3H_2O$ also beryllium yttrium carbonate	47.8	A,D
Thalenite	$Y_4Si_4O_{13}(OH)_2$	66.8	A
Thortveitite	$(Sc,Y)_2Si_2O_7$	17.7	A
Toernebohmite	$(Ca,La,Al,Mg)_3Si_2O_8F$	62.4	A
Treanorite = allanite			
Tritomite	Borosilicate of cerium and yttrium	56.5	B

Tscheffkinite	Silicate of rare earths and Ti	47.3	A
Tysonite = fluocerite			
Weibyeite, related to ancylite			
Weinschenkite	$YPO_4 \cdot 2H_2O$	52.9	D
Wiikite	Ill-defined material containing Y,Cb,Si,Ta, and Ti	20.3	A
Xenotime	YPO_4	67.8	A,E
Yttrialite	Silicate of Y and Th	51.7	A
Yttrocalcite) Yttrocerite) Yttrofluorite)	Intermediate between fluocerite and fluorite		A
Yttrocrasite	$(Y,Th,U)_2Ti_4O_{11}$?	28.6	A
Yttrotantalite	$(Fe,Y,U)(Cb,Ta)O_4$	18.2	A

* Types of occurrence

A - Granitic pegmatites
B - Syenitic pegmatites
C - Placer
D - Secondary mineral
E - Accessory mineral of granites

In addition, the rare earths also occur as accessory elements in solid solution in many minerals. The most important of these are listed in table 3. The figures given are for maximum rare earth content; the average content is much less. From consideration of the ionic radii (see table 1), the rare earths can be expected to replace calcium (ionic radius 1.06), uranium (1.05), and thorium (1.10), particularly the last two. This is verified by experience in that uranium and thorium minerals commonly contain the rare earths in appreciable amounts as do many calcium minerals. Perhaps the most important of these is apatite, $Ca_5(PO_4)_3F$. Almost all the apatite of phosphorite deposits contains hundredths to tenths of a percent of rare earths; apatite of magmatic deposits associated with nepheline syenites, such as that of the Kola Peninsula, Russia, contain as much as 2 to 3 percent of rare earths. Sphene, $CaTiSi_2O_5$, from granites, commonly contains yttrium and other rare earths.

Table 3.--Minerals containing rare earths as accessory elements in solid solution

Name	Composition	Maximum content of rare-earth oxides (Wt. %)	Type of occurrence*
Alvite, see zircon			
Apatite	$Ca_5(PO_4)_3F$	5.2	B
Auerlite, see thorite			
Cyrtolite, see zircon			
Davidite	Contains Fe,Ti,U	8.3	A
Dysanalyte, see perovskite			
Ellsworthite, see pyrochlore-microlite			
Eudialyte	$(Na,Ca)_5Zr_2Si_6O_{18}(OH,Cl)$	5.2 (21?)	B
Fersmite	$(Ca,Ce,Na)(Cb,Ti,Fe,Al)_2(O,OH,F)_6$	4.8	B
Gorceixite	$BaAl_3(OH)_7P_2O_7$	2.5	C
Hatchettolite, see pyrochlore-microlite			

Kalkowskite	$Fe_2Ti_3O_9$?	2.7	mica schist
Keilhauite, see sphene			
Koppite, see pyrochlore-microlite			
Mackintoshite	Hydrated thorium silicate	1.9?	A
Maitlandite	Hydrated thorium silicate	0.4	A
Microlite, see pyrochlore-microlite			
Naegite, see zircon		9.1	C
Nicolayite	Hydrated thorium silicate	0.4	A
Oyamalite, see zircon			
Perovskite See also loparite, table 2	$(Ca,Ce)(Ti,Cb)O_3$	usually 2-6	B,E
Pilbarite	Hydrated thorium silicate	0.7	C
Pyrochlore-microlite	$(Na,Ca,Ce)(Cb,Ta)_2O_6(OH,F)$	18.4	B,A
Rosenbuschite	Silicate of Na,Ca,Zr	2.4	B
Scheelite	$CaWO_4$	0.14	
Sphene	$CaTiSi_2O_5$	12.1	E
Thorianite	$(Th,U)O_2$	8.0	C
Thorite	$ThSiO_4$	7.2	B
Titanite = sphene			
Uraninite	UO_2	12.2	A
Wöhlerite	Complex silicate of Ca, Na,Zr,Cb	0.8	B
Zircon (including varieties above)	$ZrSiO_4$	17.7	A,E
Zirkelite	$(Ca,Fe,Th)_2(Ti,Zr)_2O_5$?	3.7	C

* Types of occurrence

A - Granitic pegmatites
B - Syenitic pegmatites
C - Placer
D - Secondary mineral
E - Accessory mineral of granites

RELATIVE ABUNDANCE OF GADOLINIUM

Despite their geochemical similarity, which is shown by the fact that practically all members of the group are present in any occurrence, the fifteen rare-earth elements show a great diversity in relative abundance from occurrence to occurrence. In table 4 are assembled all available quantitative determinations of the relative abundance of these elements in individual rocks and minerals.

The data are relatively few and their precision is considerably in doubt, especially for the rarer elements such as gadolinium. The data suggest that minerals relatively high in yttrium are relatively high in gadolinium, but the extreme value (15 percent of the total rare earths) represents only about two or three times the average content.

Table 4.--Ratio of gadolinium to total rare earths plus yttrium in rocks and minerals

Total rare earths wt. %	% Gd in total rare earths	Type of material	Reference
0.015	4.1	Earth's crust	Table 1
0.0176(a)	4.0	European Paleozoic shales	(7)
0.0174(a)	3.8	Japanese Paleozoic shales	(7)
0.0187(a)	3.8	Japanese Mesozoic shales	(7)

8.41(a)	3.9(b)	Wiikite, Finland	(11)
18.17(a)	5.9(b)	Wiikite, Finland	(11)
7.59(a)	3.4(b)	Wiikite, Finland	(11)
6.80(a)	2.1(b)	Wiikite, Finland	(11)
12.04(a)	5.8(b)	Wiikite, Finland	(11)
2.59(a)	7.7(b)	Wiikite, Finland	(11)
10.48(a)	4.8(b)	Allanite	(11)
0.135(a,c)	7.4(b,c)	Alkali feldspar pegmatite	(12)
0.0303(a)	3.3(b)	Granophyre, Finland	(12)
0.0343(a)	5.8(b)	Granophyre, Finland	(12)
0.0154(a)	5.8(b)	Diabase, Finland	(12)
0.0555(a)	5.4(b)	Diabase, Finland	(12)
0.0553(a)	5.4(b)	Diabase, Finland	(12)
0.266(a)	4.5(b)	Granite, Finland	(12)
—	ca.6(b)	Allanite, Finland	(12)
0.0412(a)	4.9(b)	Granite, Finland	(12)
0.154(a)	5.2(b)	Granite, Finland	(12)
0.261(a)	3.8(b)	Granite, Finland	(12)
0.0136(a)	5.1(b)	Granite, Finland	(12)
0.0141	5.7(b)	Granite, Finland	(12)
—	6.4(b)	Monazite, Finland	(12)
0.0307	6.7(b)	Granite, Finland	(12)
0.0193(a)	5.1(b)	Granite, Finland	(12)
—	5.6(b)	Monazite, Finland	(12)
0.392(a)	5.1(b)	Sphene, Finland	(12)
2.67(a)	7.7(b)	Apatite from pegmatite	(12)
0.47(a)	6.4(b)	Sphene, Finland	(10)
0.30(a)	6.7(b)	Sphene, Finland	(10)
0.37(a)	5.4(b)	Sphene, Russia	(10)
0.26(a)	3.8(b)	Sphene, Russia	(10)
0.0304(a)	5.9(b)	Granites, Finland	(9)
0.0126(a)	7.1(b)	Mica gneiss, Finland	(9)
0.0194(a)	5.1(b)	Mica gneiss, Finland	(9)
0.0151(a)	5.3(b)	Mica gneiss, Finland	(9)
0.0203(a)	5.5(b)	Granite, Finland	(9)
0.0316(a)	7.6(b)	Granite, Finland	(9)
0.121	3.3	Apatite-magnetite ore, Sweden	(4)
0.154	5.2	Apatite-magnetite ore, Sweden	(4)
0.375	8.0	Apatite-hematite ore, Sweden	(4)
0.0227(a)	6.6(b)	Average younger granites, Finland	(8)
0.0145(a)	5.5(b)	Average gneisses, Finland	(8)
0.0113(a)	5.1(b)	Average granulite, Finland	(8)
0.0036(a)	5.5(b)	Average greenstone, Finland	(8)
0.0024(a)	6.7(b)	Average gabbros, Finland	(8)
0.0100(a)	5.0(b)	Average schists, Finland	(8)
0.0082(a)	7.2(b)	Average leptites, Finland	(8)
55.25	7.2	Xenotime	(6)
33.65	7.7	Tscheffkinite	(6)

39.9	4.4	Cerite, Sweden	(6)
0.05	14	Scheelite, Swaziland	(5)
0.011	2.2	Clay, URSS	(1)
--	4(b)	Apatite, Georgia, URSS	(2)
--	5(b)	Apatite, Urals, URSS	(2)
--	0.6(b)	Loparite, Kola, URSS	(2)
--	5(b)	Apatite, Kola, URSS	(2)

Goldschmidt and Thomassen (3) give averages for many minerals. These averages (percent gadolinium in total rare earths) are:

8 Apatite
15 Yttrofluorite, gadolinite, and sphene
13 Thalenite and Cb-Ta minerals
4 Thortveitite, zircon
15 Xenotime
4 Allanite, monazite

Notes to Table 4

(a) Rare-earth oxides
(b) Percent Gd_2O_3/Total rare-earth oxides + Y_2O_3
(c) Yttrium not determined

RECOVERY OF GADOLINIUM

Probably the only practicable method now available for the separation of gadolinium is the ion-exchange process, as used at the Oak Ridge National Laboratory of the U. S. Atomic Energy Commission, and at Iowa State University, Ames, Iowa. As far as is known to us, monazite sands are the sole source of rare earths now utilized, but the bastnaesite occurrence in California may become a producer. One spectrographic determination recently made by the Geological Survey on this bastnaesite indicates a content of 1 percent gadolinium.

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