THE COMPOSITION CHARACTERISTICS OF THE RARE EARTHS IN MINERALS*

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Abstract

The composition of rare earths is shown by two similar curves linking the points of separate even and odd lanthanides. According to the value of the maximum, three types of rare-earth composition have been distinguished: a strongly selective (> 45-50), a selective (> 30) and a complex type (< 30). Besides the well-known maxima on Ce, Dy and Yb, abrupt maxima of lanthanides in minerals has been outlined. A correlative bond between near-lanthanides and a relative constancy in the ratios of even and odd elements of one pair has been established. The correlative bond of the separate lanthanides depends on the proximity of the ionic radius (and electronic configuration) of one pair of elements. The typical ratios of pair lanthanides are somewhat disturbed in strongly selective compositions. In minerals with maxima on Ce, Nd and Gd, Y is nearly absent, whereas in compositions with maxima of Dy and Yb, large amounts of Y are present.

Therefore in the mineralogical-geochemical respect it has been suggested to place the boundary between the cerium and yttrium groups between Tb and Dy. It is reasonable to distinguish the pair-lanthanide groups according to the leading even elements; the cerium group (Ce, La), the neodymium group (Nd, Pr), the samarium group (Sm, Eu), the gadolinium group (Gd, Tb), the dysprosium group (Dy, Ho), the erbium group (Er, Tu) and the ytterbium group (Yb, Lu).

Systematic studies of the rare earths in minerals were begun in the 1920's by V. M. Goldschmidt and L. Thomassen [1]. Although their studies were chiefly qualitative, they were sufficient to demonstrate that the rare earth minerals differ significantly among themselves in the proportions of the rare earths they contain.

Goldschmidt and Thomassen were able to differentiate several types of rare earth minerals on the basis of their composition and the relative preponderance of this or that element: a) the complex type (apatite, yttrium fluorite); b) the selectively cerium type (monazite, allanite); c) the selectively yttrium type (thalenite, thortveitite, xenotime).

Complete quantitative data on the composition of the rare-earth minerals have appeared in abundance chiefly in recent years, in the studies by I. B. Borovskii and V. I. Gerasimovskii [2], Murata et al. [3, 4], E. E. Vainshtein, A. I. Tugarinov, and N. V. Turanskaya [5], and others [6, 7, 8, 9].

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We conducted systematic studies of the composition of the rare earths represented by more than 100 specimens of different minerals of different genetic types from different localities. Inasmuch as the earlier studies [2, 3, 4, 5] report quantitative characteristics of the rare earths chiefly in cerium minerals, the present study was intended to put a particular emphasis on yttrium minerals.

The mineral specimens were collected by E. I. Semenov during his studies in the Kola Peninsula, Ukraine, Urals, Central Asia, Taimyr, Yenisei Range, and Kolyma. Several specimens were procured from other geologists in the Union whose names are given in the analytical tables. The rare-earth minerals from foreign sources were procured from the collections of the Mineralogical Museum, Academy of Sciences of the USSR, through the courtesy of G. P. Barsanov. The minerals were identified, in controversial cases, by X-ray and optical methods.

Preliminary isolation of precipitates of the sum-total of the rare earths (ΣTR_2O_3) were performed for most of the minerals by A. V. Bykova, O. F. Dorondova, M. E. Kazakova, M. V. Kukharchik, and I. S. Razina, chemist-analysts. The quantitative composition of the rare earths in the ΣTR_2O_3 or in the minerals was determined by R. L. Barinskii by the X-ray spectrographic procedure. Reliability of the analyses was 5 to 7% of the determined values, with a sensitivity of 0.1%.

Results of the X-ray spectrographic analyses are presented in the table. Figures in the columns of the table indicate percentages of the given lanthanide in the ΣTR_2O_3, which is here taken as 100%. All of the oxides are sesquioxides, with the exception of the oxides of Ce and Pr which are assumed to be dioxides, by analogy with earlier reports [3, 4]. The point here is that Ce and Pr are present as dioxides in the working standards employed in the X-ray spectrographic analyses. It should be possible to treat them as sesquioxides, for the sake of uniformity of results.

Inasmuch as the rare-earth content of the minerals is generally lower than it is in the ΣTR_2O_3, the lanthanides are determined with higher sensitivity and with greater accuracy in the precipitate than in the minerals. For that reason, whenever rare earths were determined directly in minerals, the results are qualified in the table, by the word "mineral" in the footnote. Yttrium was determined by difference, 100% minus ΣTR_2O_3, in the minerals here examined. Consequently, the results for yttrium are not quite as accurate as the results for the lanthanides.

Because the composition of the rare earths has been ascertained so far only for very few minerals, it appeared desirable to include the older analyses together with the newer data for the same minerals. For minerals which were already analyzed by the earlier investigators in detail (tens and hundreds of specimens of monazite, allanite, etc.) we report only the range of the variation for their composition.

Table 1. Composition of Rare Earths in Minerals ($\Sigma TR_2O_3 = 100\%$)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Item No.	Mineral and formula	Source and geologic features	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Remarks
1	Bastnaesite; $CeFCO_3$	Gallinas, N.M., USA; granite hydrotherm; extreme of 6 lanthanides	42.9	45.6	3.9	7.1	0.5	-	-	-	-	-	-	-	-	-	a)
2	Bastnaesite; $CeFCO_3$	Mountain Pass, Calif., USA; alkaline syenite hydrotherm; extreme of 6 high-Nd specimens	26.1	50.5	4.9	15.9	1.8	-	0.9	-	-	-	-	-	-	-	a)
3	Bastnaesite; $CeFCO_3$	Mochalin Log, Ural; alkali granite pegmatite	39	50	3.1	7.7	0.2	-	-	-	-	-	-	-	-	-	a)
4	Bastnaesite; $CeFCO_3$	Madagascar; granite pegmatite	34	53	3.8	8.5	0.7	-	0.1	-	-	-	-	-	-	-	b)
5	Bastnaesite; $CeFCO_3$	Tuva; hydrotherm of alkali granites	25	50	5.6	18	0.9	-	0.5	-	-	-	-	-	-	-	
6	Fluocerite; CeF_3	N. Kirgiziya; hydrotherm of granites	38	48.4	3.3	9.3	1.2	-	-	-	-	-	-	-	-	-	c)
7	Nordite; $Na_3Ce (Sr,Ca)\cdot(Mn,Fe) Si_6O_{17}$	Lovozero, Kola Peninsula; sodalite syenite pegmatite	34	55	4.1	7	-	-	-	-	-	-	-	-	-	-	
8	Ancylite; $Ce_4Sr_3(CO_3)_7 \cdot(OH)_4 H_2O$	Khibiny, Kola Peninsula; nepheline syenite; hydrothermal stage	32	54	4.1	9.5	0.3	-	-	-	-	-	-	-	-	-	
9	Parisite; $Ce_2Ca (CO_3)_3 F_2$	Mountain Pass, Calif., USA; hydrotherm of alkali syenites	29.9	50.5	4.3	14	1.3	-	-	-	-	-	-	-	-	-	a)
10	Parisite; $Ce_2Ca (CO_3)_3 F_2$	Mariupol, Ukraine; hydrotherm of alkali syenites	29.1	51	3.8	14.6	1.5	-	-	-	-	-	-	-	-	-	d)
11	Sahamalite; $Ce_2(Mg,Fe) (CO_3)_4$	Mountain Pass, Calif., USA; hydrotherm of alkali syenites	30	53	4	12	1	-	-	-	-	-	-	-	-	-	
12	Burbankite; $(Ce,Na,Ca,Sr,Ba) CO_3$	Bear Paw Mtn.,Montana, USA; hydrotherm of alkali rocks	25.8	53.6	4.2	15.4	1.1	-	0.8	-	-	-	-	-	-	-	
13	Calkinsite; $Ce_2 (CO_3)_3\cdot 4H_2O$	Bear Paw Mtn., Montana, USA; supergene after burbankite	30.7	52	4.5	12.3	-	-	-	-	-	-	-	-	-	-	
14	Florencite; $CeAl_3 (PO_4)_2\cdot(OH)_6$	Ural diamond placers	29.2	48.6	5.4	16.8	-	-	-	-	-	-	-	-	-	-	
15	Loparite; $(Ce,Na,Ca)(Ti,Nb)O_3$	Khibiny; neph. syenite pegmatite; hydrothermal stage	33	53	4.5	9	0.5	-	-	-	-	-	-	-	-	-	
16	Loparite; $(Ce,Na,Ca)(Ti,Nb)O_3$	Ijolites; Kola Peninsula	24	54	6	15	0.7	0.3	-	-	-	-	-	-	-	-	
17	Loparite; $(Ce,Na,Ca)(Ti,Nb)O_3$	Ijolites; Yenisei Range; Kiya	25	55	5.8	14	0.2	-	-	-	-	-	-	-	-	-	e)
18	Steenstrupine $Na_2MnCe_2(Si_5 PO_{18})(OH,F)$	Lovozero; sodalite syenite pegmatite	24	48	7.3	20	0.7	-	-	-	-	-	-	-	-	-	
19	Cordylite; $Ce_2 Ba (CO_3)_3F_2$	S.Greenland, Narsarsuk; alkali syenite pegmatite; hydrothermal stage	29	45	5.5	15	3.2	0.1	2.1	-	-	-	-	-	-	-	c)
20	Chevkinite; $Ce_4FE_2Ti_3Si_4O_{22}$	Vishnevye Gory; alkaline syenite pegmatite	34	51	3.8	11	0.2	-	-	-	-	-	-	-	-	-	f)
21	Chevkinite; $Ce_4Fe_2Ti_3Si_4O_{22}$	Keivy, Kola Peninsula; alkali syenite pegmatite	20.2	42.6	5.5	21.3	4.9	-	3.2	-	2.3	-	-	-	-	-	d)
22	Belovite; $Na_2Ce_2Sr_6 P_6O_{24} (OH)_2$	Lovozero, alkali syenite pegmatite	22	52	7.8	18	0.5	-	-	-	-	-	-	-	-	-	
23	Rhabdophane $CePO_4 \cdot H_2O$	Ditto, hydrothermal stage	39	48	3.4	9.3	0.3	-	-	-	-	-	-	-	-	-	
24	Rhabdophane $CePO_4 \cdot H_2O$	Julianehaab, S. Greenland; alkali syenite pegmatite, supergene stage	35	56	3	6	-	-	-	-	-	-	-	-	-	-	c)
25	Rhabdophane $CePO_4 \cdot H_2O$	Sumy, Ukraine; sedimentary rocks	18.0	46	8	20	3.4	0.3	2	0.3	1.3	0.2	0.5	-	0.2	-	g)
26	Rinkolite $Na_2Ca_4Ce Ti Si_4 O_{15}F_3$	Khibiny; nepheline syenite pegmatite; the La extremes of 12 analyses	27.6	45.6	4.9	16.3	2.6	-	1.6	-	1.4	-	-	-	-	-	h)
27	Rinkolite $Na_2Ca_4Ce Ti Si_4 O_{15}F_3$	Ditto; the Nd extreme of 12 analyses	15	44.2	4.8	24.2	4.3	-	2.8	0.1	2.3	0.2	0.3	-	1.9	-	h)
28	Rinkolite $Na_2Ca_4Ce Ti Si_4 O_{15}F_3$	Lovozero; nepheline syenite pegmatite	17	51	8	19	4	0.2	0.5	-	0.4	-	0.1	-	-	-	
29	Monazite, $CePO_4$	Kounrad, Kazakhstan; granite pegmatite; the La extreme of 100 specimens	37.7	49.3	3.1	9.0	0.9	-	-	-	-	-	-	-	-	-	i)
30	Monazite, $CePO_4$	Jamestown, Colo., USA; granite pegmatite; the Nd extreme of 100 specimens	13.1	41.5	6.1	32.9	4.4	-	2	-	-	-	-	-	-	-	
31	Monazite, $CePO_4$	Tommot, Yakutiya; alk. granite pegmatite	26	49	5.5	18	1	0.1	0.6	-	-	-	-	-	-	-	
32	Monazite, $CePO_4$	Borshchevochnyi Range, Transbaikal (pptd. cerium group)	20	51	7.4	18	1.8	0.1	1	-	0.3	-	0.3	-	0.2	-	
33	Monazite; $CePO_4$	Ditto (pptd yttrium group)	1.9	3.8	1	5	8	0.7	43	5.8	17	3.3	6	1	3	0.7	
34	Cerite; $Ce_2Si_2 O_7 \cdot H_2O$	Mtn. Pass, Calif., USA; hydrotherm of Alkali Syenites (the La extreme of 4 specimens)	24	49.3	5.6	18.5	1.6	-	-	-	-	-	-	-	-	-	a)
35	Cerite; $Ce_2Si_2 O_7 \cdot H_2O$	Jamestown, Colo., USA; granite pegmatite; (the Nd extreme of 4 specimens)	11	42.9	6.3	33.6	4.7	-	1.5	-	-	-	-	-	-	-	a)
36	Cerite; $Ce_2Si_2 O_7 \cdot H_2O$	Bastnaes, Sweden; skarns	31	45	5.8	16	1.1	-	0.7	-	0.3	-	-	-	-	-	

Table 1. Composition of Rare Earths in Minerals ($\Sigma\, TR_2O_3 = 100\%$) (continued)

1 Item No.	2 Mineral and formula	3 Source and geologic features	4 La	5 Ce	6 Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
37	Gorceixite; $BaAl_3(PO_4)(HPO_4)(OH)_6$	Minas Gerais, Brazil; diamond placers	17.5	39.1	6.3	26.6	6.4	-	4.1	-	-	-	-	-	-	-	a)
38	Knopite; $Ca(Ti, Fe, Nb)O_3$	Kola Peninsula; alkaline pyroxenites	23	45	5.3	22	1.8	0.1	1.3	0.2	0.4	-	0.2	-	0.5	-	
39	Knopite; $Ca(Ti, Fe, Nb)O_3$	Taimyr: alkaline pyroxenites	19	51	7.2	19	1.8	0.1	1.1	0.2	0.4	0.2	0.2	-	-	-	
40	Knopite; $Ca(Ti, Fe, Nb)O_3$	Yakutiya; carbonatites	16	47	9.5	25	2	0.2	0.4	-	0.2	0.2	-	-	-	-	
41	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	USA; granite pegmatite	0.6	1.2	0.7	25	15	0.6	53	6	15	1.7	1.8	0.7	1	0.4	
42	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Shumilovka Mine, Transbaikal: granite pegmatite	0.6	2.1	1.3	6.6	22	0.6	29	5.6	20	2.5	4.1	1	3.5	0.8	
43	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Baits-Kundui, Transbaikal; granite pegmatite	1.3	3.5	1.7	7	15	1.2	24	3.6	15	3.4	8	1.6	12	2.4	
44	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Madagascar; granite pegmatite	0.6	1.8	1.5	4.7	14	0.5	23	4	20	2.7	11	1.9	12	2.1	
45	Samarskite; $(Gd,U,Fe)(Nb,Ta)_2O_6$	Ilemeny, Ural; granite pegmatite	1	3.3	1	3.9	19	1	18	2.6	28	6.8	4.8	1	7.8	1.7	
46	Euxenite; $YNbTiO_6$	Romteland, Norway; granite pegmatite	1.1	3	1.7	5.4	4.1	0.3	6.8	1.5	14	3.4	16	2.8	33	7	
47	Euxenite; $YNbTiO_6$	Kragero, Norway: granite pegmatite	5	16	2	6	1	-	7	1.5	14	3	8	1.4	30	5.3	b)
48	Euxenite; $YNbTiO_6$	Eliseevka, Ukraine; granite pegmatite	1.9	4	0.5	1.9	9	0.5	12	2	16	3.8	11	1.9	30	5	m)
49	Euxenite; $YNbTiO_6$	Romteland, Norway; granite pegmatite	0.5	1.3	0.2	0.5	5.8	0.5	14	2.6	18	3.8	16	2.9	29	4.9	-
50	Euxenite; $YNbTiO_6$	Iveland, Norway; granite pegmatite	1	3.7	1.2	3.5	5.7	0.5	11	2.4	17	4	13	2.3	29	5.6	-
51	Euxenite; $YNbTiO_6$	Iveland, Norway; granite pegmatite	3.7	13	1	3	4	0.2	9.2	2.2	13	3	12	1.8	29	5	b)
52	Euxenite; $YNbTiO_6$	Iveland, Norway: granite pegmatite	0.8	2.5	0.9	1.9	6.7	0.2	14	2.7	18	3.7	16	2.8	25	4.6	-
53	Euxenite; $YNbTiO_6$	Korovikha, Altai; granite	1.5	4.2	1.4	4.2	5	0.5	10	1.6	19	4.8	16	3	25	4.1	b)
54	Euxenite; $YNbTiO_6$	Adun-Chilon, Transbaikal; granite pegmatite	2.5	7.4	2.7	6	11	0.7	8	2.2	16	3.7	12	2.5	21	4.4	n)
55	Euxenite; $YNbTiO_6$	Arve, Norway; granite pegmatite	1.1	3.4	1.1	3.4	7.3	0.4	17	3	22	4.5	14	3	17	3	-
56	Euxenite; $YNbTiO_6$	N. Tuva; albitite of nepheline syenites	0.6	1.2	0.4	1.2	4	0.4	8	2.5	31	7.6	20	3.1	17	3.3	o)
57	Euxenite; $YNbTiO_6$	Hitterö, Norway; granite pegmatite	2	5	1.5	4.7	11	0.9	20	3.6	22	4.5	10	2	11	2	p)
58	Xenotime; YPO_4	Arendal, Norway; granite pegmatite; (the extreme of 11 specimens of Yb type)	-	-	-	-	-	-	*13.2*	-	*2.4*	-	*21.4*	*5.4*	*46*	*11.6*	*i)*
59	Xenotime; YPO_4	St.Gotthard, Switzerland; Alpine vein (the extreme of 11 specimens of Dy type)	-	-	-	-	2.9	-	14	3	36	7	18.6	-	15.8	2.9	i)
60	Xenotime; YPO_4	Omsukchan, Magadan District; hydrotherm of granites	-	-	-	-	3.8	-	13	3.5	28	6.7	22.6	-	18.9	3.5	d)
61	Xenotime; YPO_4	Placer, Ural	1.8	6	0.5	1.5	3.7	0.4	15	2.6	20	4.8	18	2.6	20	3	b)
62	Churchite; $YPO_4 \cdot 2H_2O$	Kiya, Krasnoyarsk Krai; alkali syenites, supergene stage	2.5	6.8	1.2	4.6	4	0.6	13	21	23	5.7	17	3	14	2.5	q)
63	Yttrialite; $(Y,Th)_2Si_2O_7$	N.Yakutiya; alkali granite pegmatite	2	7	2	7	6	0.2	10	2	20	4.1	15	2.2	19	3.2	r)
64	Thalenite; $Y_2Si_2O_7$	Upsala, Sweden; granite pegmatite	0.8	2.6	0.7	1.6	1.4	0.3	20	3.2	17	3.9	12	2	19	3.4	-
65	Fergusonite; $Y(Nb,Ta)O_4$	Iveland, Norway; granite pegmatite	0.5	2	1.4	4.3	5.1	0.2	7	1.4	9	2.2	8	2	48	9	-
66	Fergusonite; $Y(Nb,Ta)O_4$	Gierrestad, Norway; granite pegmatite	1.6	4	0.8	2.4	3.5	0.9	9	1.6	18	3.8	20	3.7	26	5	-
67	Fergusonite; $Y(Nb,Ta)O_4$	Ytterby, Sweden; granite pegmatite	1.6	6	0.3	1	2	0.1	8	2	13	3.4	16	2.6	38	6	b)
68	Fergusonite; $Y(Nb,Ta)O_4$	Kuramin Range, Central Asia; granite	3.3	11	2.6	8	8	0.5	11	2.2	10	2.6	11	1.7	24	4.2	s)
69	Fergusonite; $Y(Nb,Ta)O_4$	Evje, Norway; granite pegmatite	0.4	1	0.2	0.5	1.4	0.4	8.6	1.7	19	4.9	22	4	30	5.6	-
70	Fergusonite; $Y(Nb,Ta)O_4$	Evje, Norway; granite pegmatite	0.8	2.4	0.1	0.5	1.7	-	6.6	1.5	21	5	20	3.4	31	5.8	-
71	Fergusonite; $Y(Nb,Ta)O_4$	Sabaragamuva; Ceylon; granite pegmatite	1.2	3.	1.3	4.7	8	0.5	15	2.5	16	3.8	17	3.2	20	3.8	-
72	Fergusonite; $Y(Nb,Ta)O_4$	Keivy; alkali granite pegmatite	5.7	14	1.1	3.3	7	1	13	2.3	13	3	14	2.7	16	3.5	b)
73	Hellandite; $Ca_2Y_3Al_3(SiO_4)_4(O,OH)_4$	Kragero, Norway; granite pegmatite	2	5.8	1.5	4.8	4	0.2	12	2.2	17	4.1	14	2.1	26	4.1	b)
74	Zircon; $ZrSiO_4$	N.Tuva; albitite of alkali syenites	1	3.5	0.7	1.5	1.7	0.2	3.5	0.8	15	4	23	3.6	36	5.8	t)
75	Zircon; $ZrSiO_4$	Zhdanov Alkali Massif, Ukraine; albitite	1.8	5.8	1.4	3.3	3.1	0.2	7.8	1.6	23.4	5.8	19.5	3.1	19.5	3.7	-
76	Zircon; $ZrSiO_4$	Sorug, N.Tuva; nepheline syenite pegmatite	1.7	27.2	7.3	25	8.3	0.6	6.9	1	6.1	1.5	7.3	1.5	4.8	0.8	-
77	Spessartite; $Mn_3Al_2(SiO_4)_3$	Keivy; alkali granite pegmatite	2	7	0.9	2	0.4	-	1.6	0.5	6.5	2.1	14	2.2	53	8	-
78	Siderite; $FeCO_3$	Aryskan, N.Tuva; albitite of alkali syenites	-	-	-	9	6.6	-	14.6	2	34.7	-	24.3	-	9	-	-
79	Thortveitite; $(Sc,Yb)_2Si_2O_7$	Madagascar; granite pegmatite	-	-	-	-	0.5	-	5.4	1	8	2.2	9	1.6	61	11	b)

Table 1. Composition of Rare Earths in Minerals ($\Sigma\, TR_2O_3$ = 100%) (continued)

1 Item No.	2 Mineral and formula	3 Source and geologic features	4 La	5 Ce	6 Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
80	Thortveitite; $(Sc,Yb)_2Si_2O_7$	Madagascar; granite pegmatite	2	8	3	-	-	-	-	-	17	4	12	2	44	8	-
81	Aeschynite; $(Ce,Nd)(Nb,Ti)_2O_6$	Vishnevye Gory; alkali syenite pegmatite	15	52	7	16	2.3	0.2	3	0.4	2.1	0.4	0.7	0.1	0.9	0.2	-
82	Aeschynite; $(Ce,Nd)(Nb,Ti)_2O_6$	Ilmeny; alkali syenite pegmatite	14	48	7.3	22	3.1	0.1	1.8	0.2	1.8	0.4	0.9	-	0.4	-	b)
83	Aeschynite; $(Ce,Nd)(Nb,Ti)_2O_6$	Tatarka, Enisei Range; alkali syenite pegmatite	2.2	13	6.7	22	17	2	13	2.5	11	1.5	5.5	0.8	2.2	0.5	e)
84	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_1)O(OH)$	Ilmeny; hydrotherm of granites (the extreme of 40 specimens of La type)	41.1	44.9	3.4	9.6	1	-	-	-	-	-	-	-	-	-	i)
85	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	N.Carolina, USA; granite pegmatite (the extreme of 40 specimens of Nd type)	18.3	41.9	5.3	22.2	7.7	-	4.6	-	-	-	-	-	-	-	a)
86	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Kalai-Makhmud River, Turkestan Range; granite pegmatite	24	48	5.8	19	2	0.1	0.8	0.1	0.4	-	-	-	-	-	-
87	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Kuramin Range; granite	23	55	6	14	0.9	0.1	0.6	-	0.1	-	0.1	-	0.6	-	s)
88	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	S.Yakutiya; para-gneiss	24	59	3.6	13	0.3	-	-	-	-	-	-	-	-	-	v)
89	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Keivy; alkali granite pegmatite	22	54	6	15	1.2	-	0.5	- -	0.4	0.1	0.3	-	0.6	0.1	-
90	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Kamennaya Taibola, N.Karelia; granite pegmatite	14	32	6.5	17	7.4	0.4	10	2	6.2	1.3	1.7	0.2	1.1	0.3	-
91	Allanite; $CaTRFeAl_2(Si_2O_7)\cdot(SiO_4)O(OH)$	Sinyaya Pala, N.Karelia; granite pegmatite	1.3	2.2	0.2	0.4	1.1	0.2	15	2.7	2.7	6.5	17	2.7	20	4.1	-
92	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Vishnevye Gory; alkali syenite pegmatite	22	59	5.1	12	1.3	0.1	0.3	-	-	-	-	-	-	-	-
93	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Korarfvet, Sweden; granite pegmatite	5	20	5.2	14	9.5	0.7	8	1.8	15	3.2	7	1.2	8	1.4	ad)
94	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Impilakhti, S.Karelia; granite pegmatite	4.2	16	4.3	11	8.8	0.4	8.6	2	15	2.8	10	1.5	13	2.5	y)
95	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Alakurtti, N.Karelia; granite pegmatite	3	11	3	12	22	0.5	25	4	13	1.5	2.5	0.5	1.7	0.4	z)
96	Pyrochlore; $(Na,Ca,TR)_2(Nb,Ta,Ti)_2(O,OH,F)_7$	Yauri-Ioki, Kola Peninsula; greisen	1.8	6.2	3.5	10	9	0.2	11	2.3	16	3.5	14	2.6	17	2.8	aa)
97	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	N.Caucasus; granite pegmatite	2.3	9	4	14	10	0.2	12	1.9	14	3	10	1.8	15	2.9	ab)
98	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Hitterö, Norway; granite pegmatite	2.1	6.5	2.8	8	9	0.3	19	3.1	16	3.1	11	2	15	2.3	-
99	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Iveland, Norway; granite pegmatite	1.6	5	2	6.5	9.3	0.3	18	2.5	17	3.5	13	2.3	16	2.1	-
100	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	0.9	3	2.9	7	8	0.3	19	2.8	17	3.5	12	2	18	2.9	-
101	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	1.4	3.5	1.5	5.4	7.5	0.5	18	2.9	17	3.7	14	2.5	19	3.1	-
102	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Birkeland, Norway; granite pegmatite	1.4	3.7	1.7	6	8	0.2	13	2.4	37	4	8	1.2	12	1.7	-
103	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Birkeland, Norway; granite pegmatite	0.9	2.5	2	6.5	9	0.4	22	3.6	20	4	13	2	12	2	-
104	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	N.Yakutiya; alkali granite pegmatite	4.2	10	1.5	4.7	3.7	0.3	10	2	22	4.8	15	2.5	17	2.7	ac)
105	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	2.5	7	3.5	8	7	0.2	16	2.6	15	3.3	11	1.5	19	3.3	b)
106	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	1.2	4	2.5	7	8	0.3	18	2.7	17	3.5	12	2	19	3	-
107	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	3.4	12	5.7	12	5.8	0.3	8	1.6	13	2.6	12	1.9	19	2.8	b)
108	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Keivy; alkali granite pegmatite	5.8	19	3.3	7	1.8	0.1	2.6	0.5	7.1	1.9	12.6	2.2	31	4.8	-
109	Gadolinite; $(TR,Y)_2FeBe_2Si_2O_{10}$	Ytterby, Sweden; granite pegmatite	1.7	6	2.6	9	8	0.3	12	2	13	2.7	11	2	25	4.5	-
110	Britholite; $TR_8Ca_4Si_2O_{24}(OH)_2$	Khodzha-Achkan River, Turkestan Range; alkali syenite pegmatite	28	52	6	13	0.4	-	0.4	0.1	-	-	-	-	-	-	ae)
111	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Khibiny; apatite-nepheline rocks	24	48	6.1	18	1.7	0.2	1	-	0.6	0.1	0.2	-	-	-	-
112	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Lovozero; ijolites	22	51	5.9	17	1.7	0.2	1.6	0.2	0.4	-	-	-	-	-	-
113	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Lovozero; alkali syenite pegmatite	21	45	6.8	21	3.7	0.3	1.2	0.1	0.3	-	0.3	-	0.2	-	-
114	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Sumy District, Ukraine; phosphates	18	42	6.3	21	4	0.3	4	0.6	2	0.3	1	0.1	0.4	0.1	-
115	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	N.Caucasus; phosphates	13	34	5.5	19	7	1.5	8	1.3	4.7	0.9	2.6	0.4	1.7	0.4	-
116	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Podolia, Ukraine; phosphates	6.5	23	7.5	2.6	13	2	13	2	4.2	0.8	1.4	0.1	0.6	0.1	-
117	Apatite; $Ca_{10}P_6O_{24}(OH)_2$	Elovka, Transbaikal; granite pegmatite	5.1	11.4	4.4	6.8	24.1	0.7	26.8	4	9.8	1.9	2.1	0.9	1.3	0.7	af)
118	Chindusuite; $mMnO_2\cdot nTiO_2\cdot pSiO_2\cdot qH_2O$	Lovozero; sodalite syenite pegmatite hydrothermal stage	3.1	21	6.8	25	12	1.4	9.5	1.6	9	1.9	4.1	0.8	2.9	0.6	-
119	Halloysite; $Al_4Si_4O_{10}(OH)_8\cdot 4H_2O$	Lovozero; nepheline syenite; hydrothermal stage	26	20	7	25	5.4	1	5.3	0.9	3.9	0.8	2.1	0.3	2	0.4	-

Table 1. Composition of Rare Earths in Minerals ($\Sigma\ TR_2O_3 = 100\%$) (continued)

1 Item No.	2 Mineral and formula	3 Source and geologic features	4 La	5 Ce	6 Pr	7 Nd	8 Sm	9 Eu	10 Gd	11 Tb	12 Dy	13 Ho	14 Er	15 Tm	16 Yb	17 Lu	18 Remarks
120	Apophyllite; $KCa(Si_4O_{10})_2F\cdot H_2O$	Lovozero; nepheline syenite pegmatite	17	33	6.1	21	6	0.6	5.8	0.8	4	1	2.4	0.2	1.7	0.3	-
121	Fluorite; CaF_2	Keivy; alkali granite pegmatite	5	10	1.1	3	2.8	0.2	2	0.5	7	2	16	2.5	41	7	-
122	Fluorite; CaF_2	Kara-Oba, Kazakhstan; hydrotherm of granites	2.2	6.5	1.7	5.9	5	0.2	11	1.7	14	3.3	13	2.8	28	4.6	ag)
123	Fluorite; CaF_2	Hundholmen, Norway; granite pegmatite	4.3	13	3.7	9	4.7	0.3	10	2	13	3	13	1.9	19	3.3	-
124	Andradite; $Ca_3F_2(SiO_4)_3$	W.Transbaikal; Skarns	9	21	8	14	3.8	0.2	4.7	1	10	2.2	9	1.7	13	2.5	ah)
125	Scheelite; $CaWO_4$	Kara-Kamys, E.Kazakhstan; hydrotherm of granites	13	40	7.2	17	9.6	1.3	5.8	0.9	3.1	0.8	1	0.1	0.4	-	-
126	Sphene; $CaTiSiO_5$	Khibiny; sphene-apatite-nepheline rocks	20	45	6.5	21	3	0.3	2.3	0.3	1	0.2	0.4	-	0.2	-	-
127	Sphene; $CaTiSiO_5$	Yakutiya; para-gneiss	13.5	48	8.7	21	4.3	0.3	1.6	0.3	0.8	0.2	0.5	-	0.6	0.1	v)
128	Sphene; $CaTiSiO_5$	Borshchevochn. Range, Transbaikal; granites	7	23	10	27	9.4	0.8	7.8	0.9	6	1.3	2.5	0.4	3	0.6	ai)
129	Sphene; $CaTiSiO_5$	Iveland, Norway; granite pegmatite	2.5	8	2.5	9	7	0.7	18	2.5	17	3.6	12	1.5	14	2	aj)
130	Sphene; $CaTiSiO_5$	Iveland, Norway; granite pegmatite	1.6	5.8	3.8	11	6	0.5	9.3	1.5	11	2.7	13	2.5	26	5	aj)
131	Eudialyte; $(Na,Ca)_4\ FeZr\ (Si_6O_{18})\ (OH,Cl)$	Lovozero; nepheline syenite pegmatite	19	42	6	20	3.3	0.3	2.5	0.5	2.5	0.4	2.1	0.2	1.1	0.2	-
132	Eudialyte; $(Na,Ca)_4\ FeZr\ (Si_6O_{18})\ (OH,Cl)$	Lovozero; eudialyte luyavrite	14	37	5.7	17	6	0.8	6	0.8	4.7	0.8	3.6	0.6	2.6	0.4	- -
133	Eudialyte; $(Na,Ca)_4\ FeZr\ (Si_6O_{18})\ (OH,Cl)$	Lovozero; sodalite syenite pegmatite	11	35	7	22	7.2	1.6	6.7	1	4.4	0.9	1.9	0.4	0.5	0.2	-
134	Eudialyte; $(Na,Ca)_4\ FeZr\ (Si_6O_{18})\ (OH,Cl)$	Botogol, Buryat-Mongolia; alkali syenite pegmatite	11.1	18.9	3.2	8.9	3	0.5	5.7	1.1	14.8	4	14	2.4	10.5	1.9	ak)
135	Thorianite; ThO_2	Ceylon: Placers	10	41	9	25	6.3	0.3	3.1	0.5	1.9	0.5	0.8	0.2	1.1	0.2	-
136	Uraninite; UO_2	Chupa, N.Karelia; granite pegmatite	0.6	1.3	1	4	12	0.7	19	3.7	21	4	13	2.7	14	2.7	-
137	Thorite; $ThSiO_4$	Lovozero; nepheline syenite pegmatite	22	55	6	15	1.9	-	0.3	-	-	-	-	-	-	-	-
138	Epidote; $Ca_2Al_3(Si_2O_7)\ (SiO_4)\ O\ (OH)$	Talitskii Massif, Altai; granite	17.3	41.2	4.9	16.8	3.8	0.5	4.7	0.8	3	0.8	3.6	0.7	1.4	0.3	al)

Remarks on Table 1

(a) According to Murata et al. (b) "Mineral." (c) According to A.V. Kosterin and N.V. Turanskaya. (d) N.V. Turanskaya, Analyst. (e) Collected by I.P. Tikhonenkov. (f) Collected by E.M. Eskova. (g) Collected by O.V. Krashennikov. (h) According to N.V. Turanskaya and Yu. S. Slepnev. (i) According to E.E. Vainshtein et al. (j) Collected by E.I. Dolomanov. (k) "Khlopinite" (also chlopinite, propably Ti-poor euzenite). (l) "Ampangabeite." (m) Mineral: "ampangabeite." (n) Mineral; collected by V.A. Kornetova. (o) Collected by V.B. Alexandrov. (p) "Blomstrandite" (probably betafite). (q) Collected by V.I. Noneshnikova. (r) Collected by Yu. P. Ivenson. (s) Mineral; collected by I.E. Smorchkov. (t) Cyrtolite; collected by V.B. Alexandrov. (u) Collected by V.B. Alexandrova; analyzed by N.V. Turanskaya. (v) Collected by V.A. Galyuk. (w) Collected by A.N. Labuntsov. (x) "Toerneboehmite." (y) Collected by A.P. Kalita. (z) Obruchevite; collected by A.P. Kalita (yttrian pyrochlore). (aa) Collected by I. Kupriyanova. (ab) Collected by G.D. Afanasev. (ac) Mineral; collected by E.G. Troshchenko. (ad) "Hjelmite". (ae) Collected by V.I. Stepanov. (af) Collected by Z.V. Vasileva. (ag) Collected by L.P. Ermilova. (ah) Collected by E.A. Nechaeva. (ai) Collected by N.I. Zabavnikoa. (aj) "Yttrotitanite". (ak) Collected by K.A. Zhuk-Pochekutov. (al) Collected by V.V. Lyakhovich.

The analyses in the table are grouped as follows:
Nos. 1 through 19 - Selectively cerium minerals;
Group 1a: Markedly selective cerium minerals.
Nos. 20 through 40 - Selectively cerium minerals;
Group 1b: Selectively cerium minerals.
Nos. 41 through 45 - Group 2: Selectively gadolinium minerals.
Nos. 46 through 78 - Group 3: Selectively yttrium minerals.
Nos. 79 through 80 - Group 32: Selectively yttrium-ytterbium minerals.
Nos. 81 through 138 - Group 4: Complex minerals.

(A) CLASSIFICATION OF RARE EARTHS ACCORDING TO COMPOSITION

Analysis of the data on composition of the rare earths may be facilitated considerably by the use of graphic methods. For example, there is the well known method of a diagrammatic representation of the TR composition by means of a broken line connecting the points indicative of both odd and even lanthanide compositions (Fig. 1a) (Pm may be omitted here, because of its absence from the earth's crust). However, the pattern becomes far more interesting if two curves are drawn, instead of one, for the odd and the even lanthanides respectively (Fig. 1b) [12]. Such curves, as one may see, are generally simple and smooth and they have only a few peaks (1 or 2, as a rule).

These curves so drawn are true images of the odd and the even lanthanide curves. Indeed, the Dy maximum on the even TE curve is analogous to the Ho maximum on the odd TR, as Dy is right next to Ho. The same holds also for the Sm-Er couple on the aeschynite TR curve

(Fig. 1b). The Sm and Er minima are analogous to the Eu and Tm minima, etc. Therein lies apparently an expression of a direct relationship, a correlation, between the proportions of the odd and the even elements (neighbors of each other in the table) in the following couples: Ce-La; Nd-Pr; Sm-Eu; Gd-Tb; Dy-Ho; Er-Tm; Yb-Lu. This odd-even correlation between the coupled elements enables us to represent both the even and the odd (its cognate) element by one single point on the horizontal curve. Analogies of the odd and the even TR elements are made conspicuously clear by the diagrams constructed for the purpose (Fig. 2).

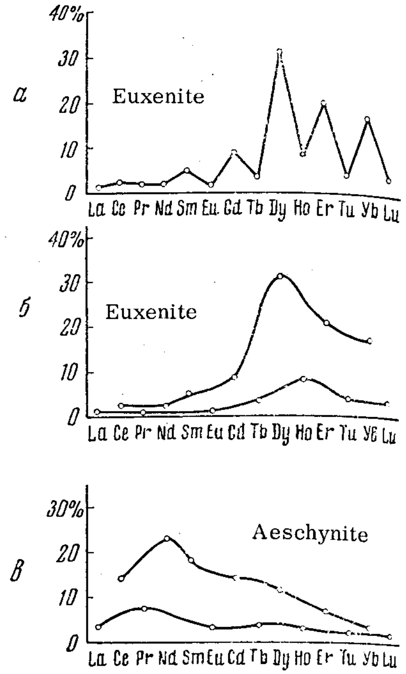

Fig. 1. Different methods of representing composition of the rare earths.

The TR composition curves may be classified as "simple" (Figs. 2a, 2e) or "complex" (Fig. 2l), depending on their shape. There is only one peak in the simple curves, but there are several peaks in the complex curves. The simple curves have only one arm, if their peaks represent Ce or Yb, but two arms in all other instances. The simplest of the simple curves may be approximated as single simple continuous functions. For example, the even lanthanide curves for loparite (cerian perovskite) or fergusonite (Figs. 2a, 2i) may be represented crudely by a descriptive function of the type of $C = C_0 \times 10^{K(Z_0 - Z)}$.

In this case, "C" and "Z" stand for the concentration and the atomic number of the element in question, with "C" as the maximum; K is the tangent of the slope angle of the $C = f(z)$ curve which is a line on the logarithmic scale. For loparite, $K = 0.127$ and $Z_0 = 70$.

The even curve for samarskite (Fig. 2e) may be approximated by a function of the type $C = \frac{C_0 \times A^2}{(Z - Z_0)^2 + A^2}$, where "A" is one half of the breadth of the curve at one half of its maximum. In this particular case, $A = 1.27$ and $Z_0 = 64$. Inasmuch as the even and the odd element curves are similar, their descriptive functions tend to resemble each other.

The community of fortunes of individual elements in the lanthanide group, their "trans-migrations" only by groups, "chain"-like, the conjugation of the even and the odd elements, so clearly visible in the curves showing proportions of the lanthanides not only in the minerals

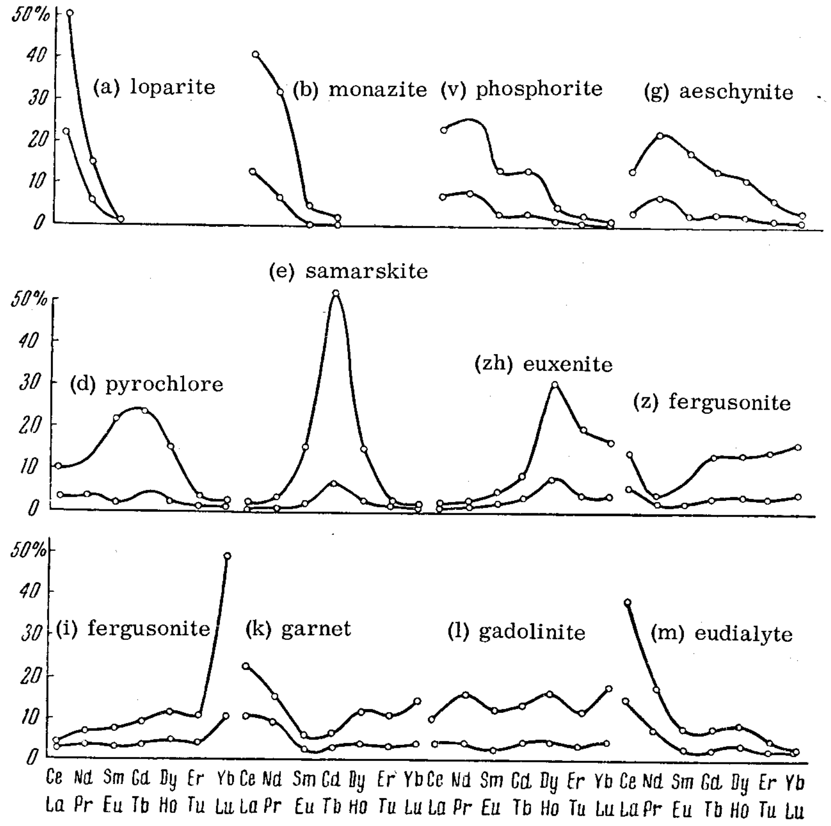

Fig. 2. Composition of rare earths in different minerals.

but also in the chemically separated sums of the rare earths (Fig. 5), are plainly visible in the curves. This means that the fundamental relationships governing distribution of the rare earths are the same both for the mineralogic and for the chemical materials.

The averages of ionic radii, atomic weights, neutron-capture cross-sections, etc., are among the major (diagnostic) characteristics, in the instance of the rare-earth minerals and of the groups of the rare earths themselves. Thus the average ionic radius of the lanthanide group may be represented as:

$$r_{\text{ave.}} = \frac{(r_{La} \times C_{La}) + (r_{Ce} \times C_{Ce}) + \dots}{100} = \frac{\Sigma r_i c_i}{100},$$

where r_i is the ionic radius of the element and c_i is its concentration in the ΣRE_2O_3. The $r_{\text{ave.}}$ is at its maximum, 1.02 Å, for the bastnaesite lanthanides (No. 1 in the table). The lowest r_i, 0.82 Å, is observed in the lanthanides of thortveiteite, where it is very close to the radius of Yb. The average atomic weight of the lanthanides in bastnaesite and thortveitite is 140 (like Ce) and 167 (like Er) respectively.

The effective average maximum neutron-capture cross-section, for slow neutrons, is shown by the samarskite rare earths (No. 41) and is 24980 barns; the minimum, 40 barns, is shown by the bastnaesite rare earths (No. 1).

V. Goldschmidt and L. Thomassen [1] proposed two categories in their classification of the rare earths in minerals according to composition, the "complex" and the "selective".* The greater the maximum on the composition curve, the greater is the "selectivity" of the composition. Depending on the size of the maximum, one may distinguish the following types of composition: markedly selective (> 45 to 50%); selective (> 30%); complex (< 30%). In addition to the size of the maximum, the degrees of selectivity may be characterized also by the "K" and the "A" coefficients from the equations previously cited. The smaller the "A", the greater the "K", — the more selective the composition.

The composition curves are simple, in the case of the selective (especially the markedly selective) categories of the rare earths, with only one single maximum and with steeply sloping arms. In the case of the complex category, the composition curves are complicated and they contain several maxima (weakly expressed, as a rule). Serious difficulties arise occasionally in deciding whether the rare-earth composition in question should be referred to the selective or to the complex category.

Typically selective or markedly selective compositions are most characteristic, occupying extreme positions in the lanthanide series (Ce and Yb). Elements in the intermediate positions in this series present a more complicated case. Thus curves of the type shown in Figure 2d have practically identical maxima for the two neighboring even elements, Gd and Sm. Such compositions are weakly selective with respect to these two elements, but are highly selective at the same time, with respect to the small part of the rare-earths "spectrum" from Sm to Gd, inasmuch as their content of lanthanides outside the limits of this part of the "spectrum" falls off abruptly. The TR compositions of this type, represented by simple curves, may be classified rationally as samarium-gadolinium selective ones, since the typically or the markedly selective gadolinium compositions are exceptionally rare. The broad cerium-neodymium TR maximum was noted in zircon No. 76; the samarium-neodymium maximum in aeschynite No. 83; the dysprosium-gadolinium in samarskite No. 44; the erbium-dysprosium in zircon No. 75.

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*The complex category includes compositions with relatively uniform proportions of the lanthanides; the selective category, compositions in which one or more of the lanthanides are definitely preponderant.

In the instance of the "m" type curves, Figure 2, there is also a supplementary Dy maximum in addition to the principal maximum of Ce. It is clear a composition of this type is not particularly selective, and yet it may be hardly called complex, because the main maximum is so definitely preponderant over the supplementary one.

The "wave-like" pattern is characteristic of the transition from a selective composition (one maximum) through a complex composition to another selective composition (one maximum) (Fig. 3, Curves 1 through 5). As the degree of selectivity becomes smaller, the slopes of the curves become progressively less steep, to the point where any further flattening-out of the main peak becomes impossible without a break in the smoothness of the curve. When that happens, a minimum makes its appearance on the curve, together with a hint of a new supplementary maximum which grows bigger as the first (main) maximum flattens out.

Up to this time, in minerals, we knew of the selective rare-earths' compositions with the Ce, the Dy, and the Yb maxima (Fig. 2b, 2zh, 2i respectively). As shown both in the table and in Figure 2, however, there are minerals in nature whose rare earths have the Nd and the Gd maxima (Fig. 2g, aeschynite, and Fig. 2e, samarskite, respectively). Thus we find cerium, neodymium, gadolinium, dysprosium, and ytterbium compositions of the lanthanides in the minerals.

The content of Sm and Gd which falls on the maximum in the curve is about the same in some specimens of samarskite. In zircon (No. 75) the Er content is also rather close to the maximum. This leads us to the idea that there may be some rare earth minerals in nature with the composition maxima embracing all of the even elements: Ce, Nd, Sm, Gd, Dy, Er, Yb. However, the relative abundance of minerals with this or that kind of maxima in the composition curve is highly variable. The most common ones are the minerals with the cerium maximum. Yttrium minerals have generally the Dy and the Yb maxima in their lanthanides. Minerals with the Gd and the Nd maxima are far more rare. No minerals could be discovered so far with clearly defined Sm and Er maxima. The foregoing considerations suggest the following sequence of the relative abundance of the composition maxima for the even lanthanides in minerals:

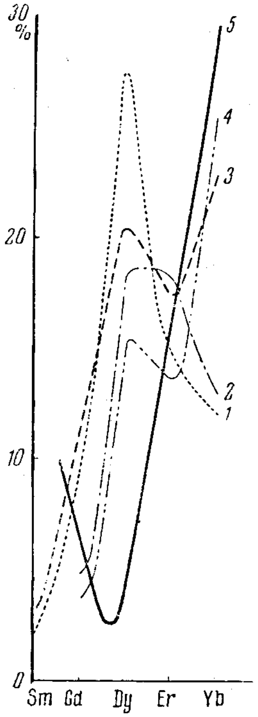

Fig. 3. The "wave pattern" of transitions from one maximum to another.

Ce, Dy, Yb, Gd, Nd, Er, Sm. The relative abundance of the composition minima is in the reverse order of this sequence.

The abundance sequence of the maxima for the odd elements is analogous to that of their even cognates: La, Ho, Lu, Tb, Pr, Tm, Eu. The relative abundance of the elements themselves is characterized also by their maximum concentrations (per cent): 42.9 La; 59 Ce; 9.5 Pr; 33.6 Nd; 22 Sm; 1.6 Eu; 5.3 Gd; 6 Tb; 37 Dy; 7.6 Ho; 23 Er; 5.4 Tm; 61 Yb; 11.6 Lu. Thus, if this percentage exceeds 50 for Ce, Yb, and Gd, it does not attain even 10 for any of the odd elements, with the exception of La.

The clarke relationships of the elements are reflected, to some extent, in the abundance sequences of the lanthanide composition maxima in minerals, as well as in the percentage concentrations represented by such maxima on the composition curves. Indeed, the fact that Sm, Eu, Er, and Tm never yield any maxima on the composition curves, and are generally in the minima, indicates that these elements are extremely deficient in the earth's crust.

We must take into account nevertheless the content of the given element in minerals in which the maximum is represented by some other element, as we now pass to a discussion of the clarke sequence of the lanthanides. Thus, although there are very few minerals showing an independent neodymium maximum, large amounts of Nd are present in the abundantly distributed cerium minerals. We are justified therefore in placing Nd next to Ce, with respect to its relative abundance. The same reasoning may be followed also for certain other lanthanides.

Further statistical data on composition of the rare earths in minerals and on the relative abundance of the minerals themselves may serve apparently in verifications and corrections of the sequences here stated as well as of the currently accepted relationships between the lanthanide clarkes in the earth's crust.

Among the cerium type compositions of the rare earths in minerals, we may distinguish three types: the normal, the cerium anomalous, the cerium-free anomalous. The vast majority of the minerals have their TR's of the normal type. Such minerals are characterized consistently by the relationships already reported [3, 4, 5]: the relatively constant proportions of cerium (about 40 to 50%) and of praseodymium (about 5%); the inversely proportional relationship between La and Nd (La + Nd approx. constant). Anomalous minerals with tetravalent cerium are also known whose TR consist almost entirely of cerium. Cerianite, CeO_2, is one of these; it was first discovered in endogenic carbonatite deposits in Canada. We ascertained composition of the TR in cerianite which was formed on a weathering of bastnaesite in pegmatites of Madagascar. Its composition is as follows: $La_6Ce_{91}Pr_{.09}Nd_{2.1}$. Since this test material is ocherous, one might think that the presence of La, Pr, Nd is due to a contamination. However, it has been proved experimentally that there exists a series of solid solutions $(Ce^{VI}, Th, U)\,O_2 - TR_2O_3$. Characteristically, there is no enrichment of Pr in cerianite, because, in this particular case, there is apparently no formation of Pr^{IV}.

Thus cerianite is practically 100% the oxide of one single element—Ce. We are dealing here not only with a complete rupture of rigid bonds (La + Nd about constant) characteristic of ordinary cerium compositions but also of the common chain bonds, so characteristic of the trivalent rare earths. The decisive preponderance of cerium over lanthanum may be illustrated by zircon (No. 76) and by several other minerals.

The most recently published data of Hildebrand [10] on a most curious rhabdophane of the cerium-free anomalous composition of its TR, from Connecticut, USA show: $La_{37.6}\,Ce_{0.8}\,Pr_{0.8}\,Nd_{44.4}\,Sm_{7.5}\,Eu_{1.5}\,Gd_{7.4}$. This rhabdophane contains practically no cerium or praseodymium, in contrast with the other cerium minerals. These two elements had passed apparently into their anomalous tetravalent forms and were parted as an independent phase, $(Ce, Pr)O_2$.

Curiously, the lanthanide chains were not disturbed in this rhabdophane, despite the lapse of two elements (Ce and Pr) from the lanthanide series, between lanthanum and neodymium.

The following anomalous TR composition was established for halloysite (No. 119): $La_{26}\,Ce_{20}\,Pr_7\,Nd_{25}$. Lanthanum here is higher than cerium or any other element, so that, in the case of this sort, we may speak of the lanthanum maximum of the TR in minerals. However, we do not yet recognize a distinctive lanthanum type of the rare earths, inasmuch as the case in question is the first one of the kind and still remains to be studied in detail. This halloysite example is an illustration of an incomplete withdrawal of cerium, as against its nearly complete withdrawal in the instance of the rhabdophane. In cerium-free anomalous minerals of this type, there is a disturbance of the analogy between the even and the odd lanthanide curves and these curves intersect each other.

For a series of minerals (fluorite, strontianite, pyromorphite, microcline, etc.) there were frequent reports on an enrichment by europium, as evidenced by optical spectrographic data. Europium is present in such minerals in its divalent state and replaces Sr, Pb, and K, resembling them in the size of their ionic radii. However, we found about the same amounts of europium in the minerals we had examined, both strontium (nordite, fluorite) and lead (anglesite), as are present in ordinary cerium minerals. The reports on the specific role of europium in some minerals may be attributed frequently to the fact that spectrographic optical analysis is most sensitive for this particular lanthanide.

(B) LANTHANIDE COUPLES

More than three quarters of the total rare earths in minerals consist generally of the even elements which play a leading part, in many respects, and by which the fortunes of the odd elements are also determined. The content of an odd element is higher in proportion to the content of its even neighbors. However, this even-odd correlation is generally more close between the given odd element and some particular one of its even neighbors. The following correlations are indicated by the analysis: Ce-La; Nd-Pr; Sm-Eu; Gd-Tb; Dy-Ho; Er-Tm; Yb-Lu. In such manner the odd elements to the left of Pm, in the rare-earth series (with "z", the atomic number lower than 61) are correlated with their even neighbors on the right, whereas the odd elements to the right of Pm ("z" higher than 61) are correlated with their even neighbors on the left.

Such grouping of the couples is sustained most convincingly by Figure 4 and by the analogy between the curves for the even and for the odd lanthanides constructed on the basis of the principle of their coupling, as here formulated (Fig. 2). There is no correlation and no analogy between the curves, if we group the lanthanide couples differently (e.g., Yb-Tm, Er-Ho,etc.).Characteristically also, chemically (first of all, chromatographically), in the separation of the couples, the greatest difficulties arise in the cases of Nd and Pr, Sm and Eu, Yb and Lu.

The following characteristic ratios within the lanthanide couples are indicated by the general averages for all of the minerals: Ce:La = 3; Nd:Pr = 3; Gd:Tb = 6; Dy:Ho = 5; Er:Tm = 6; Yb:Lu = 6. The Sm:Eu ratio is very much higher and may be given tentatively as 10 to 20. One fact stands out conspicuously, namely: Ce:La ≈ Nd:Pr; Gd:Tb ≈ Dy:Ho ≈ Er:Tm ≈ Yb:Lu. A breakdown of the rare-earth series into two sections is indicated accordingly (La to Nd and Gd to Lu); this break is at the Sm - Eu couple, immediately next to Pm (z = 61). It is possible that these two sections of the lanthanide series were formed by two different branch-variants of the nuclear process.

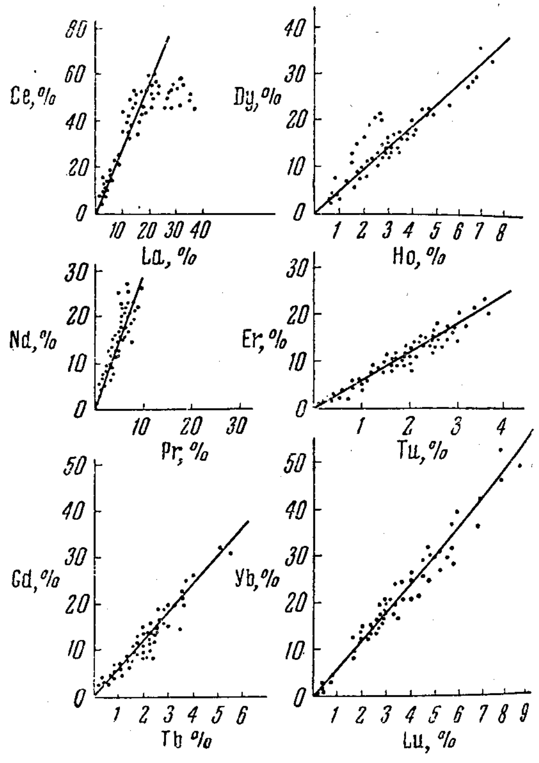

Fig. 4. Proportions of odd and even lanthanides.

The phenomenon of the lanthanide couples may be explained possibly by the similarity of the ionic radii of the couples. According to N. V. Belov and G. B. Bokii, their ionic radii are as follows: La - 1.04, Ce - 1.02; Pr - 1.00, Nd - 0.99; Sm - 0.97, Eu - 0.97; Gd - 0.94, Tb - 0.89; Dy - 0.88, Ho - 0.86; Er - 0.85, Tm - 0.85; Yb - 0.81, Lu - 0.80 Å. It is evident therefore that the ionic radii are about the same for Lu and Yb, Pr and Nd, and are equal for Tm and Er, Eu and Sm.

The approximate equality of the ionic radii in the lanthanide couples may be related to the similar distribution of their 4 f electrons in their orbits which is not the same for elements belonging to different couples (thus Yb and Lu have fourteen f electrons each). Curiously, there is no coupling on the basis of atomic radii in the lanthanides. Consequently, the phenomenon of the lanthanide couples is characteristic apparently for compounds with ionic bonds.

The diagram in Figure 4 shows that the Ce - La correlation has been definitely weakened. We also know of examples where La > Ce [11]. This may be due to the "extreme left" position of La in the rare-earths series, to the point that La is the only one of the rare earths that has no 4 f electrons. Moreover, the anomalous La-Ce relationships may be caused by the capacity of cerium to assume the tetravalent state.

Insofar as the degree of similarity between the ionic radii of the lanthanide couples is not the same, there may be differences also in the extent of their correlations. After conclusive determinations of their ionic radii and of their electronic configurations, it should be highly desirable to ascertain the relationship between their atomic proportions and the ionic radii. It should be interesting also to find out whether there is a coupling among the actinides which resemble the lanthanides.

The characteristic ratios between the even and the odd lanthanides obtained by analysis of the rare earths in minerals are apparently very close to the ratios of their clarkes. This enables us to utilize these ratios in minerals in correcting the currently accepted lanthanide clarke ratios. For example, V. M. Goldschmidt's clarke ratio Yb:Lu = 3.5 is too low, in all probability, while his Er:Tm = 12 ratio is too high. Curiously, F. Clarke reports Er:Tm = 5.

The analogy between the curves of the even and of the odd lanthanides (expression of the diagnostic relationships), and the smoothness and the common simplicity of these curves are indicative of the correctness of the analyses of the rare earths in minerals. A whole series of old decipherings by many others pretending at a quantitative reliability of their results, should be treated now only as qualitative findings, because they fail to meet the required criteria. The characteristics of the lanthanide composition curves, as shown here, justify extrapolations, in the instance of the selective compositions.

The ratios between the coupled even-odd lanthanides are only approximately constant. For example, although the normal Er:Tm = 6, this ratio may vary from 4.5 in samarskite to 7.5 in eudialyte, i.e., more than 1.5 times. The typical lanthanide ratios are most commonly observed in compositions of the complex type which are represented by complex curves with several gently sloping maxima. For example, the Er:Tm ratio is fairly constant and is approximately 6 for all gadolinites whose lanthanides are of the complex type (Nos. 97-109 in the table).

The widest variations in the ratio of the coupled even-odd lanthanides are observed in the TR compositions of the selective type. For example, Gd:Tb = 8 and Dy:Ho = 9 in a samarskite with a strong gadolinium maximum (No. 41 in the table), whereas Yb:Lu = 4.5 and Er:Tm = 4.5. The first two of these ratios are apparently characteristic for elements at their maxima and the too-low ratios for elements at their minima, in curves representing composition of the markedly selective type. The excessively low ratios may be compensated, in some cases, by some excessively high ones but may be tied, in some other cases, to a constant ratio between the total even and the total odd lanthanides. Indeed, the sum-total of the even elements remains fairly constant, in the vicinity of 85% (of Σ TR), in many minerals, excepting cerium minerals.

The selective compositions show occasionally that an odd lanthanide may be influenced by an even one, both within and outside the even-odd couple. Thus, in the two examples of the lanthanide compositions in fergusonite (Nos. 65 and 72 in the table), Tm is relatively high in the very same lanthanides (No. 65), which show also a markedly high ytterbium maximum. This may be explained by the position of Tm, intermediate between Er and Yb in the rare earths series. Although Tm is generally correlated with Er, the abrupt rise in the Yb content brings about an increase in the content of its neighbor, Tm, but not of Er. On the contrary, in the case of a markedly high dysprosium maximum, the Er:Tm ratio rises above its ordinary level.

In such manner, if the maximum in the selective composition is to the right of the couple in question, the ratio within the couple falls below its ordinary level; if the maximum is to the left—the ratio within the couple increases.

We must take into account the fact that the characteristic ratios between the coupled even and odd elements are subject to smaller variations at different TR compositions in one and the same mineral than in several different minerals. For example, in fergusonite: Er:Tm $\approx$ 6 and Yb:Lu $\approx$ 5.4 show very little variation. On the other hand, the abnormal Dy:Ho = 9 ratio is found both in the selectively gadolinium mineral, samarskite, and in the gadolinium-type TR composition of an entirely different complex mineral, pyrochlore. Thus not only the crystal structures but also the TR compositions, that is, positions and size of their maxima, play a decisive part in establishing the ratios between the coupled lanthanide elements.

(C) CLASSIFICATION OF RARE EARTH ELEMENTS

As we know, Sc and Y (atomic numbers 21 and 39 respectively) are often included with the lanthanide group consisting of 15 similar elements, from La through Lu (atomic numbers 57 and 71 respectively). Indeed, there exist minerals containing Sc and practically no lanthanides, such as cassiterite and wolframite. Also, most of the lanthanide minerals, and especially the cerium group, contain no Sc.

The Y problem is more involved. All of the known yttrium minerals contain lanthanides, whereas most of the lanthanide minerals (not all) contain Y. The lanthanides amount only to about 30% of the rare earths in xenotime, euxenite, fergusonite, and many other minerals, whereas 70% of the $\Sigma\,TR_2O_3$ is Y itself functioning as the leading or the principal element. We must refer to such minerals therefore as yttrium minerals and not as dysprosium or ytterbium minerals.

As we know, the ionic radius of Y is similar in its size to the ionic radii of Dy and Ho and that it is for this reason that the fractionation of this group is particularly difficult in chemistry. There is every indication that it is feasible to treat Y as a member of the lanthanides, in mineralogical and geochemical research, and to deal with the rare earths (TR) as with a combination of the lanthanides ("Ln") and yttrium.

Very small quantities of yttrium are present not only in the cerium but also in the neodymium (aeschynite) and the gadolinium (samarskite) minerals. On the other hand, yttrium is preponderant in the rare earths with the Dy and the Yb lanthanide maxima. There is a direct correlation apparently between Y and the heavy lanthanides (Dy, Ho, Er, Tm, Yb, Lu) with the ratio of Y:Σ (Dy-Lu) approximately equal to 3. Characteristically, in this connection, the Y content is high in the eudialyte rare earths, on account of the enrichment of this mineral with heavy lanthanides. There is a lowering of the Y-heavy lanthanides ratio in the TR compositions whose maxima of the center fall on (Gd, Dy).

A correlation with certain specific lanthanides is indicated also for Sc. The rare earths in thortveitite, the principal scandium mineral (Nos. 79 and 80) have their maximum characteristically at Yb. According to Wylie [7], the Australian fergusonite is significantly enriched with Sc and its lanthanide maximum falls on Yb. Thus a definite association is noted for Sc and Yb specifically, and not for Sc and the yttrium earths. This relationship was first suggested by T. Sahama and V. Vahatalo [6] who discovered Sc "highs" in Yb-enriched wiikite.

The Sc-Yb correlation is explained by the closeness of the ionic radius of scandium to the ionic radii of Yb and Lu, which are the smallest ones among the lanthanides. Scandium is found, however, also in minerals whose lanthanide maxima fall on Dy and Gd (samarskite and others).

There exists a traditional separation of the rare earths into the cerium and the yttrium groups which is accepted in chemistry.

The boundary between these two groups is drawn between Sm and Eu on the basis of solubility differences of the compounds, or between Gd and Tb on the basis of the electronic structures.

The foregoing data on composition of the rare earths in minerals show that the break-down of the series into the cerium and the yttrium groups is entirely inadequate. Indeed, how would one classify the rare earths with the Nd maxima (Nos. 83, 118, 128) or with the Gd maxima (Nos. 41-44, 95, 117)? There is practically no Ce or Y group, the neodymium and the gadolinium respectively. Chemistry knows some rare-earths compositions with the Sm maxima but without any Ce or Y. Depending on positions of the maxima, it is possible accordingly to distinguish five groups of the rare earths: the cerium, the neodymium, the samarium, the gadolinium, the yttrium. The boundary between the gadolinium (or the cerium group by the traditional understanding) and the yttrium groups must be drawn between Tb and Dy. It is not permissible to draw this boundary between Gd and Tb for, were that done, it would mean a rupture of a closest link between an even and an odd element of a couple.

On the basis of their studies of the rare earths in monazite, Murata et al. [3] proposed to divide the cerium earths into two subgroups: the lanthanum (La, Ce, Pr) and the neodymium (Nd, Sm, Gd). In chemistry, the yttrium earths are divided commonly into three subgroups: the terbium (Eu, Gd, Tb), the erbium (Dy, Ho, Er, Tm) and the ytterbium (Yb, Lu). This latter classification seems to be irrational, from the mineralogic-geochemical point of view, because it either makes combinations of dissimilar elements or breaks up the closely related even-odd couples. It is more appropriate to divide the groups into subgroups on the basis of the preponderant even elements in the couples. Thus the cerium group may be divided into the following subgroups: the cerium (Ce, La), the neodymium (Nd, Pr), the samarium (Sm, Eu), the gadolinium (Gd, Tb), while the yttrium group may be divided into the dysprosium (Dy, Ho, Y), the erbium (Er, Tm) and the ytterbium (Yb, Lu) subgroups.

It is rational also not to classify separately the cerium and the yttrium groups but to think instead in terms of the primary groups: neodymium, cerium, samarium, gadolinium, dysprosium, erbium, and ytterbium.

The division of the rare earths into the cerium and the yttrium groups is customary in chemical analysis. As shown in Figure 5, however, in the analysis of monazite, the maximum in the so-called yttrium group falls on Gd and not on Y or the yttrium group at all (Dy, Er, Yb).

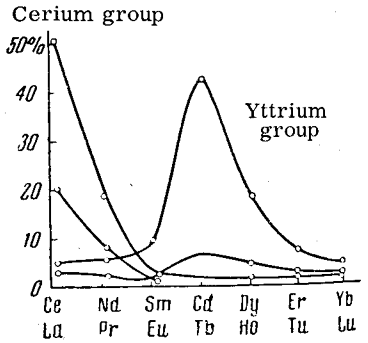

Fig. 5. Composition of rare earths in precipitates of cerium and of yttrium groups of monazite.

This is an illustration of the conventional way of characterization of the rare earths provided by the chemical analysis of minerals. There is no real need to divide the Σ TR_2O_3 into the cerium and the yttrium groups. The color of the precipitate is already a sufficient indication of its qualitative composition. As to the quantitative characterization of the Σ TR_2O_3 precipitate, it is only rational at once to pass it on for its X-ray spectrographic or the spectrographic analysis.

The dependence of the TR composition on the composition and structure of the minerals is to be reported in our next communication.

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