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RARE EARTHS IN MINERALS

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1. The elements of the group of rare earths, from La to Lu, with atomic numbers from 57 to 71 inclusive, constitute one of the most interesting series within Mendeleev's periodic table.

The specific physical-chemical properties of the rare earth elements (1), their co-occurrence under natural conditions (in minerals, ores and soils) are associated with the specific features of the electronic structure of the atoms of these elements: the gradual completion of the *4f*- and *5d*-concentric orbits while the 6 *s*-orbits are filled up (2).

The quantitative identification of the rare earth elements by the routine methods of analysis involves considerable difficulties, and the obtaining of pure samples of some of them is a rather cumbersome procedure. This is why their distribution in the Earth crust has been but poorly investigated.

2. The actual concept of the distribution of rare earths in the Earth crust, and of the quantitative relations between them, is largely based upon data by Goldschmidt and Tomassen (3).

One of the present authors (4) undertook to analyse quantitatively with the aid of the X-ray spectroscopic method the rare earths present in minerals occurring in the USSR. The experimental data obtained made him arrive at conclusions somewhat different from those generally adopted with regard to the quantitative relations between the elements of this group and the dependence of their distribution in the various rocks of the Earth crust upon the nature of these rocks.

Quantitative X-ray spectrum analysis of the elements of the TR group was carried out with the aid of spectrographs with bent crystals, according to Johann and Cauchoix, by the method of internal standards. Experimentally obtained transitional coefficients between the relative intensities of the lines and the content of the elements by weight were used (5).

3. Table 1 contains the results of a quantitative analysis of 23 minerals.

The average relative content of atoms of the elements of the cerium group, as borne out by this table, is as follows: 57 La : 58 Ce : 59 Pr : 60 Nd = 0.66 : 1 : : 0.20 : 0.41, *i. e.* Ce > La > Nd > Pr > Sm (Sm has been identified for five minerals).

Goldschmidt's and Tomassen's data which are commonly adopted in geological and geochemical literature, lead to the following atomic ratio: 57 La: 58 Ce: 59 Pr: :60 Nd = 0.23 : 1 : 0.16 : 0.58, *i. e.* Ce > Nd > La > Pr.

Thus, according to Goldschmidt La : Nd is 0.4, whereas from our data it is 1.6.

Among all the samples analysed the correlation between the individual elements of the cerium group is found to coincide with that reported by Goldschmidt only in two samples of apatites, from the Volkov deposits (the Urals), and from the Vakis-Djvari deposits (West Georgia), both of which correspond to basic rocks.

Table 1

Name of sample and of rock to which it is confined	Ce	Rd/Ce	La/Ce	Pr/Ce	ΣTR, %
Apatite from Volkovsky deposit the Urals (gabbro)	1	0.90	0.50	0.40	~ 1
Apatite Kuftuay, Lovozersky tundras (nephelite syenites)	1	0.41	0.52	0.15	~ 1
Grey apatite from the Vakis-Djvari deposit, West Georgia (gabbro)	1	0.65	0.45	0.22	~ 1
Loparite from urtite of Mt. Vavnbed (nephelite syenites)	1	0.30	0.60	0.20	~ 30
Loparite from urtite of Mt. Eingporr (nephelite syenites)	1	0.40	0.60	0.20	~ 30
Loparite from luyavrite of Mt. Vavnbed, Lovozersky tundras (nephelite syenites)	1	0.36	0.60	0.20	~ 30
Loparite from Mt. Ninchurt, Lovozersky tundras (nephelite syenites)	1	0.32	0.41	0.12	~ 30
Loparite from Mt. Aluayv, Lovosersky tundras (nephelite syenites)	1	0.34	0.62	0.17	~ 30
Monazite from the Kounrad deposit, North-western near-Balkhash (granites)	1	0.24	1.10	0.30	~ 60
Monazite from the Kounrad deposit, North-western near-Balkhash (granites)	1	0.24	0.83	0.14	~ 60
Monazite of the Taraka deposite (granites)	1	0.44	0.51	0.14	~ 60
Monazite Sukhoy Padunok of the Tarak deposit (granites)	1	0.44	0.64	0.19	~ 60
Monazite from pegmatite, Elizavetinsky mine, South Urals (granites)	1	0.43	0.63	0.19	~ 60
Monazite from a pegmatite of the Uruskiskan river, South Urals, Mironovsky mine (granites)	1	0.50	0.70	0.20	~ 60
Granite monazite, Uruskiskan river, settlement Andyrmensky (granites)	1	0.44	0.90	0.25	~ 60
Parisite from Mariupol (nephelite syenites)	1	0.36	0.73	0.16	~ 60
Parichlore from Kurochkin log, the Vishnevye mounts of the Urals (nephelite syenites)	1	0.28	0.74	0.23	~ 4
Nordite from Mt. Changusuay, Lovozersky tundras (nephelite syenites)	1	0.29	1.05	0.20	~ 18
Orphite, Lovozersky tundras (nephelite syenites)	1	0.45	0.52	0.18	~ 20
Orthite from the Baby-djid river, North Kirghizia (granites)	1	0.34	0.70	0.18	~ 23
Soquan clay, Moscow province	1	0.49	0.46	0.19	~ 0.01
Palaeozoic shale (Europe) (6)	1	0.30	0.48	0.14	~ 0,017
Mesozoic shale (Japan) (6)	1	0.43	0.46	0.12	~ 0.02
Mesozoic shale (Japan) (6)	1	0.40	0.29	0.11	~ 0.02

The mean ratio Ce:Nd:La:Pr = 1 : 0.41 : 0.66 : 0.20. If we take $\Sigma\ Ce_2O_3 = 100$ per cent (minus the yttrium group), the following content of the individual elements of the cerium group will be obtained (resulting from a total of 24 analyses) Ce_2O_3, 43.0%; Nd_2O_3, 17.7%; La_2O_3, 28.5%; Pr_2O_3, 8.6%; Sm_2O, 2.2 %.

From Table 1 it may easily be inferred that in minerals associated both with asic rocks and with granites and nepheline syenites, the ratio of the elements f the cerium group does but little deviate from the average; and in two inerals only, *viz.* the monazite from the north-west near-Balkhash and the ordite from Lovozersky tundras do we find La > Ce.

Table 2 illustrates the quantitative relation between the elements of the yttrium roup, obtained from 8 analyses of minerals. A comparison of the data contained in this table with Goldshmidt's data leads to the following results:

According to Goldschmidt: 39 Y > 64 Gd = 66 Dy = 70 Yb > 68 Er > 71 Lu > 65 Tb = 67 Ho = 69 Tu > 63 Eu.

According to Borovsky: 39 Y > 64 Gd > 66 Dy > 68 Er > 70 Yb > 63 Eu > 65 Tb ≥ 67 Ho ≥ 69 Tu ≥ 71 Lu.

Table 2

Semi-quantitatve X-ray-spectrum Analysis of Elements of the Yttrium Group (in per cent)

Name and origin of the sample	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu	Y
Palaeozoic shale (Europe)	2	14	2	10	3	6	0.6	6	2	35
Palaeozoic shale (Japan)	3.5	10	25	9	2	4	0.4	3	1	64
Liparite, Kola peninsula	7	45	5	25	2	5	2	3	—	10
Monazite, Taraka . . .	1	15	2	10	1	5	—	4	1	64
Monasite, Baschelok . .	1	14	2	9	1	6	1	2	2	62
Monazite, Sukhoy padunok	—	15	2	10	1	4	0.6	3	0.3	62
Monazite, Baley	1.5	16	2	13	1.5	4	1	4	—	57

The most essential in the rearrangement of the sequence of elements is according to our data the mutual transposition of 63 Eu and 71 Lu, the former being shifted from its tenth place to the sixth place.

Our data demonstrate, moreover, a regular decrease in the relative quantities of elements of the yttrium group, accompanied by an increase both in even and odd atomic numbers. Especially overestimated has been by Goldschmidt the rôle of Y within this group of elements.

No less striking appears the difference between our data and those obtained by Goldschmidt if we are to compare the relative contents of elements of the cerium and yttrium groups. The highest content in the yttrium group has been found in three apatites, two of which are confined to basic rocks, while the third is associated with nephelite syenites.

The relative content in the elements of this group has been found to vary but very little in all the eight analyses. In Table 3 is to be found the content of rare earths in three apatites and one loparite sample (ΣTR being put at 100 per cent).

The quantitative relations between the individual elements both of the cerium and yttrium group of rare earths are found to vary within a rather narrow range in minerals differing as to their genesis and confined to different rocks (basic, granites or nephelite syenites). The $\Sigma\, Ce_2O_3$ to $\Sigma\, Y_2O_3$ ratio is subject to no important variation either, being the highest in apatites.

If we are to judge by what has been reported above for minerals of the USSR, it may well be assumed that a sharp differentiation between the elements of rocks and those of nephelite syenites is scarcely like to take place.

The ratios of elements belonging to the group of rare earths, as suggested by the present author, vary materially from those given by Goldschmidt; they are, however, in fair agreement with more recent individual measurements made by some other students (6).

Table 3

	Apatite, Vakis-Djvari deposit, West Georgia, in %	Apatite, Volkovsky deposit, Urals, in %	Loparite, from Mt. Vavnbed, in %	Apatite, from Kirovsky mine, Kola peninsula, in %
57 La_2O_3 . . .	17	15	26	27
58 Ce_2O_3 . . .	35	30	44	34
59 Pr_2O_3 . . .	8	11	9	7
60 Nd_2O_3 . . .	23	25	17	16
62 Sm_2O_3 . . .	2	2	2	2
63 Eu_2O_3 . . .	1	0.5	0.05	0.8
64 Gd_2O_3 . . .	4	5	0.6	5
65 Tb_2O_3 . . .	0.6	0.7	0.5	0.5
66 Dy_2O_3 . . .	3	4	0.3	3
67 Ho_2O_3 . . .	0.3	0.2	0.02	?
68 Er_2O_3 . . .	2	2	0.05	1
70 Yb_2O_3 . . .	1	0.8	0.03	?
71 Lu_2O_3 . . .	0.1	0.1	—	—
39 Y_2O_3 . . .	3	4	0.1	3
69 Tu_2O_3 . . .	—	—	0.02	--

The validity of the ratios obtained for the elements of the yttrium group does not seem to be affected by the fact that our results are lacking analytical data for yttrium minerals; nor do we feel obliged to restrain the scope of our generalizations, in so far as apatite, monazite, orthite, loparite are the most widespread minerals containing rare earths.

It should be pointed out, moreover, that the relations recorded for the elements within the TR group contained in sedimentary rocks hold true in the case of minerals, as well. Further accumulation of experimental data is necessary, however.

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