American Mineralogist, Volume 63, pages 869–873, 1978

Relation of the relative concentrations of lanthanides in titanite to type of host rocks

MICHAEL FLEISCHER

U.S. Geological Survey
Reston, Virginia 22092

Abstract

Recalculation of 271 published analyses of the relative proportions of lanthanides and yttrium in titanite has led to ranges and averages for samples from seven types of rocks. The averages show that in the sequence alkalic pegmatite, alkalic rock, gabbro and pyroxenites, granodiorite, granite, granite pegmatite (order of decreasing Σ), the average contents of the lightest lanthanides (La, Ce, and sum of La to Nd) decrease, the contents of the intermediate lanthanides (Sm to Ho and their sum) increase, the contents of the heaviest lanthanides (Er–Lu and their sum) increase, the content of Y increases, and the ratio La/Nd decreases. The averages indicate that geological environment has an important effect on the relative concentrations of the lanthanides in titanite. However, these relative concentrations show large degrees of overlap from group to group, so that analyses of individual samples are not sufficient to identify the host rock.

Titanite, in which the lanthanides replace calcium isomorphously, has generally been considered to have a "complete" assemblage of lanthanides, *i.e.* to have a non-selective assemblage of all the lanthanides and yttrium, as would be predicted from the sevenfold coordination of the lanthanides in the mineral. However, the 33 analyses gathered by Semenov (1963) showed great variation, including cerium-selective compositions from alkalic and from ultramafic rocks. Fleischer and Altschuler (1969) summarized 51 analyses to show that, although the relative concentrations of lanthanides from a given type of rock have wide ranges, the average values showed a consistent trend, indicating a strong effect of conditions of formation. More than 200 new analyses have been published during the past nine years, permitting the calculation of more reliable averages for various rock types.

The averages, omitting those for gneisses, are plotted in three diagrams. Figure 1 is a triangular diagram with apices the sums of the atomic percentages of the lightest lanthanides (La–Nd), the intermediate lanthanides (Sm–Ho), and the heaviest lanthanides (Er–Lu). The graph shows, as does Table 1, the normal changes in relative concentrations of the lanthanides from alkalic pegmatites to alkalic rocks to gabbros to granodiorites to granites to granitic pegmatites. The averages of Σ and of the sum of the lightest lanthanides (La–Nd) decrease, those of the intermediate lanthanides (Sm–Ho) and heaviest lanthanides (Er–Lu) increase, with an especially large increase of the heaviest lanthanides in samples from granitic pegmatites. Figure 2, in which Σ [the sum of the atomic percentages (La+Ce+Pr)] is plotted against the ratio 100Y/(Y+Ln), (where Ln = total lanthanides), shows that yttrium is also concentrated with the heavy lanthanides, as would be expected from the ionic radii. These variations are in accord with those found by Murata *et al.* (1957), who analyzed other minerals.

Previous averages by Lyakhovich and Balanova (1971), based on far fewer analyses, have been recalculated and are given in Table 2. Their average for "granites of palingenic intrusives" (the term is not explained) is close to that for granodiorites, *etc.* (Table 1, column 4); their average for basic rocks is close to that for alkalic rocks (Table 1, column 2), and their average for alkalic rocks is intermediate between those for alkalic rocks and alkalic pegmatites (Table 1, columns 2 and 1).

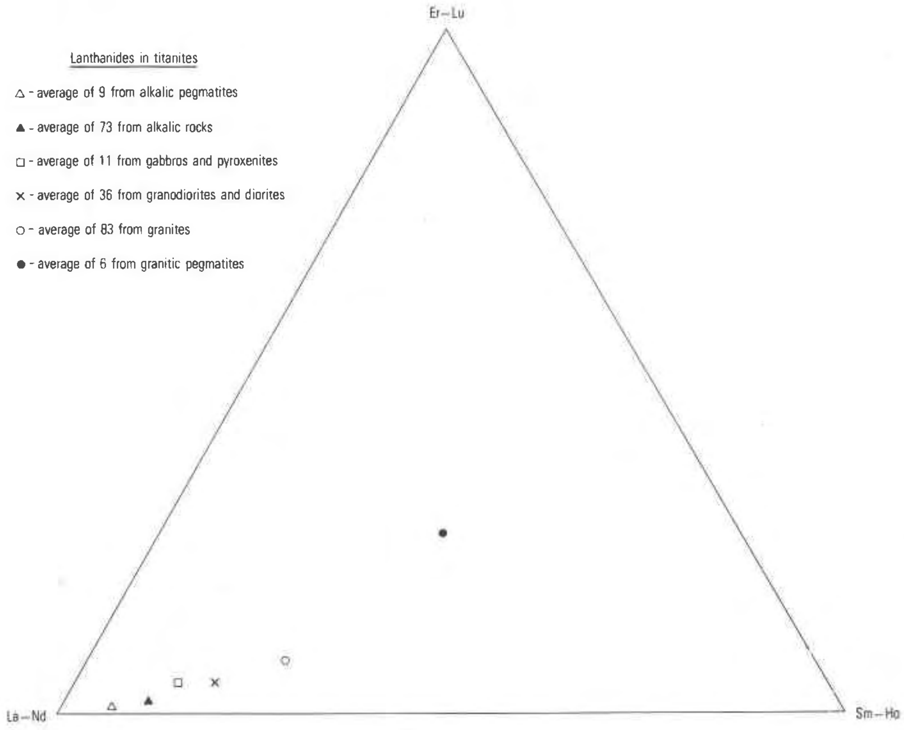

Fig. 1. Plot of average concentrations (in atomic percent) of lanthanides. Triangular diagram with apices lightest lanthanides (sum La–Nd), intermediate lanthanides (sum Sm–Ho), heaviest lanthanides (sum Er–Lu) in titanites from 6 types of rocks.

Figure 3 shows the variation of the ratio La/Nd with Σ, the average ratio increasing nearly linearly with Σ[1].

It is evident, however, from the data in Table 3 that the fields of relative concentrations of the lanthanides in titanites from different types of rocks overlap considerably, so that a single analysis is insufficient to determine the type of source rock. The ranges given in Table 3, however, include a relatively small number of extreme values, so that the variation shown gives a somewhat distorted view of the true distribution. Thus, for columns 2 and 6, alkalic rocks and granites respectively, if one eliminates the extreme 5 percent and 10 percent of these two large groups of analyses, the ranges for Σ and the ratio La/Nd are shown in Table 4.

Most of the overlaps disappear, with very little change in average. There are, however, considerable overlaps among the analyses of columns 1, 3, 4, and 5 of Table 1, and it is impossible to decide from a single analysis which group the sample came from. In part, this is a problem of nomenclature and the use of terms such as "alkalic granite," "quartz monzonite," or "granitoid," with petrographic or chemical data insufficient for classification. More detailed studies might sharpen the criteria by which the relations of relative concentrations of lanthanides could be correlated with host rocks.

Two previous studies have suggested that the variations of relative concentrations of lanthanides in accessory titanite might be useful in deciphering the history of granitic intrusives. Uskov (1967) gave data on the relative concentrations of lanthanides in four intrusives in the Tien-Shan Range, and suggested that granitic rocks of the different phases could be distinguished by the relative concentrations of the lanthanides of accessory sphene. His data are given only as graphs; these seem to show decrease of Ce and La and increase of Sm, Gd, and Yb from phase I to

[1] A critic remarks that a plot of La+Ce+Pr against La/Nd is partly a plot of La against La. This is correct, but for 271 titanites studied, La/Σ is greater than 0.5 in 1 sample and greater than 0.33 in 15 additional samples, so that the effect is small. The average ratio La/Nd has been shown (Fleischer, 1965) to be a useful empirical guide to variations in types of host rocks.

Table 1. Average composition of lanthanides in titanites from various types of rock: (1) alkalic pegmatites; (2) alkalic rocks (including syenites); (3) gabbros and pyroxenites; (4) granodiorites, *etc.* (including diorites, monzonites, adamellites); (5) granites; (6) granitic pegmatites; (7) gneisses and migmatites

	Atomic percent of total lanthanides						
	1	2	3	4	5	6	7
La	17.8	16.9	16.6	14.3	8.7	4.0	7.6
Ce	45.3	43.0	38.8	34.8	29.7	13.3	23.6
Pr	9.9	6.3	5.7	7.1	5.3	5.3	4.4
Nd	19.8	21.3	21.2	20.6	23.6	14.8	23.4
Sm	2.5	4.1	4.6	5.7	8.0	7.8	6.4
Eu	0.2	0.2	0.4	0.3	0.8	0.9	1.3
Gd	2.3	3.7	4.1	5.9	7.4	9.3	6.6
Tb	0.1	0.2	0.4	1.3	1.1	1.7	0.8
Dy	1.0	2.2	2.4	3.8	6.3	11.9	9.1
Ho	0.3	0.4	0.9	1.0	1.4	4.6	2.7
Er	0.6	1.2	2.3	2.1	3.4	8.8	6.2
Tm	-	-	0.1	0.3	0.6	1.4	0.7
Yb	0.2	0.5	1.9	1.9	3.1	14.2	6.8
Lu	-	-	0.1	0.3	0.6	2.0	0.4
$\frac{100Y^*}{(Y+Ln)}$	11.8(5)	13.9(48)**	25.2(7)	30.8(16)	31.0(54)	67.0(3)	35.9(11)
Number of analyses	9	75	11	36	83	8	14
La+Ce+Pr	73.0	66.2	61.1	56.2	43.7	22.6	35.6
La→Nd	92.8	87.5	82.3	77.4	67.3	37.4	59.0
Sm→Ho	6.4	10.8	13.3	18.0	25.0	36.2	26.9
Er→Lu	0.8	1.7	4.4	4.6	7.7	26.4	14.1
RE_2O_3	2.07	1.58	0.63	1.35	2.32	4.48	1.92
La/Nd	0.90	0.79	0.78	0.69	0.365	0.27	0.32

* number of determinations given in square brackets
** probably high, many analyses gave (Y+Tb).

Table 2. Ranges of compositions of lanthanides in titanites from various types of rocks (numbers correspond to those in Table 1)

	1	2	3	4	5	6	7
La	14.8-22.1	4.8-36.0	8.4-27.7	2.3-36.0	1.2-32.1	1.6- 9.8	0-15.7
Ce	42.2-48.9	21.0-56.6	14.7-48.6	10.6-47.8	3.7-53.2	6.3-18.4	0-43.6
Pr	3.7-23.4	2.0-12.8	2.6- 9.6	2.1-12.0	0-11.3	1.3-10.7	0- 7.4
Nd	15.8-23.6	14.7-31.7	16.4-27.7	10.7-32.6	6.4-33.2	9.4-20.9	0-30.6
Sm	0- 5.3	1.3-12.1	1.6-13.2	0-13.5	1.6-19.1	3.4-10.6	0-11.7
Eu	0- 0.5	0- 3.3	0- 1.1	0- 2.8	0- 2.7	0- 3.3	0- 3.3
Gd	1.3- 3.6	0.8-11.5	2.3- 8.6	0.9-18.3	2.0-17.8	0-18.1	0-13.2
Tb	0- 0.3	0- 4.9	0- 2.0	0- 8.8	0- 4.9	0- 3.3	0- 3.2
Dy	0- 1.8	0-16.2	0.6-11.3	0.5-12.7	0-17.5	0-21.2	0.1-33.6
Ho	0- 1.4	0- 1.7	0- 4.2	0- 4.6	0- 7.9	2.2-13.7	0- 8.8
Er	0- 1.9	0- 7.2	0-10.5	0-10.4	0-14.2	0-12.6	0.1-18.0
Tm	0- 0.1	0- 1.1	0- 0.4	0- 3.1	0- 4.6	0- 2.4	0- 3.2
Yb	0- 0.4	0- 3.6	0- 8.1	0- 9.9	0-16.7	6.4-24.5	0-31.6
Lu	0- 0.1	0- 0.8	0- 0.2	0- 3.1	0- 3.5	0- 4.7	0- 3.1
$\frac{100Y}{Y+Ln}$	0-17.5	1.5-43.6	9.2-50.3	10.3-67.3	5.8-71.4	60.7-78.4	9.0-72.6
Σ	67.5-82.2	29.9-80.5	29.8-76.5	16.0-82.7	6.3-75.6	12.2-31.0	0-64.1
La-Nd	87.6-98.0	76.3-96.3	46.9-94.0	30.5-95.3	12.7-91.9	23.8-51.7	0-91.8
Sm-Ho	1.9-11.4	3.3-36.1	5.0-34.5	4.2-45.7	6.2-53.2	27.6-48.7	8.0-48.1
Er-Lu	0.1- 1.9	0-10.7	0-18.6	0.1-25.4	0.2-34.8	15.6-44.2	0.2-51.9
$\%RE_2O_3$	0.1- 2.49	0.14-4.81	0.22-1.31	0.12-4.09	0.16-8.00	0.97-8.04	0.68-4.25
La/Nd	0.79-1.03	0.18-2.02	0.30-1.69	0.08-2.73	0.07-2.32	0.15-1.03	0.10-0.61

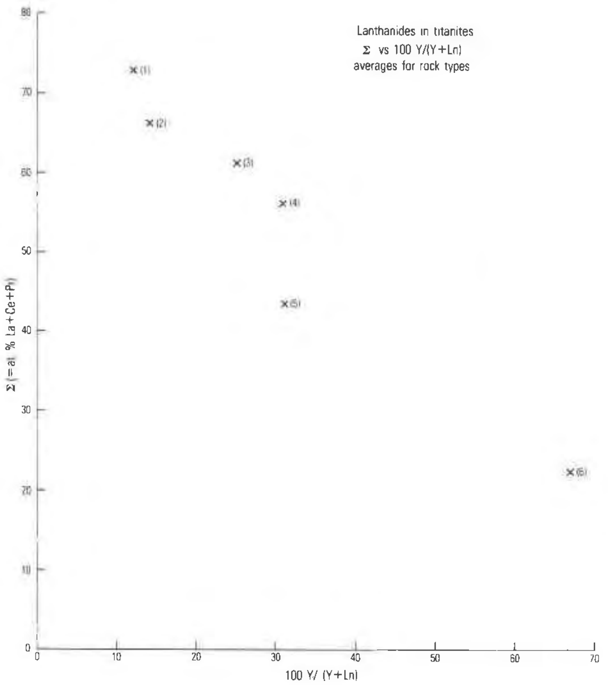

Fig. 2. Plot of Σ (= atomic percent La+Ce+Pr) *vs.* 100 Y/(Y+Ln); averages for titanites from 6 types of rocks.

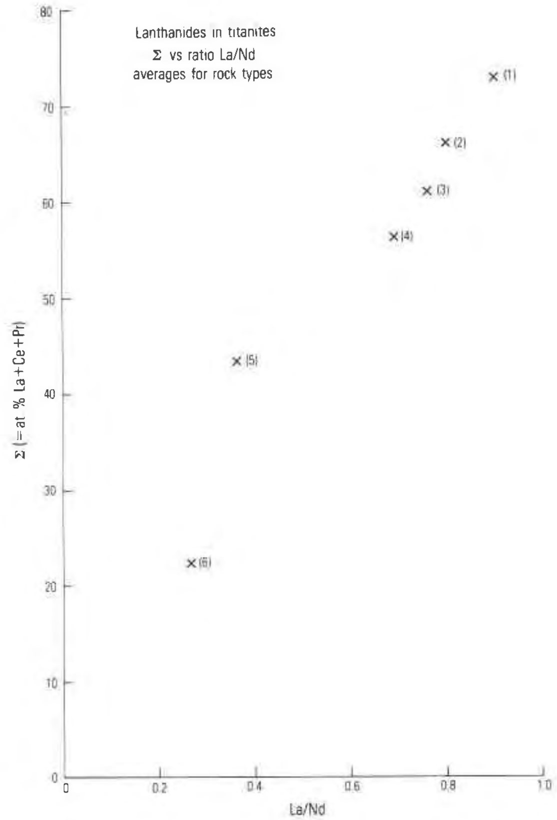

Fig. 3. Plot of Σ (= atomic percent La+Ce+Pr) *vs.* ratio La/Nd; averages for titanites from 6 types of rocks.

Table 3. Average composition of lanthanides in titanites from various types of rocks, as calculated by Lyakhovich and Balanova (1971)

(1) av. of 30 granites of palingenic intrusives, (2) av. of 15 alkalic rocks, (3) av. of 3 basic rocks, (4) av. of 4 gneisses and migmatites.

Element	1	2	3	4
La	12.8	17.1	14.1	4.8
Ce	35.5	47.2	43.4	17.9
Pr	7.8	6.3	7.9	4.1
Nd	20.0	20.2	21.7	20.6
Sm	5.9	3.5	4.6	6.8
Eu	0.5	0.3	0.5	-
Gd	5.6	2.7	3.2	11.7
Tb	0.9	0.3	0.4	1.6
Dy	4.5	1.3	1.9	9.2
Ho	0.9	0.2	0.3	4.2
Er	2.5	0.5	0.7	9.5
Tm	0.4	-	0.1	0.8
Yb	2.3	0.4	1.0	8.6
Lu	0.4	-	0.2	0.2
100Y/(Y+Ln)	-	-	-	-
Σ=La+Ce+Pr	56.1	70.6	65.4	26.8
La-Nd	76.1	90.8	87.1	47.4
Sm-Ho	18.3	8.3	10.9	33.5
Er-Lu	5.6	0.9	2.0	19.1
ΣRE_2O_3	1.73	3.56	-	1.60
La/Nd	0.64	0.84	0.65	0.24

phase III, but the graphs cannot be read accurately enough to compare with the data of Table 1. Dodge and Mays (1972) found that Σ for titanite is lower than that for coexisting apatite; Σ for titanite of granitic rocks of the Sierra Nevada ranged from 31 to 74, av. 52 (compare columns 3 and 4 of Tables 1 and 2). The values of Σ for titanite appeared to increase from west to east in the area studied.

Copies of the calculated atomic percentages for the 271 individual analyses summarized here, with references and localities, will be deposited in the U.S. Geological Survey libraries at Reston (Virginia), Denver (Colorado), and Menlo Park (California).

Table 4. Effect of discarding extreme values

	Alkalic Rocks		Granites	
	Σ	La/Nd	Σ	La/Nd
All data of Table 1	29.9-80.5	0.18-2.02	6.3-75.6	0.07-2.32
Discarding 5% at each extreme	56.8-74.9	0.52-1.18	16.6-69.1	0.09-0.90
Discarding 10% at each extreme	61.2-73.9	0.60-0.97	21.7-66.3	0.11-0.80

They are available in U.S. Geological Survey Open-File Report no. 78-530 which may be obtained from:

Open File Services Section
U.S. Geological Survey
Box 25425
Federal Center
Denver, Colorado 80225

by payment of the cost of reproduction.

References

Dodge, F. C. W. and R. E. Mays (1972) Rare-earth element fractionation in accessory minerals, central Sierra Nevada batholith. *U.S. Geol. Surv. Prof. Pap. 800-D*, 165–168.

Fleischer, M. (1965) Some aspects of the geochemistry of yttrium and the lanthanides. *Geochim. Cosmochim. Acta, 29*, 755–772.

—— and Z. S. Altschuler (1969) Relationship of the rare-earth composition of minerals to geological environment. *Geochim. Cosmochim. Acta, 33*, 725–732.

Lyakhovich, V. V. and T. T. Balanova (1971) Average contents and composition of rare-earth elements in accessory minerals of granitic rocks. (in Russian) *Geokhimiya, 1971*, 131–143.

Murata, K. J., H. J. Rose, Jr., M. K. Carron and J. J. Glass (1957) Systematic variation of rare-earths in cerium-earth minerals. *Geochim. Cosmochim. Acta, 11*, 141–161.

Semenov, E. I. (1963) *Mineralogy of the Rare Earths.* (in Russian) Izdat. Akad. Nauk S.S.S.R., Moscow.

Uskov, M. N. (1967) The crystallochemical features of the distribution of the rare-earths in accessory sphene. (in Russian) *Konst. Svoistva Mineral., 2*, 94–103.

Manuscript received, April 7, 1978; accepted for publication, June 12, 1978.