

Rare earths in some niobate-tantalates.

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Summary. Rare-earth distribution has been determined for fourteen niobate-tantalates containing essential rare earths. Those minerals with more than about 15 % TiO_2 (and corresponding to either priorites or members of the euxenite-polycrase series) have Yt as the dominant rare earth with the heavier lanthanons¹ in excess of the lighter lanthanons. Those minerals with less than about 4 % TiO_2 and less than about 30 % $(\text{Yt}, \text{Ln})_2\text{O}_3$ (and corresponding to samarskites) also have Yt as the dominant rare earth but they show a marked concentration of Gd + Tb + Dy over the other lanthanons. It is tentatively suggested that this power of selective lanthanon enrichment may be characteristic of samarskite among the niobate-tantalates examined.

THE identification of those metamict minerals containing essential Nb, Ta, and rare earths is not a straightforward matter. Crystal morphology is the most valuable single diagnostic feature, but frequently the minerals have poorly developed faces or occur massive. Thus it is that in the field it is not always possible to distinguish between mineral groups, and consequently laboratory data assume considerable importance. Both X-ray and differential thermal techniques have been employed (e.g. Berman, 1955; Kerr and Holland, 1951) but the methods do not always give clear-cut results. Chemical data are certainly more useful and, as will be shown, division into certain mineral series or groups can be made on such data alone. Nevertheless, the rare-earth niobate-tantalates have not been extensively analysed, partly, no doubt, because of the difficulties they present to the analyst. Estimation of Nb and Ta has always required considerable skill using the classical methods, and the modern methods are not devoid of problems especially for minerals rich in Ti.² Data on the individual rare earths are noticeably scarcer than data on Nb and Ta and it seemed worth while carrying out a small-scale survey of readily available minerals like samarskite and members of the euxenite-polycrase series to determine if and in what

¹ Lanthanon, and the symbol Ln, is a general term for all the rare-earth elements from La to Lu; Sc and Yt are not included.

² The method of Williams (1952) seems to need modification for minerals like euxenite.

respects distribution of the rare earths varied in the different minerals. Members of the rare earth group are taken to consist of Sc (atomic number $Z = 21$), Yt ($Z = 39$), and the lanthanons, with atomic numbers $Z = 57$ to $Z = 71$ inclusive; Pm ($Z = 61$) is sensibly absent in nature.

Identification of the minerals.

The more common rare-earth niobate-tantalates can be conveniently divided into two major groups on the basis of Ti content:

Those with *Ti exceeding about 15 % TiO_2* include polymignite, members of the euxenite–polycrase series, and members of the aeschynite–priorite series. Few analyses of polymignite are available but the mineral is here unique in containing essential Zr. Sufficient analyses of the other minerals are available to convince both casual and careful observers of the chemical complexities of the series; unfortunately the basis for division in the euxenite–polycrase series revolves round the Nb, Ta, and Ti contents whereas that for division in the aeschynite–priorite series depends on the rare-earth (and Th) content. In euxenite the atomic ratio $Ti/(Nb+Ta)$ is less than 3 whereas in polycrase it exceeds 4 (Brøgger, 1906); contents of TiO_2 in the series range from about 15 to 35 wt. %; usually Nb exceeds Ta although the ratio Nb/Ta can vary at least by a factor of ten. The name tanteuxenite has been proposed for minerals otherwise euxenite when Ta_2O_5 exceeds Nb_2O_5 on a wt. % basis; no new name has been proposed for Ta-rich polycrase. The description tantalian euxenite or tantalian polycrase would seem adequate to imply knowledge of Nb, Ta, and Ti contents in the mineral. In aeschynite the lighter lanthanons (La, Ce, &c.) are the dominant constituents of the rare earths whereas in priorite Yt and the heavier lanthanons (Gd, Dy, &c.) are dominant; further, in aeschynite Th is higher (e.g. 15 % ThO_2) than it often is in priorite (e.g. 8 % ThO_2). In the series TiO_2 varies from about 20 to 35 % and although the extent of the variation in the ratio Nb/Ta is not well known no Ta-rich varieties have been described.

It must be appreciated that a partial chemical analysis for the elements or chemical groups Nb and Ta, Ti, and Yt and heavier lanthanons will not enable a distinction to be made between priorite and a member of the euxenite–polycrase series. Knowledge of the U and Th contents is, however, useful in so far as U can be and often is higher in members of the euxenite–polycrase series than in priorite; moreover, Th can be and often is higher in priorite than in members of the euxenite–

polycrase series; and the atomic ratio U/Th is generally higher in members of the euxenite-polycrase series than in priorite.

The minerals described in this paper as members of the euxenite-polycrase series all have fairly low Th contents (table I, cols. 1-10) and the U/Th ratios at least exceed unity. X-ray diffraction patterns of the specimens after heating in air at 700° C. for 6 hours (Berman, 1955) can be divided into three types. Those of minerals nos. 1, 2, 3, 6, and 10 (table I) gave comparable patterns similar to that for (heated) lyn- dochite, a rare-earth niobate-tantalate rich in the lighter lanthanons (Butler, 1957c); those of minerals nos. 4, 5, 7, and 8 gave comparable patterns similar to that of samarskite from North Carolina (no. 12) after the latter had been heated in air at 1000° C. for 2½ hours; mineral no. 9 gave a unique pattern.

Those rare-earth niobate-tantalates with *Ti below about 4% TiO₂* include the fergusonite-formanite series, yttrotantalite, and samarskite. The basis for division in the fergusonite-formanite series is the Nb/Ta (atomic) ratio which exceeds unity for fergusonite and is below unity for formanite; rare earths nearly always total above 30% and average nearer 40% (Yt, Ln)₂O₃. Samarskite usually contains between 10 and 25% rare earths; Nb is dominant over Ta. Both U and total Fe usually exceed 4%, whereas some members of the fergusonite-formanite series can be low in both these constituents. Yttrotantalite is chemically similar to samarskite except that Ta dominates over Nb.

The minerals described in this paper as samarskite have rare earths totalling between 12 and 25% (Yt, Ln)₂O₃ (table I, cols. 11-14); semi-quantitative tests showed that the Nb/Ta ratio was appreciably greater than unity. X-ray diffraction patterns of the specimens nos. 11, 12, and 14 after heating in air at 1000° C. for 2½ hours were similar (and comparable with those of specimens nos. 4, 5, 7, and 8 after they had been heated in air at 700° C. for 6 hours); that for specimen no. 13 gave a unique pattern.

Analytical methods.

Rare earths plus thorium were determined via the fluorides, perchlorates, and oxalates using a modified method after Gordon *et al.* (1949) described elsewhere (Butler, 1957b). The separation is probably not suitable for the quantitative estimation of Sc as its oxalate is not completely insoluble under the chosen conditions of oxalate precipitation; however, absence of Sc in the minerals (i.e. not in the separated oxides) was confirmed spectrographically (sensitivity about 0.07% Sc₂O₃).

TABLE I. Analytical data for some Nb-Ta-Yt-Ln minerals. Nos. 1-10 are thought to be either priorites or members of the euxenite-polycrase series; nos. 11-14 are thought to be samarskites. Individual rare earths were determined spectrographically in and reported on the basis of chemically separated (Y, Ln)₂O₃ + ThO₂, (Sc₂O₃ and Eu₂O₃ below 0.1 % throughout, La₂O₃ below 0.1 %, Pr₂O₃ below 0.3 %, and Lu₂O₃ below 0.1 % where indicated by —. No data for Ho₂O₃. Total rare-earth oxides of the formula shown, TiO₂, and ThO₂ were determined chemically on a mineral basis. R²⁺, ionic radii (A.) of trivalent rare-earth cations. δ , percentage standard deviations of estimate of individual rare earths from duplicate spectrograms; the higher values for La₂O₃ and Pr₂O₃ are for lower concentration estimates.

	R ³⁺ .	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	δ .
Yt ₂ O ₃	0.92	59.2	59.5	47.0	46.8	47.0	39.7	49.8	45.8	44.4	46.0	44.7	44.0	49.2	58.6	5
La ₂ O ₃	1.14	0.10	0.60	0.15	0.12	0.12	0.12	0.40	0.35	0.10	0.38	—	—	—	0.13	7-10
CeO ₂	1.07	0.52	—	1.47	0.96	0.57	1.10	1.25	2.79	1.45	2.48	0.92	0.50	1.28	0.89	7
Pr ₂ O ₃	1.06	—	—	0.63	0.56	—	0.65	0.53	1.12	0.66	0.78	0.50	0.65	0.76	—	7-10
Nd ₂ O ₃	1.04	0.93	0.85	3.74	2.08	1.37	3.01	1.98	7.90	3.60	5.75	2.58	3.84	3.46	1.97	5
Sm ₂ O ₃	1.00	1.16	0.85	3.17	1.72	1.94	4.75	2.22	7.24	3.88	2.18	5.55	10.2	6.97	3.20	5
Gd ₂ O ₃	0.97	4.04	3.30	6.95	5.06	6.70	9.64	6.26	11.7	9.77	3.26	16.9	27.6	12.8	10.9	6½
Th ₄ O ₇	0.93	1.31	1.02	1.59	1.25	1.45	2.24	1.54	2.56	2.23	0.81	3.70	4.90	3.40	2.93	6
Dy ₂ O ₃	0.92	7.00	6.47	9.14	7.75	10.5	11.8	10.6	11.0	12.0	2.98	16.0	13.6	13.6	14.2	5
Er ₂ O ₃	0.89	8.32	7.14	9.72	10.9	10.2	9.35	8.06	6.77	10.0	5.65	4.15	1.21	4.82	3.88	13
Tm ₂ O ₃	0.87	0.84	1.10	1.00	1.37	1.13	0.93	0.93	0.58	0.97	1.06	0.26	—	0.52	0.33	10
Lu ₂ O ₃	0.86	8.82	11.6	10.0	12.4	6.55	6.17	9.68	3.60	6.99	11.2	1.35	0.11	2.81	2.19	5
Yb ₂ O ₃	0.85	0.83	1.30	0.96	1.69	1.70	0.76	0.83	0.50	0.84	3.75	0.25	—	0.46	0.39	30
ThO ₂	—	6.18	1.29	11.20	7.78	10.10	9.27	5.20	12.80	n.d.	16.20	2.38	tr.	nil	nil	—
Sum	—	99.25	95.02	106.72	100.44	99.21	99.49	99.28	114.71	96.89	102.48	99.24	107.21	100.08	99.61	—

(Yt, Ln) ₂ O ₃	25.96	27.71	30.07	23.10	20.30	28.28	21.77	25.47	(20.85)	20.86	16.85	17.70	12.44	24.68	
TiO ₂	25.0	24.3	29.6	24.9	20.5	24.4	27.0	20.0	25.0	21.8	2.10	2.17	1.60	1.20	
ThO ₂	1.71	0.36	3.79	2.07	2.28	2.89	1.44	3.73	n.d.	4.04	0.41	tr.	nil	nil	

1. Skilnabo, Västergötland, Sweden.
2. Mattawan Township, Nipissing District, Ontario, Canada.
3. South West Africa.
4. Nansoke, Uganda.
5. Kjaelevann, Vegusdal, Norway.
6. Arendal, Norway.
7. Brazil.
8. Vaalputs portion of Nousees, 5 miles east of Nousees Homestead, South-west Africa.
9. Fitamalama, Madagascar.
10. Rio Ligonha, Moçambique.
11. Bjortjenn, Iveland, Norway.
12. Mitchell Co., North Carolina, United States. B.M. 68781.
13. Divino Ubá, Minas Gerais, Brazil. B.M. 1926,246.
14. Madras, India.

Thorium was determined by decomposing the HF-insoluble fluorides with sodium bisulphate and precipitating thorium as iodate using the method of Meyer and Speter (1910); it was found advantageous to ice-cool the solution prior to addition of sodium sulphite and to allow the solution to become completely iodine-free (i.e. decolorized) prior to addition of ammonium hydroxide. Titanium was determined colorimetrically using the yellow Ti-H₂O₂ compound; uranium was estimated approximately using the method of Bowie (1949). Individual rare earths were determined spectrographically on the chemically separated rare earth plus thorium oxides (Butler 1957*a*); it was not found possible to estimate Ho with adequate precision although it probably reaches 2% Ho₂O₃ for the samples rich in Dy and Er. The errors of determination associated with the spectrographically determined oxides are shown in table I (that for chemically determined Th is relatively negligible). The summations of the individual oxides should be, say, $\frac{1}{2}$ -2% less than 100 according to the Ho₂O₃ content and it is possible to use this knowledge of the total to 'improve the data' for the individual oxides by adjusting the oxide percentages in proportion to their variances (squares of actual deviations) using Merriman's method of least squares. For oxides from minerals 2, 3, and 8 with totals of 95, 107, and 115 respectively improved values for oxide percentage estimates might be of use were it not for the probability that Ho₂O₃ is likely to be nearer, say, 2 or 3% than $\frac{1}{2}$ %; with or without improved estimates the rare-earth distribution trends are the same. For oxides from mineral 12, however, the total is 107.2, but Ho₂O₃ is absent (i.e. below $\frac{1}{2}$ %): improved estimates have been obtained to give more precise data for this very gadolinium-rich mineral.

Table II, col. 12, shows the atomic percentages of the lanthanons in the total lanthanons derived by Merriman's method from the data in table I, col. 12. All other data in table II are derived directly from corresponding data in table I.

Previous work.

The determination of rare earths by classical chemical methods has marked limitations and often the best that can be accomplished is an estimation of Ce and a division into the cerium group (La, Ce, Pr, Nd, and Sm), the terbium group (Eu, Gd, and Tb), and the yttrium group (Yt, Dy, Ho, Er, Tm, Yb, and Lu) (Hillebrand *et al.*, 1953). Nevertheless, several analysts were bold enough to publish figures for, specifically, Er₂O₃ half a century ago, before, indeed, the exact number of elements

TABLE II. Atomic percentages of lanthanons in total lanthanons excluding Ho. For localities see Table I. (Z, Atomic number.)

Z.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.
La 57	0.34	—	0.35	0.31	—	0.27	1.03	0.70	0.22	1.07	—	—	—	0.31
Ce 58	1.68	1.94	3.28	2.29	1.47	2.34	3.06	5.24	2.96	6.62	1.88	1.82	2.67	2.32
Pr 59	—	—	1.42	1.35	—	1.40	1.31	2.12	1.37	2.11	1.03	1.09	1.60	—
Nd 60	3.07	2.81	8.54	5.09	3.60	6.55	4.97	15.2	7.55	15.7	5.40	6.53	7.39	5.25
Sm 62	3.70	2.71	6.96	4.05	4.95	10.0	5.40	13.4	7.85	5.79	11.2	16.7	14.4	8.25
Gd 64	12.4	10.1	14.7	11.5	16.3	19.4	14.6	20.9	19.0	8.31	32.8	43.5	25.3	27.0
Tb 65	3.98	3.03	3.26	2.74	3.42	4.40	3.50	4.43	4.19	1.99	6.95	7.46	6.52	7.05
Dy 66	21.4	19.3	18.8	17.1	24.9	23.1	23.9	19.1	22.7	7.37	30.0	20.8	26.2	34.1
Er 68	24.2	20.8	19.5	23.6	24.3	17.9	17.8	11.5	18.5	13.6	7.61	1.81	9.04	9.10
Tm 69	2.42	3.10	1.98	2.91	2.58	1.76	2.02	0.97	1.77	2.53	0.47	—	0.97	0.77
Yb 70	24.9	33.0	19.5	25.8	14.7	11.5	20.7	5.90	12.5	26.2	2.40	0.16	5.13	4.98
Lu 71	2.31	3.63	1.84	3.48	3.77	1.40	1.75	0.82	1.49	8.69	0.44	—	0.83	0.88

constituting the lanthanon group was established. The appearance of their results in subsequent and modern textbooks is no reason for not regarding the data as tentative or even highly approximate. The first worker to produce acceptably accurate semi-quantitative data for minerals like euxenite and samarskite was, of course, Goldschmidt. Together with Thomassen (Goldschmidt and Thomassen, 1924), he evolved an X-ray spectrographic technique and showed these minerals to be poor in La, Ce, &c., but rich in Yt and the heavier lanthanons like Dy, Er, and Yb. Only one samarskite and six members of the euxenite-polycrase series were analysed and the semi-quantitative data did not suggest a distinction between the different minerals on a basis of rare-earth distribution. However, Goldschmidt demonstrated that any lanthanon with an odd atomic number was invariably less abundant than those lanthanons with adjacent (and even) atomic numbers; he also explained the absence of Eu ($Z = 63$) as due to the ease of reduction of Eu^{3+} to Eu^{2+} and the consequent disassociation of the larger divalent ion (radius 1.24 Å.) from the smaller trivalent lanthanon ions (varying from 1.14 Å. for La^{3+} to 0.85 Å. for Lu^{3+}).

Bjørlykke (1935) used X-ray spectrographic methods to study rare earths and other elements, including Ti, occurring in eight samarskites and seventeen different members of the euxenite-polycrase series. He concluded that '... the distribution of the rare earth elements [in the samarskites] is very like that of the euxenites. . .'. However, in his list of estimated intensities of K_{α} and L_{α} lines obtained in X-ray spectrograms of the minerals it is noticeable that the Yb line intensity is below 1 on an arbitrary scale 0–10 for 6 of the 8 samarskites and above 1 for 12 of the 17 members of the euxenite-polycrase series; further, the Dy line is the most intense lanthanon line in 7 of the samarskites. He confirmed that all 25 minerals were poor in the lighter lanthanons La, Ce, Pr, and Nd.

Using a refined X-ray spectrographic technique Sahama and Vähätalo (1939) were able to produce percentage concentration figures for individual rare earths in several niobate-tantalates. The materials referred to by the authors as samples of wiikite were ill-defined mixtures of alteration products of pegmatitic minerals like euxenite or samarskite, and were evidently capable of very wide compositional variations (Lokka, 1928). Nevertheless, all the wiikites were consistent in having Yt as easily the most abundant rare earth, and Yt and the heavy lanthanons Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were from 2.5 to 19 times as abundant as the other lanthanons on an atomic basis.

Discussion.

Cols. 1-10 of table I show data for ten niobate-tantalates rich in TiO_2 from widespread localities where Nb is thought or known to dominate over Ta. The total rare-earth percentages vary only between 20 and 30 and, as expected, do not correlate with either ThO_2 or TiO_2 content. Yt is easily the most abundant rare earth in all the samples but, again, cannot be correlated with total rare-earth content. On an atomic basis Yt represents between about 55 (nos. 6 and 8) and 75 (nos. 1 and 2) % of the rare earths and invariably the heavier lanthanons, viz Gd, Tb, Dy, (Ho), Er, Tm, Yb, and Lu, substantially exceed the lighter lanthanons. Lanthanon distribution in the minerals is thus markedly different from that obtaining in the lithosphere (fig. 1) where the average abundance of the Z-even lanthanons falls fairly regularly from Ce to Yb by a factor of very approximately 10 and those of the rarer Z-odd lanthanons fall from La to Lu by a factor probably exceeding 10 (excluding the highly unstable Pm, $Z = 61$). It is possible that one or more of the minerals crystallized from an environment impoverished in the lighter lanthanons (relative to the average lithosphere abundance of the lanthanons) by previous crystallization of, say, the most common rare-earth mineral monazite, which contains the light lanthanons almost to the exclusion of Yt and the heavy lanthanons (Murata *et al.*, 1953). This type of pre-enrichment can hardly have obtained for all the 10 minerals here analysed and it may be concluded that they are of the type described by Goldschmidt and Thomassen as showing a selective rare-earth assemblage. Nevertheless, the degree of selectivity is not as high as in, say, thalenite or thortveitite, and it will be seen from table II that minerals nos. 1-9 each contain at least 3 lanthanons exceeding 15 at. % of the total lanthanons (omitting Ho): there are accordingly no marked peak concentrations of individual lanthanons. Moreover, the lanthanons vary appreciably from specimen to specimen; Ce, for instance, varies by a factor of $3\frac{1}{2}$ from 1.4 to 5.2 at. % in the lanthanons and Yb varies by a factor of $6\frac{1}{2}$ from 5.9 to 33 at. % on the same basis. Dy, however, is much less variable (17.1 to 24.4 at. % in minerals 1-9 and 7.3 at. % in mineral 10) and it is quite probably the optimum-sized lanthanon for the euxenite (or priorite) structure; Yt^{3+} and Dy^{3+} have identical radii.

In a plot of lanthanon concentration against atomic number three trends are discernible. Thus the minerals from Västergötland, Sweden (no. 1), Ontario, Canada (no. 2 and fig. 2), South-west Africa (no. 3), and Nansoke, Uganda (no. 4), are comparable in showing a more or less regular increase in concentration for Z-even lanthanons with increasing

atomic number. Er^{3+} and Yb^{3+} are, of course, slightly smaller than Dy^{3+} and their presence in excess of Dy does not impose much strain on the crystal structure, more especially as more than half of the rare-earth positions in the lattice are occupied by Yt^{3+} . It is not, however, possible

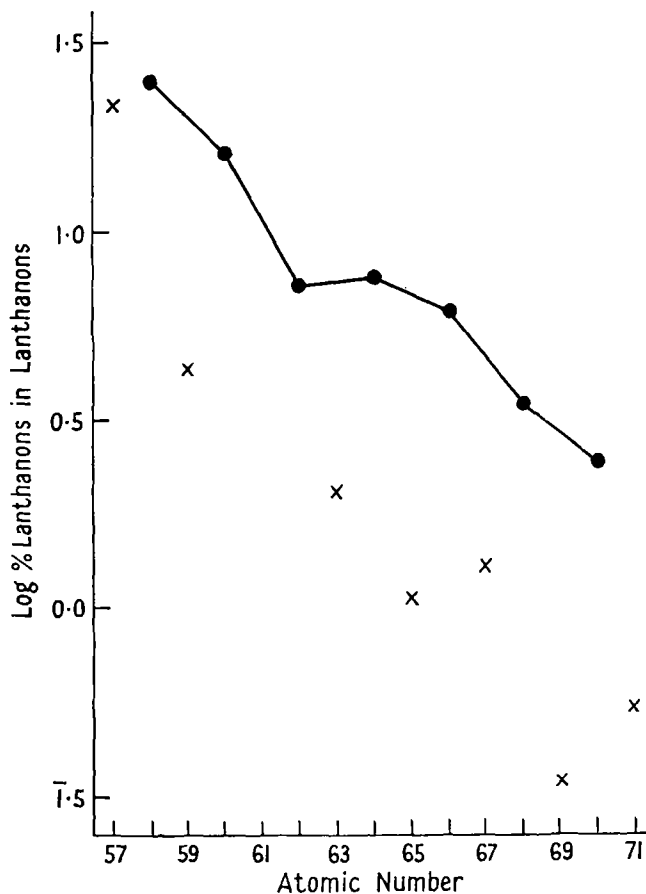


FIG. 1. Lanthanum distribution in 'average meteorites' after Suess and Urey (1956). Points representing the Z-even lanthanons are joined.

to decide if the relative concentration of Er and Yb compared with that in the other minerals was due to rate of crystallization or temperature of crystallization of the mineral rather than a relative concentration of Er and Yb in the environment in which the minerals crystallized. The Z-odd lanthanons also reflect the concentration of the smaller-sized

lanthanons in minerals nos. 1-4. Tb always exceeds Pr which in turn exceeds La but there is not invariably an increase in concentration of either Tm or Lu over Tb. There is, however, an appreciable increase in the ratio Tm/Tb over that obtaining in the lithosphere (fig. 1). The irregular trend of Lu/Tm or Lu/Yb ratios is possibly emphasized by the

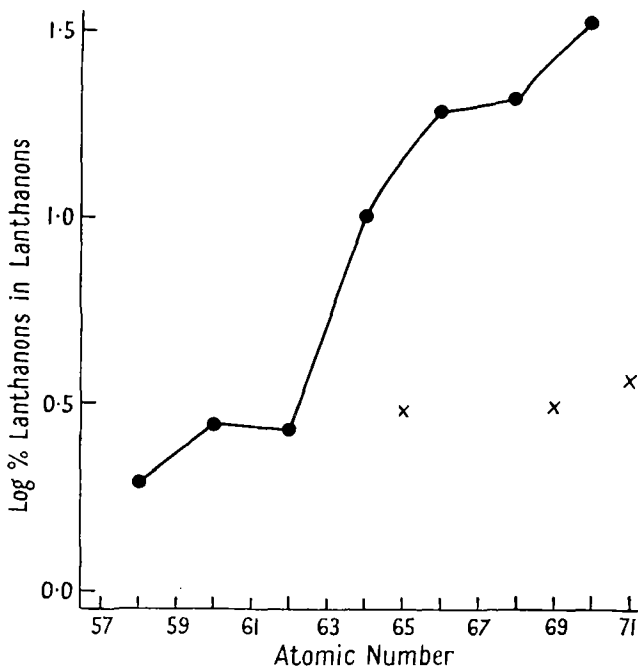


FIG. 2. Lanthanon distribution in Ti-rich niobate-tantalate, Mattawan Township, Nipissing District, Ontario, Canada (no. 2). Points representing the Z-even lanthanons are joined.

high standard deviation associated with the determination of Lu; however, it is also likely that it indicates that there is no tight distinction in lanthanon distribution between these four minerals and those in the following groupings.

The minerals from Vegusdal, Norway (no. 5), Arendal, Norway (no. 6), Brazil (no. 7), Nousees, South-west Africa (no. 8), and Fitamalame, Madagascar (no. 9), show, like those in the first grouping, about 20 at. % Dy and about 3-4 at. % Tb in their lanthanons but the concentrations of Er and Yb and of Tm and Lu tend to fall from that of Dy and Tb respectively (fig. 3, specimen no. 6).

Their higher Gd content is a consequence of the limited range in both total rare-earth content of the mineral and the Yt content in the rare earths. These four minerals are the only ones with Gd, Tb, and Dy

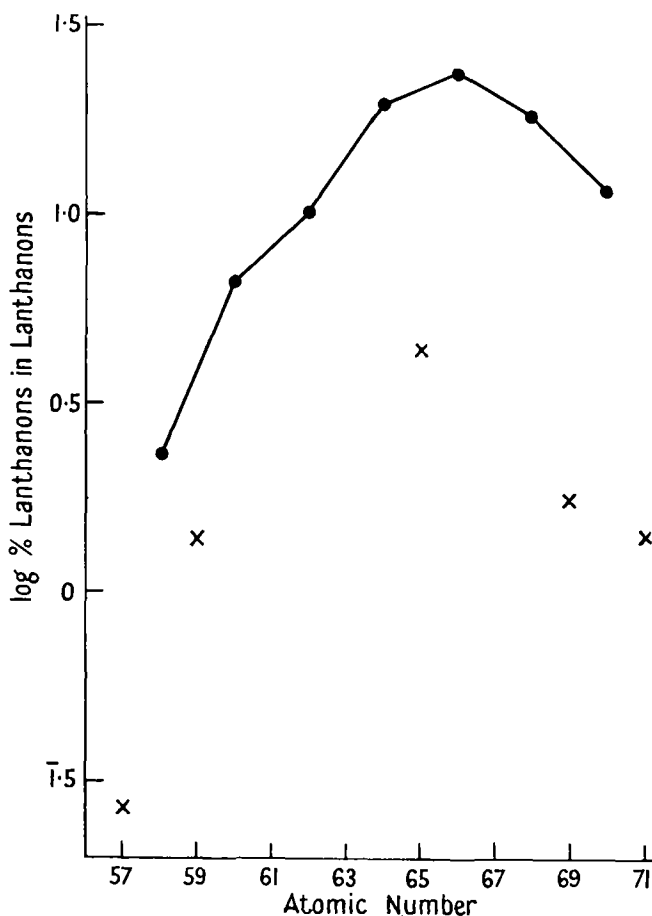


FIG. 3. Lanthanon distribution in Ti-rich niobate-tantalate, Arendal, Norway (no. 6). Points representing the Z-even lanthanons are joined.

totalling above 40 at. % of the lanthanons and in the mineral from Nousees, South-west Africa, Gd exceeds Dy, although by rather less than in the lithosphere. The tolerance of these minerals to lanthanons with ionic sizes above that of Dy^{3+} and Yt^{3+} is well seen in the latter mineral where $Nd + Pr + Ce$ exceeds 22 at. % in the lanthanons; the

weak concentrating factor of the mineral for a particular sized lanthanon was insufficient to offset the relatively high concentration of the lighter lanthanons in the environment from which the mineral crystallized.

The mineral from Rio Ligonha, Moçambique, shows a lanthanon distribution unique for the Ti-rich niobate-tantalates here investigated

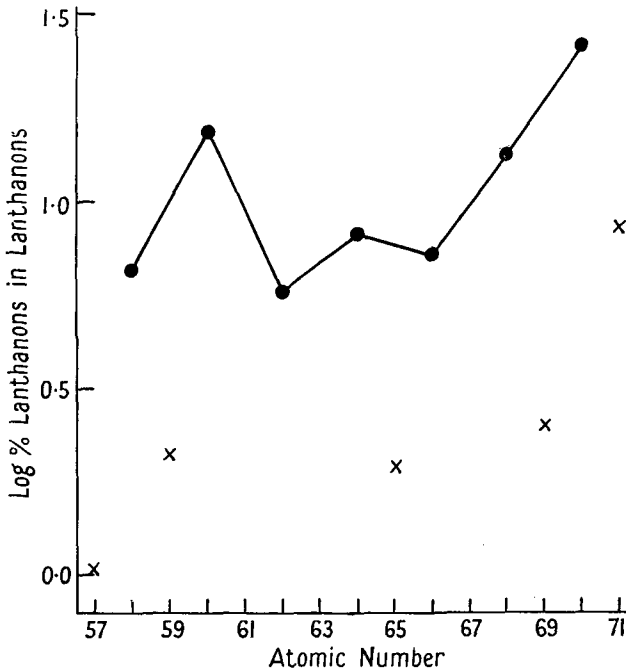


FIG. 4. Lanthanon distribution in Ti-rich-niobate tantalate, Rio Ligonha, Moçambique (no. 10). Points representing the Z-even lanthanons are joined.

(fig. 4). There are peak concentrations for Nd ($Z = 60$) and Yb ($Z = 70$) among the Z-even lanthanons and for Lu ($Z = 71$) among the Z-odd lanthanons; Pr ($Z = 59$) and Tb ($Z = 65$) show similar concentrations. This concentration-distribution type has been observed in a more severe form in davidite by Dixon and Wylie (1951). It is possible that the smallest lanthanons occupied sites in the mineral structurally dissimilar to those occupied by the largest lanthanons; this is difficult to prove for a metamict mineral. An alternative explanation is that the middle-sized lanthanons, especially Gd, Tb, and Dy, were relatively impoverished in the fluid from which the mineral formed by the previous (or contemporaneous) crystallization of another mineral strongly concentrating

just those lanthanons; samarskite would fill this role admirably. The high Lu content in the Moçambique mineral (0.93 % Lu_2O_3) and the relatively high Lu/Yb ratio is of considerable interest in view of the lack of Sc (brief mention of a similar state of affairs in a sample of fergusonite has been made by Wylie (1954)). Lu^{3+} and Sc^{3+} have ionic sizes 0.81 Å. and 0.85 Å. respectively and diadochy is clearly possible for the pair of elements; on size consideration alone it could be supposed that Sc would have little difficulty in substituting for Lu in minerals rich in Lu and the heaviest lanthanons. However, Sc breaks away from Lu at an early stage in magmatic differentiation and is a well-noted trace element in the common rock-forming ferromagnesian minerals, due to the substitution of Sc^{3+} (0.81 Å.) for Fe^{2+} (0.74 Å.). Presumably the capture of much of the larger Lu^{3+} (0.85 Å.) by Fe^{2+} would impose an excessive strain in the lattice of ferromagnesian minerals, but data on Lu in such minerals are lacking. This size strain may be a reason why the electronegativity approach suggested by Ringwood (1955) does not here apply.

The electronegativity (E) of Lu at 1.05 volts is 0.25 volts less than that of Sc; according to Ringwood this should favour substitution of Lu (over Sc) for a suitably sized ion (where diadochy between all 3 ions would be possible). The difference in behaviour between Sc and Lu may more conveniently be correlated with their differences in ionization potentials; the ratio [Ionization potential $\text{Sc}(\text{Sc}^{2+} \rightarrow \text{Sc}^{3+})$]/[Ionization potential $\text{Lu}(\text{Lu}^{2+} \rightarrow \text{Lu}^{3+})$] is 1.29 which, according to Ahrens (1952 and 1953) is rather high for close geochemical coherence to be expected. This somewhat weak coherence of Sc and Lu is in contrast to that for the largest trivalent rare earths La and Ce even though their size difference expressed as a percentage of the mean exceeds that of Sc and Lu (6.4 % against 4.8 %). The ionization potentials of La and Ce are closely similar and geochemical coherence is further helped by the absence of any common lithophile element with ionic radius near to or just a little larger than that of La. Only Hg^{2+} (1.10 Å.), Sr^{2+} (1.12 Å.), and Pb^{2+} (1.20 Å.) have radii between 1.07 Å. and 1.22 Å.

It has been stressed that the minerals nos. 1–10 need not be members of the euxenite–polycrase series on the basis of U and Th contents and ratios; they may be members of the priorite–aeschynite series albeit near the priorite end. If the mineral from Nousees, South-west Africa, is considered as a member of the latter series then its high atomic proportion of Yt and the heavier lanthanons compared with the lighter lanthanons would stamp it as being very near the theoretical priorite

end member of the aeschynite-priorite series; the light lanthanons La-Sm inclusive account for only 16 at. % of the total rare earths.

Data for these minerals—in particular those showing the restricted abundance of the light lanthanons—formed a basis for suggesting that lyndochite, with 55 at. % of light lanthanons constituting its rare earths, was chemically more comparable to a mid-compositional member of the aeschynite-priorite series than to members of the euxenite-polycrase series (Butler, 1957*c*). Nevertheless, it is to be appreciated that this survey is a preliminary and small-scale one; minerals morphologically like euxenite and compositionally similar to lyndochite are not necessarily rare.

Cols. 11-14, table I, show data for four niobate-tantalates poor in TiO_2 , with Nb exceeding Ta, and with ThO_2 below 1%. The total rare-earth contents vary from about 12 to 25 at. % and these data are not inconsistent with all four minerals being samarskite. Yt is easily the dominant rare earth and its percentage range (in total rare earths) is like that in the Ti-rich niobate-tantalates previously discussed. It accounts for 53 at. % of the rare earths in the North Carolina mineral (data from improved estimate) and 70 at. % in the Madras mineral.

The distribution of the lanthanons differs markedly from that described for the Ti-rich niobate-tantalates as it is evident that the four samarskites show fairly strong selective assemblage tendencies; Gd, Tb, and Dy are preferentially concentrated and together constitute 72, 70, 58, and 68 at. % of the lanthanons in minerals nos. 11-14 respectively (table II). Only five of minerals nos. 1-10 showed Gd+Tb+Dy exceeding 40 at. % of the lanthanons and the highest percentage was 46 (for no. 9). The data in table II also indicate that lanthanons heavier than Dy are consistently rarer in the lanthanons from the samarskites than in those from the other minerals except for Tm and Lu in the Nousees, South-west Africa, mineral. The percentages of La, Ce, Pr, Nd, and Sm are comparable.

The samarskite from Mitchell Co., North Carolina, shows a remarkably high at. % of Gd in the lanthanons which almost equals that of all the other lanthanons together (fig. 5 shows the lanthanon distribution); Gd is even more than half as abundant as Yt (25 at. % to 40 at. %). Gd in the mineral is only 4.36 wt. % Gd_2O_3 —a figure below that found in a number of gadolinites. Gadolinites, however, are, with respect to the rare earths, minerals of the complete-assemblage type and Gd can be exceeded by other (*Z*-even) lanthanons; moreover, the atomic ratio Yt/Gd is usually greater than 4. To date the samarskite from Mitchell

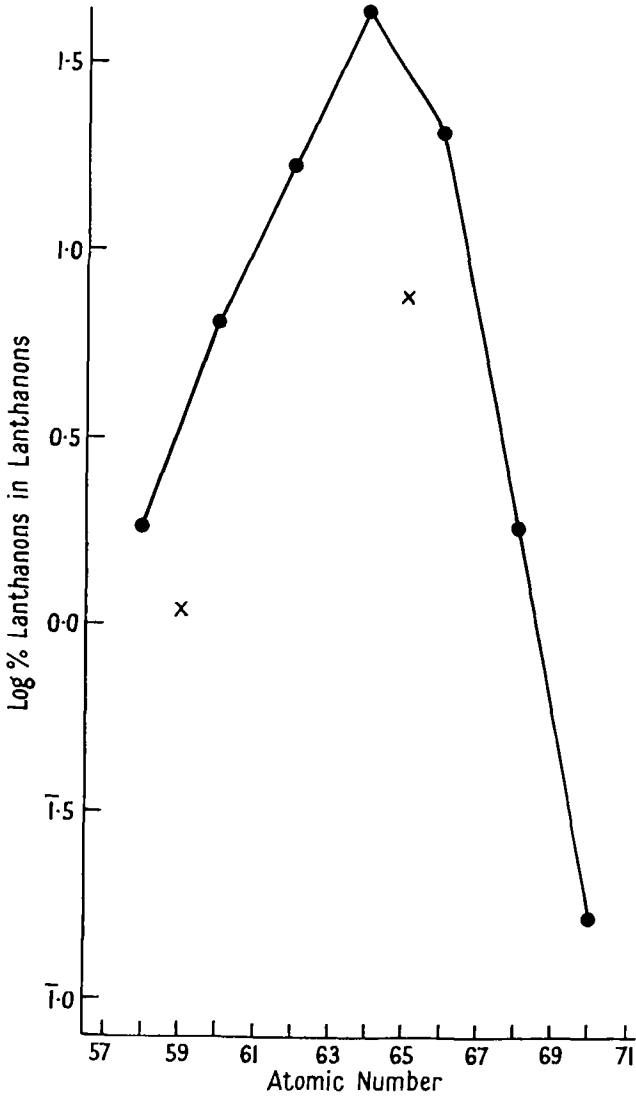


FIG. 5. Lanthanon distribution in Ti-poor niobate-tantalate (= samarskite), Mitchell County, North Carolina. B.M. 68781. Points representing the Z-even lanthanons are joined.

Co., North Carolina, is unique in its high concentration of Gd relative to the other rare earths and as a source for either Gd or Tb would be most valuable.

The remaining three samarskites have comparable lanthanon distributions but with Gd about 25 at. % in the lanthanons and Dy near or slightly higher; Tb ranges from only 6.5 to 7.5 at. % in all four

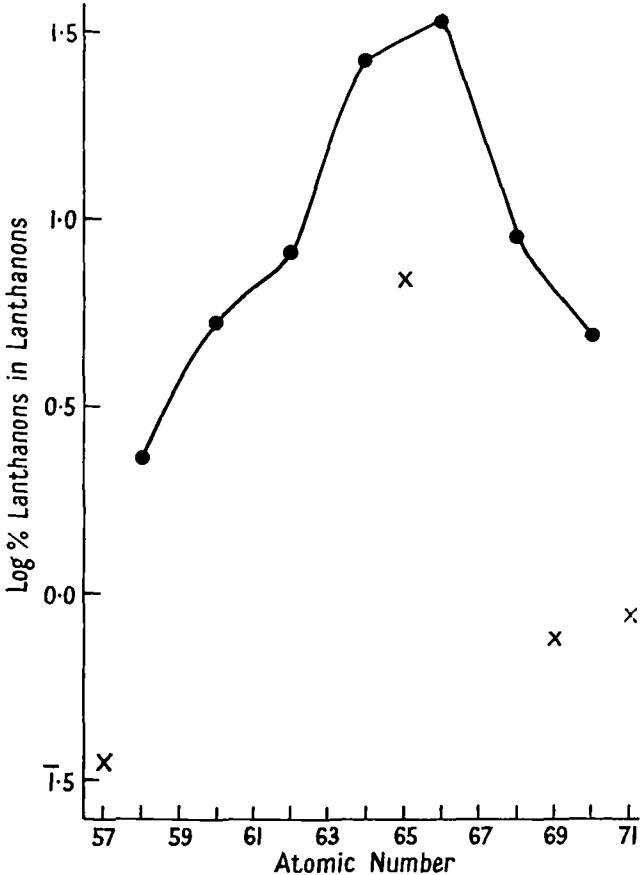


FIG. 6. Lanthanon distribution in Ti-poor niobate-tantalate, Madras, India. Points representing the Z-even lanthanons are joined.

samarskites, recalling its limited variation compared with the other lanthanons (2 to 4.4 at. %) in the Ti-rich niobate-tantalates.

The samarskite from Madras shows the least selective rare earth assemblage of the four samarskites (fig. 6), but its lanthanon distribution is distinct enough from those for minerals nos. 1-10. It is tempting to suggest that this selective concentration of Gd, Tb, and Dy and relative

rejection of Er, Tm, Yb, and Lu is a property of samarskites in general; that is, that they concentrate Gd, &c., and reject Er, &c., from the environment in which they crystallize. Contemporaneous crystallization of samarskite with davidite could explain the peculiar lanthanon distribution in the latter mineral.

However, more than four analyses are needed before generalizations can be more than guessed at; a very Yt-rich (say greater than 90 at. % of the rare earths) and lanthanon-poor samarskite may well show a more dispersed lanthanon distribution, as those lanthanons differing in size and other crystallization properties from Yt would produce correspondingly less size strain in the lattice than when total lanthanons were more nearly equal in abundance to Yt.

In conclusion, it is relevant to refer to current research at Imperial College on rare earths in members of the fergusonite-formanite series, which to date indicates that lanthanon distribution in fergusonites ($(\text{Yt,Ln})_2\text{O}_3 > 30$ wt. %) is more akin to that in the Ti-rich niobate-tantalates (nos. 1-10) than to that in samarskites (nos. 11-14). (Wylie, 1954, has reported data on an Australian formanite.) In particular a fergusonite from North Carolina, U.S.A., $(\text{Yt,Ln})_2\text{O}_3$ 43.30 wt. % showed Dy and Er approximately equal and both exceeding Gd; Yt accounted for 67 at. % of the rare earths.

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