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RARE EARTHS AND THORIUM IN LYNDOCHITE

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INTRODUCTION

In 1927 Ellsworth described an occurrence of and gave an analysis for a black niobate associated with the feldspar of a pegmatite dike in Lyndoch Township, Renfrew County, Ontario. Compositionally and in crystal form the mineral resembled euxenite except that it was low in U_3O_8 (0.74%) and high in CaO (4.86%) and ThO_2 (4.95%); further the Nb_2O_5 and the total $Nb_2O_5 + Ta_2O_5 + TiO_2$ were higher than for then known euxenites, even allowing for the presence of microscopic inclusions of columbite. The mineral was named lyndochite and it has not been recorded outside the type locality since.

Lyndochite has been re-examined with a view to ascertaining the distribution of rare earths (Sc, Yt and the lanthanons) in euxenites and closely allied minerals. It is clear that the original analysis is not wholly correct and the evidence suggests that chemically the mineral resembles eschynite more than euxenite.

EXPERIMENTAL

The crystals of lyndochite available from the type locality exhibited no faces and, as Ellsworth found, they contained foreign microscopic inclusions. A polished section was prepared and I am indebted to my colleague, Anthony P. Millman, for the following description of the material. "Lyndochite takes an excellent polish and is pale greyish white in reflected light in air with weak yellowish internal reflections. With crossed nicols and oil immersion the mineral is isotropic and shows strong yellowish brown internal reflections. The lyndochite in polished section is seen to contain as principal impurity a mineral (*P*) occurring as unreplaced residuals with deeply carious margins indicating replacement by lyndochite. *P* is white in reflected light in air compared with lyndochite and shows no reflection pleochroism or internal reflections. With crossed nicols (polariser rotated 5°) *P* shows distinct anisotropism from pale greyish white to dark grey. Twinning is absent but an incipient parting is visible and the mineral contains minute exsolution spindles or rods. The reflectivity as determined with the Cooke microphotometer was 14.7% for green light in air (Ilford spectrum green filter). This is extremely close to the published data for columbite of 15% for green light in air. A subsidiary mineral (*Q*) occurs as curvilinear veinlets (20 thick) replacing the lyndochite along fractures and partings with charac-

teristic embayed margins. *Q* is darker in reflected light in air than both lyndochite and *P*. The total content of impurities in the lyndochite was judged to be below 4%."

Presumably the mineral *P* in the lyndochite is that which Ellsworth satisfactorily showed by a partial chemical analysis to be columbite. No attempt was made to purify the lyndochite and it is to be observed that the concentrations of thorium and the rare earths determined on the impure mineral must be very near to those for the pure lyndochite. Rare earths plus thorium were determined via the fluorides, perchlorates and oxalates using a modified method after Gordon *et al.* (1949) described elsewhere (Butler 1957). 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 decolorised (i.e. iodine-free) prior to addition of ammonium hydroxide. The low U_3O_8 content was confirmed by the method of Bowie (1949). Individual rare earths were determined spectrographically by a method to be described elsewhere. The percentages of ThO_2 and rare earth oxides in the mineral were found to be 10.77 and 21.05 respectively (analyst: Miss Rosemary Hall); ThO_2 was examined spectrographically and found to be free from rare earths, etc. Results for the individual rare earths are presented in Table 1.

DISCUSSION

The new ThO_2 percentage is more than twice that originally obtained and the value of 10.77% is unprecedentedly high for a euxenite; moreover, the ratio Th/U (atomic) must exceed 10 which, together with the low U_3O_8 content is quite atypical of euxenites. Eschynites or priorites, on the other hand, have comparable ThO_2 and low U_3O_8 contents (e.g. Chernik, 1929). The original analysis of lyndochite showed $(Ce,La,Di)_2O_3$ as 4.34% and $(Yt,Er)_2O_3$ as 18.22% which was compatible with the mineral being considered as a relative to the polycrase-euxenite group. Goldschmidt and Thomassen (1924) noted the preponderance of Yt and the heavier lanthanons in euxenites, and unpublished results from this laboratory have confirmed their findings. To date, 17 members of the euxenite-polycrase group and 2 tanteuxenites have been analysed for rare earths, and Yt invariably exceeds the lanthanons on an atomic basis; further the ratio heavier/lighter lanthanons is always greater than 2:1 and can exceed 10:1. Polycrase-euxenite from Mattawan Township, Nipissing District, Ontario, shows a typical rare earth distribution (Table 1, Col. 4) with Dy, Er and Yb the dominant lan-

TABLE 1

	1	2	3	4
Sc ₂ O ₃	*	—	*	*
Yt ₂ O ₃	13.1	5	28.8	74.5
La ₂ O ₃	1.50	7	2.28	*
CeO ₂	13.5	5	19.5	.49
Pr ₆ O ₁₁	1.69	7	2.46	*
Nd ₂ O ₃	17.0	5	25.0	.71
Sm ₂ O ₃	4.40	5	6.26	.69
Eu ₂ O ₃	*	—	*	*
Gd ₂ O ₃	5.41	6½	7.41	2.57
Tb ₄ O ₇	0.50	10	.66	.77
Dy ₂ O ₃	2.94	5	3.91	4.90
Ho ₂ O ₃	—	—	—	—
Er ₂ O ₃	1.09	13	1.41	5.28
Tm ₂ O ₃	0.48	9	.62	.79
Yb ₂ O ₃	1.20	5	1.51	8.38
Lu ₂ O ₃	0.2	35	.25	.92
ThO ₂	33.80	—	—	—
Total	96.81		(100.07)	(100.00)

- Col. 1. Percentage composition of rare earths plus thorium, separated from lyndochite, Lyndoch Township, Renfrew County, Ontario. Sc₂O₃ and Eu₂O₃ below the sensitivity limit of 0.1%.
- Col. 2. Percentage standard deviations of estimates of individual rare earths from duplicated spectrograms.
- Col. 3. Atomic percentage composition of rare earths except Ho from lyndochite. (Calculated to 100%).
- Col. 4. Atomic percentage composition of rare earths from polycrase-euxenite, Mattawan Township, Nipissing District, Ontario. (Calculated to 100%.) Sc₂O₃, La₂O₃ and Eu₂O₃ were below 0.1% in the oxides; Pr₆O₁₁ was below 0.5%. Ho₂O₃ was very approximately half as abundant as Tm₂O₃. The sum of the spectrographic estimates was 94.52% and the mineral contained 27.71% RE₂O₃ (Analyst: Miss Rosemary Hall).

thanons. The new analysis of lyndochite shows a similar rare earth total—21.05% against 22.56%—but the distribution of the individual rare earths shows quite a different pattern. Yt, Nd and Ce are, in that order, the chief constituents on an atomic basis (Table 1, Col. 3); together they account for 75% of the rare earths, although 10 of the remaining rare earths are represented. The distribution of the lanthanons (Fig. 1) shows that Nd and Ce were preferentially accepted in the lyndochite structure but the tolerance of the mineral in accepting ions of smaller size (eg. Dy⁺³, radius 0.92 Å) was more limited. Thus the preponderance of Yt⁺³ (radius 0.92 Å) was probably due to its relatively high concentra-

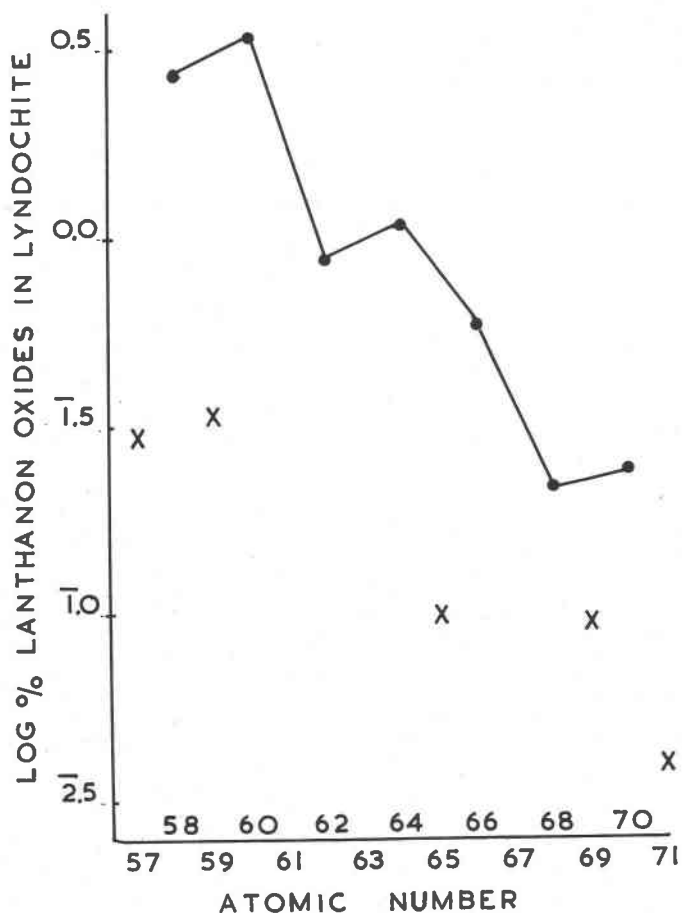


FIG. 1. Distribution of the lanthanons in lyndochite from Lyndoch Township, Renfrew County, Ontario. Points representing the Z-even lanthanons are joined.

tion in the solutions giving rise to lyndochite, rather than its being easily accommodated in the lyndochite structure. The mineral shows moderate selective assemblage tendencies in its lanthanon content (Goldschmidt and Thomassen, 1924) although the degree of selectivity is not so high as in, say, the monazites which contain but low amounts of Gd and the heavier lanthanons (Wylie, 1950, Murata *et al.* 1953) and have La/Ce ratios 4 or more times higher than in lyndochite; a further distinction is that monazites are poor in Yt. Among the Nb-Ta minerals containing essential rare earths both eschynite and polymignite show cerium earths in excess of yttrium earths; polymignite contains essential ZrO_2 and cannot, thus, be considered with either the euxenite-polycrase series (Ti

varying) or the eschynite-priorite series (ratio light/heavy lanthanons varying). It is evident that lyndochite *chemically* resembles eschynite rather than previously analysed members of the euxenite-polycrase group.

Morphologically, however, lyndochite is distinct from eschynite, and Ellsworth observed that "Owing to the roughness and distortion of the faces it has not been possible to make sufficient exact measurements to be sure to what extent the interfacial angles differ from those of euxenite, but several fairly accurate contact measurements suggest a close similarity of forms and angles." The forms he identified as present were {100}, {010}, {110}, {310} or {410} or both, {201} and {111}. The angles between faces of these forms cannot be reconciled with those between observed faces of eschynite which has an axial ratio very different from that of euxenite; they would, however, compare with angles between faces of the same forms in columbite and it is recalled that Ellsworth observed inclusions in the lyndochite to be "... plainly remnants of columbite in process of assimilation by the lyndochite..." Dr. Millman's observations confirm that lyndochite has partly replaced columbite and it is thus possible that lyndochite is a pseudomorph of eschynite after columbite. Against this, however, it is to be noted that either {310} or {410} is rare in columbite and, further, that the habit of the columbite associated with lyndochite and described by Miller (1897) is either platy or nodular. Further, Berman (1955) found that 7 suitably heated specimens of euxenite gave x -ray diffraction patterns very similar to that of suitably heated lyndochite. If this evidence is taken to preclude the likelihood of lyndochite being a pseudomorph after columbite, then lyndochite can be regarded as a cerian-thorian-U-poor variety of euxenite in the euxenite-polycrase series, chemically analogous to eschynite in the eschynite-priorite group.

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REFERENCES

- BERMAN, J. (1955), Identifying metamict minerals by x -ray diffraction: *Am. Mineral.*, **40**, 817.
- BOWIE, S. H. U. (1949), A prospector's handbook to radioactive mineral deposits. H. M. Geological Survey.

- BUTLER, J. R. (1957), *Geochim. et Cosmochim. Acta* (in press).
CHERNIK, G. P. (1929), *J. Russ-Phys. Chem. Soc.*, **61**, 735-773.
ELLSWORTH, H. V. (1927), *Am. Mineral.*, **12**, 212-218.
GOLDSCHMIDT, V. M., AND THOMASSEN (1924), *Videnskapsselskapets Skr. I. Mat. natur.* **KI**, No. 5.
GORDON, LOUIS, VANSELOW, C. H., AND WILLARD, HOBART H. (1949), *Anal. Chem.*, **21**, 1323-1325.
MEYER, R. J., AND SPETER, M. (1910), *Chem. Zeit.*, **34**, 306.
MILLER, WILLET G. (1897). Ont. Bureau Mines 7th rept., Pt. III.
MURATA, K. J., ROSE, H. J., JR., AND CARRON, M. K. (1953), *Geochim. et Cosmochim. Acta*, **4**, 292-300.
WYLIE, A. W. (1950). *Australian J. Appl. Sci.*, **1**, 164-171.

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X-RAY POWDER DATA FOR ULEXITE AND HALOTRICHITE

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During a study, described elsewhere in this journal, on an optical property exhibited by fibrous minerals, routine *x*-ray diffraction analyses were made of the specimens. It was found that the three principal diffractions of ulexite had not been reported nor had any diffraction data on halotrichite.

The *x*-ray powder data for two ulexite samples and the ASTM data are presented in Table 1. Note the use of molybdenum radiation in the ASTM data, which probably accounts for the omission of the most prominent diffractions in the lower angle region. The chemical analysis for the ulexite specimen from Boron, California is given in Table 2.

The *x*-ray powder data and the chemical analysis for the halotrichite specimen studied are presented in Tables 3 and 4, respectively.

A General Electric XRD3 diffractometer unit with nickel filtered copper radiation was used. The samples were ground to pass 325 mesh and packed in a $3\frac{1}{2}'' \times 1''$ sample holder avoiding orientation as much as possible.

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