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## The composition of rhabdophane

RHABDOPHANE is a hydrated phosphate of cerium, yttrium, and other rare earth elements of which Palache *et al.* (1944) say 'the proportions of the elements occurring with cerium have not been fully determined'.

An early analysis of the mineral by Hartley (1882) on a specimen from Cornwall indicated a substantial rare earth content; other analyses have been recorded from Salisbury, Connecticut (Brush and Penfield, 1883), Julianehaab, Greenland (Böggild, 1903), the Kiyu alkali massif (Semenov, 1959), the Lovozero alkali massif (Gerasimovskii, 1937; Vlasov *et al.*, 1959), and Idaho (Adams, 1968). These analyses are semi-quantitative or incomplete and report only total rare earth elements or the ratios of those elements.

This contribution presents a new analysis of rhabdophane from the type locality at Fowey Consols Mine, Cornwall, which indicates quantitatively the distribution of the rare earth elements. Recent XRD studies on this material (Atkin *et al.*, 1983) have shown that it has unit cell dimensions of  $a$   $6.960 \pm 0.003$  and  $c$   $6.372 \pm 0.006$  Å.

*Microprobe analysis.* The analysis for twenty-six elements given in Table I was obtained with a Cambridge Scientific Instruments Microscan 5 electron microprobe using the standards and techniques described by Bowles (1975, 1978)

TABLE I. *Microprobe analyses of rhabdophane from Fowey Consols Mine, Cornwall*

	Wt. %		Molecular proportions calculated to 4 oxygen atoms	
	A	B	A	B
La <sub>2</sub> O <sub>3</sub>	12.19	11.07	0.187	0.171
Ce <sub>2</sub> O <sub>3</sub>	11.85	13.26	0.180	0.204
Pr <sub>2</sub> O <sub>3</sub>	1.02	0.85	0.015	0.013
Nd <sub>2</sub> O <sub>3</sub>	21.18	15.74	0.314	0.236
Sm <sub>2</sub> O <sub>3</sub>	3.49	2.93	0.050	0.042
Eu <sub>2</sub> O <sub>3</sub>	1.78	1.59	0.025	0.023
Gd <sub>2</sub> O <sub>3</sub>	3.24	3.46	0.045	0.048
Tb <sub>2</sub> O <sub>3</sub>	0.34	0.33	0.005	0.005
Dy <sub>2</sub> O <sub>3</sub>	1.69	1.68	0.023	0.023
Ho <sub>2</sub> O <sub>3</sub>	0.40	0.44	0.005	0.006
Er <sub>2</sub> O <sub>3</sub>	1.12	1.13	0.015	0.015
Tm <sub>2</sub> O <sub>3</sub>	0.51	0.42	0.007	0.005
Yb <sub>2</sub> O <sub>3</sub>	0.40	0.76	0.005	0.010
Y <sub>2</sub> O <sub>3</sub>	4.02	8.33	0.089	0.186
CaO	0.26	0.24	0.012	0.011
Fe <sub>2</sub> O <sub>3</sub>	0.38	0.32	0.012	0.010
ThO <sub>2</sub>	—	0.10	—	0.002
U <sub>3</sub> O <sub>8</sub>	0.42	0.18	0.004	0.002
P <sub>2</sub> O <sub>5</sub>	28.59	28.02	1.006-1.01	0.995-1.00
H <sub>2</sub> O	7.12*	9.15*	0.987-0.99	1.280-1.28
	100.00*	100.00*		

\* H<sub>2</sub>O added to give total = 100%, measurement of evolved water of specimen A gave 7.9%. Lu, Hf, Al, Mn not detected (< 0.01%); Ti, Si, Pb detected (0.01-0.03%)

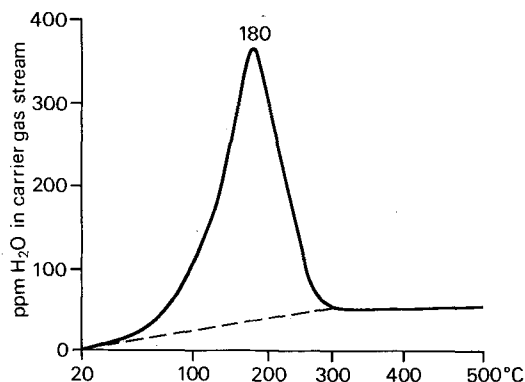


FIG. 1. Evolved water profile for rhabdophane (7 mg sample, heating rate 10 °C/min).

together with standards from Drake and Weill (1972) and Smellie *et al.* (1978). Full ZAF correction of the results was obtained using a version of the Mason-Frost-Reed (1969) program expanded to consider a sufficient number of elements.

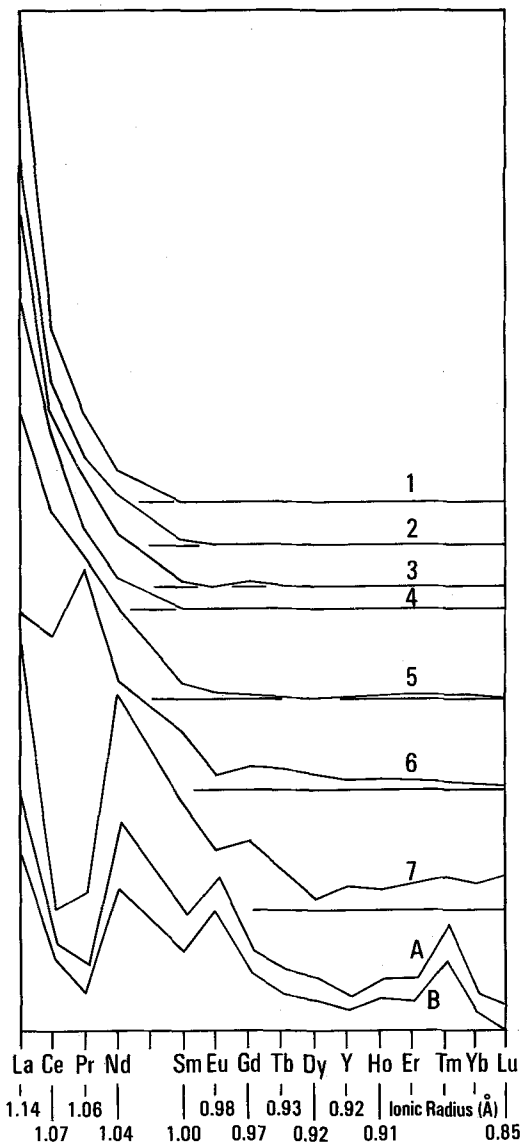
**Measurement of water content.** The water content of sample A was determined by evolved gas analysis (Morgan, 1977). Seven mg of the powdered material, taken from near the microprobe analysis site, were heated in a DTA furnace and the evolved water transported by a dry nitrogen stream to a non-dispersive infra-red water analyser. The resulting water-evolution profile is shown in fig. 1. The quantity of water evolved, measured from the peak area, is 7.9% which is in reasonable agreement with the deficit on the microprobe analysis.

Rhabdophane contains one water molecule per formula unit, this being accommodated in 'zeolitic' channels in the structure (Mooney, 1950). Palache *et al.* (1944) quote experiments carried out by

FIG. 2. The rare earth pattern of rhabdophane from various environments. The vertical axis shows the RE composition expressed as a ratio of the RE concentration in average chondritic meteorites and normalized to 100% total REE plus yttrium. This enables comparison to be drawn between the present quantitative work and earlier relative analyses. Yttrium is included in a position indicated by its ionic radius and the base line of each pattern has been shifted for clarity. Key: 1. Lovozero. Supergene enrichment of nepheline syenite pegmatite; 2. Lovozero. As above but after belovite; 3. Yenisei Ridge. Weathering crust of alkali syenites; 4. South Greenland. Supergene enrichment of sodalite syenite pegmatite; 5. Mongolia. Supergene enrichment after bastnaesite in alkali granosyenite; 6. Ukraine. Sumy region. From sedimentary rocks; 7. Connecticut. Encrustation on limonitic ores; A, B. Two spheroids from Fowey Consols Mine, Cornwall. Source: 1-6 Semenov (1969); 7 Hildebrand *et al.* (1957); A-B this work.

Hartley (1884) which indicated that the water was 'retained on heating to 200° or more'. Fig. 1 shows that the bulk of the water had been released by 200 °C at a heating rate of 10 °C/min. Subsequent thermogravimetric analysis showed that all the water was expelled from 5 mg of sample A after being held at 160 °C for 1 hour.

**Discussion.** Rhabdophane is usually described as a hydrated cerium phosphate with cerium as the predominant rare earth element, which implies that the others are present. Vlasov (1966) classified rhabdophane as a 'selective cerium mineral'. Whilst



it is true for many of the analyses in the literature, particularly those of rhabdophane from magmatic rocks (fig. 2), that cerium is the predominant rare earth element, this statement does not hold true universally. In sedimentary rocks (Semenov, 1959) the heavy rare earth element content of rhabdophane becomes detectable and neodymium to gadolinium and yttrium are significant. Similarly, in encrustations on limonitic ores (Hildebrand *et al.*, 1957), the amount of neodymium (38.5% of total rare earth elements) is greater than the proportion of lanthanum (27.5%) and far greater than the proportion of cerium (0.7%). Yttrium is quoted as 13%. The material from Cornwall, analysed here, bears some similarities with that from the encrustations described by Hildebrand *et al.* (1957) in that neodymium is the predominant rare earth element ( $Nd > La \sim Ce$ ) with significant quantities of yttrium (4–8%  $Y_2O_3$ ) and about 3% of each of the oxides of samarium and gadolinium.

These considerations suggest that whilst rhabdophane is frequently formed in an environment rich in cerium, and is therefore often cerium-rich, where it is formed in the presence of other rare earth elements, notably neodymium, it can just as readily accommodate those elements in its structure. Genesis, therefore, appears to be more important than the crystal structure in determining the composition of rhabdophane and the mineral should not be categorized as 'cerium selective' or 'apatite type'.

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