

154. Rare Earths in Scheelite.

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Servigne's micro-method for the detection of rare earths by their luminescence in fused calcium tungstate gave high results for the more efficient luminophores when applied to natural scheelite. Only 5% of the reported abundance of europium in scheelite from Forbes Reef was found by chemical and spectroscopic analysis. Absorption bands of neodymium are also unusually intense in this mineral.

SERVIGNE (*Compt. rend.*, 1940, **210**, 440) reports 0.05—0.1% of europium in scheelite from Forbes Reef, Swaziland. As this would constitute an unsurpassed natural concentration of europium, together with a degree of segregation from other rare earths not before observed, and as the chemistry of its isolation would be easy, his findings have been tested by direct chemical means. He employed a micro-method, photographing the luminescence spectrum of a coating of scheelite on the interior of a discharge tube with argon and mercury filling and thus excited chiefly by Hg λ 2537 (*ibid.*, 1937, **204**, 863; 1938, **207**, 905; 1939, **209**, 210; *Bull. Soc. chim.*, 1940, **7**, 121). In the last paper he claimed that in calcium tungstate, by his technique and contrary to usual experience, each of several luminophores gives a reliable quantitative indication of its abundance over a wide range of low concentrations in presence of the others. This finding for artificial scheelite prepared at 1100° was applied to 15 samples of natural mineral of which the origin would be hydrothermal or pneumatolytic. The abundance of the earths found by him throws doubt on the validity of his assumption that natural scheelite behaves similarly as a base for luminescence to the artificial product. The fact that he found both to show identical X-ray patterns is not sufficient ground for this assumption. The luminescence depends upon the presence of 10⁻³—10⁻⁵% of rare earth and upon the situation of the earths at points of lattice defect. The necessary degree of defect is therefore below anything detectable by X-ray methods. He gives the effective decreasing order of luminophore strength in artificial scheelite as follows:

	Sm.	(Eu)	Pr.	(Tb)	Dy).	(Er)	Tm).	Nd.	Gd.	
(a)	3(9)	2(6)	1(3)	(0)	(4)	(0)	(0)	(2)	(2)	
(b)	100	500	100	1	10	<1	—	—	—	× 10 ⁻⁴ %
(c)	25	25	10	10	80	15	—	50	65	× 10 ⁻⁴ %

In line (a) is given the number of times each rare earth was found by him to be the most abundant (or, in brackets, of unsurpassed abundance) in one or other of the 14 out of 15 natural scheelites which he found to contain rare earth. His estimate of the amount of each in Forbes Reef scheelite, in line (b), is compared with the author's, from chemical and spectroscopic analysis, in line (c). It is apparent from (a) that Servigne does in fact estimate those earths which he finds to be the best luminophores to be the most abundant in natural scheelites. His estimate for Forbes Reef earths differs very widely from the author's through an over-estimation of the strong luminophores. His estimates, moreover, show little of the coherence of the rare earths as a group which is always found in natural sources; *i.e.*, there is usually no great divergence from a certain proportionality between one earth and its neighbours in atomic number sequence, though the cerium or yttrium group, or even the middle members may predominate. Much the least coherent member of the group is, however, europium, which owing to its comparatively strong bivalence has become separated to the extent of about 80% in essentially rare-earth minerals, which are always of magmatic origin, and is found as a more widely distributed trace element in commoner minerals. The proportion to samarium found by the author in Forbes Reef scheelite is 80—100 times greater than in Travancore monazite and a few times greater than its probable lithospheric ratio (Goldschmidt, J., 1937, 655). Similar comparatively high europium proportions have been found in the rare earths from some pitchblendes (Marsh, *Phil. Mag.*, 1929, **7**, 1005).

Ordinarily the absorption coefficient of a rare earth is nearly constant in strength in presence of other rare earths, or in varying chemical combinations, but in Forbes Reef scheelite a much more intense absorption spectrum than usual is found. The orange neodymium bands 5850 and 5740 Å. are, for the extraordinary ray, about 20 times more intense than is usual for solution bands in this region, *i.e.*, the augmentation is of a similar order to that of the luminescent power of europium in this mineral over the artificial product.

EXPERIMENTAL.

Isolation of the Rare Earth from Scheelite.—The ground mineral was freed from magnetic impurity, treated with dilute acid to remove a little calcite, and then added (45 g.) to fused sodium hydroxide (80 ml.). The cooled mass was lixiviated, and the solution filtered. The residue was dissolved in dilute nitric acid (400 ml.) in very slight excess, and the solution decanted or filtered from a small residue. Sodium hydroxide was then added dropwise till a precipitate formed. This was taken up in nitric acid, and a slight hydrogen sulphide precipitate removed. The solution was then reprecipitated with sodium hydroxide, and again taken up in nitric acid. After two oxalate precipitations a yield of 21 mg. of rare-earth oxides was obtained.

Another 50 g. of mineral were treated with successive quantities of hydrochloric acid till it was decomposed. The acid was evaporated, nitric acid added, and this evaporated. Water was added, the solution decanted from tungstic acid, and the rare earth recovered by hydroxide and oxalate precipitations as before. This was compared by arc spectroscopy with the previous yield. The rare-earth mixtures appeared identical. The former method of isolation is to be preferred. The two yields were united and again precipitated as oxalate. Yield, 45 mg. of oxides = 0.05% in the mineral.

Spectra of the Forbes Reef Scheelite Rare Earths.—(1) *Arc.* Lanthanum and lutecium were not found and there was only a trace of ytterbium. Yttrium, gadolinium, and dysprosium were found in considerable quantity. Europium appeared to exceed 3%. Cerium, praseodymium, neodymium, samarium, and terbium were identified. (2) *Absorption.* Neodymium gave the predominant spectrum: 20 mg. of oxide in 2 ml. of solution gave absorption bands equal to 1 g./l. of neodymia in solution. The neodymium content in the rare earth is therefore 10%. Erbium and holmium absorption bands were also identified on examining 20 mg. of oxides in 0.05 ml. of solution through 5 cm.

On the basis of the spectrum analysis and on general grounds of coherence of the group the estimate (*d*) was made. A mixed oxide was then prepared from pure materials to the composition of (*d*) and its arc spectrum compared with the scheelite extract. On the basis of this comparison a revised estimate (*e*) of the composition of the scheelite extract was made, the chief difference being a reduction in the estimate for cerium.

	Ce.	Pr.	Nd.	Sm.	Eu.	Gd.	Tb.	Dy.	Ho.	Y.	Er.
(<i>d</i>)	15	2	10	5	5	12	2	12	2	32	3 %
(<i>e</i>)	7	2	10	5	5	14	2	15	2	35	3 %

Luminescence of Scheelites.—A comparison of the cathodoluminescence of a number of scheelites was made with the aid of a Hilger constant-deviation spectroscope in order to determine if the Forbes Reef scheelite used by Servigne and by the author had comparable luminescent properties. The most striking feature found in the Forbes Reef luminescence was a pair of narrow bright red emission bands 6160 and 6120 Å, identified as due to europium. They were less brilliant in a Rhodesian scheelite but were not seen in samples from Cumberland, Nevada, Bern, Bohemia, Piedmont, and Rhodesia (Mazoe Mine). They establish the similarity of the author's sample to Servigne's. The Forbes Reef scheelite gave the brightest luminescence of any sample examined. Observations on Bohemian and Piedmont specimens confirmed that the author's technique, although different from Servigne's, gave indications of similar relative abundances of the rare earths, *e.g.*, high samarium but little europium in the Piedmont specimen, and not much rare earth in the Bohemian specimen.

Absorption Bands of Scheelite.—The absorption bands 5850 and 5740 Å. for the extraordinary ray found by Becquerel (*Ann. Chim. Phys.*, 1888, **14**, 170) were detected in 1.6 mm. of Forbes Reef scheelite. In solution the minimum concentration which the same spectroscope could detect was 1 g./l. of neodymia in 1 cm. thickness. The neodymium content of the scheelite has been shown to be 5×10^{-3} %, or 3×10^{-1} g./l., and the bands were detected in 1.6 mm., equivalent to 1 cm. of 0.5×10^{-1} g./l., or 20 times less than the minimum required for detection in solution.

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