An occurrence of vanadiferous nodules in the Permian beds of South Devon.

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THE object of this note is to place on record an interesting occurrence of vanadiferous nodules on the coast of South Devon. I have to thank Lord Clinton, the owner of the property on which the nodules occur, for the assistance and encouragement he has given me in this matter, and Lieut.-General Sir William Furse, the Director of the Imperial Institute, for kindly arranging to have chemical analyses carried out by Miss Hilda Bennett in the Institute Laboratory. I also have to thank Mr. Thomas Crook, of the Imperial Institute, for the trouble he has taken to write up this short paper on the basis of my notes and the laboratory work done at the Institute.

The nodules referred to above are to be found in the red marls immediately underlying the Budleigh Salterton pebble bed,[1] to a depth of at least 400 feet; they are also to be seen in the red clay on the beach as waterworn specimens. On the cliff face they stand out clearly as dark cores surrounded by aureoles of greenish clay. In the natural section provided by the cliff face they are traceable for about half a mile on either side of Straight Point, with a maximum development west of the base of West Down Beacon, near Budleigh Salterton. Inland, the principal exposure is in Mr. F. E. Carter's brickfield in Withycombe Raleigh parish, about $1\frac{1}{2}$ miles from the coast; and it seems not unlikely that the nodules occur over the whole area between these exposures, viz. at least 1,000 acres.

Where the nodules are found in landslips or wet ground, the aureole is no longer observable, and the nodule itself becomes a pulverulent

[1] In the Geological Survey memoir and map (Sheet 339, 1913) the Budleigh Salterton pebble bed marks the base of the Trias, and the underlying red marls are mapped as Permian. Some authors (e.g. H. B. Woodward, Geology of England and Wales, 1887, p. 235, fig. 36) have included these red marls in the Trias.

sandy ball of a sepia colour. In the white sandstones which occur interbedded with the marls, nodular sepia banding may be seen. Stored under conditions of dryness, the dark portions of the nodules develop a yellow bloom.

The nodules are small in mass in proportion to the mass of the clays in which they are embedded, but they are easily distinguishable by the bleached aureoles surrounding them. As the cliffs break away by weathering, the nodules are lost or redistributed in the beach accumulations, while new nodules are exposed. Bleached beds resembling the aureoles extend for long distances. They can be seen at Exmouth, Lympstone, Woodbury, and Exeter in one direction, and at Ottery St. Mary in Triassic beds to the east.

Fossiliferous strata, in which the fossils are now represented almost wholly by casts of molluscs, form part of the nodule-bearing beds. The position and growth of any nodule appears to have no direct connexion with the position of any fossil. The fossiliferous strata have so far been observed to have a thickness of about fifty feet, but they may be much thicker.

The nodules are often roughly spherical in shape, with dark surface ribs, and in appearance often look like the crowns of sea lilies. When broken they show a roughly concentric structure, ill-defined blackish shells alternating with shells of light-coloured material. Radiating planes of the blackish material traverse the shells and stand out as ribs on some of the nodules. The nodules are of various sizes from finely disseminated bleached spots to large balls. The largest so far found was spherical in shape; it measured eight inches in diameter and weighed twenty-one pounds.

A specimen (fig. 1) examined at the Imperial Institute was spherical in shape and about four inches in diameter. When cut hemispherically it showed a blackish nucleus followed by a shell of light-coloured material. This was succeeded by a shell about half-an-inch thick of blackish material, from which bands of roughly the same thickness radiated outwards, appearing as ribs on the surface.

Two samples were prepared from this specimen, one of the light-coloured and one of the blackish material, and these gave the following analyses (p. 612).

The analyses show that the material of the nodule consists essentially of indurated siliceous clayey material. The light-coloured portions contain appreciable amounts of lime and carbon dioxide as compared with the blackish portions, these together with silica

making up most of the defect of vanadic oxide shown by the light-coloured as compared with the blackish material. No appreciable amounts of lead, copper, sulphur, or phosphorus appear to be present

FIG. 1. Vanadiferous nodule (sawn in half) from the shore west of Budleigh Salterton, South Devon. (Actual size.)

in the nodule examined, and the comparative percentages of iron oxide, magnesia, potash, and soda in the two different portions analysed do not indicate a state of combination with the vanadic oxide. The lime, which is concentrated in the light-coloured portion of the nodule, is largely if not wholly present as calcium carbonate. It would therefore appear that the vanadium is present as an impregnation of vanadium oxide, possibly hydrated.

Analyses of Vanadiferous nodule.

(By Miss Hilda Bennett, M.A., B.Sc., A.I.C.)

		Blackish portion.	Light-coloured portion.
Silica	SiO_2	51·86	59·05
Titanium dioxide...	TiO_2	0·71	0·88
Alumina	Al_2O_3	14·16	15·14
Vanadium as pentoxide	V_2O_5	13·96	1·91
Iron as ferric oxide	Fe_2O_3	2·32	2·85
Cobalt and nickel oxides ...	CoO, NiO	0·18	0·06
Manganous oxide...	MnO	trace	not detected
Lead oxide	PbO	not detected	—
Copper oxide	CuO	trace	—
Magnesia	MgO	2·85	2·47
Lime	CaO	0·70	3·06
Soda	Na_2O	0·56	0·88
Potash	K_2O	4·60	4·86
Carbon dioxide	CO_2	0·38	2·54
Sulphur (soluble in acid) ...	S	0·08	—
Combined water	H_2O+	4·16	3·58
Moisture	H_2O-	3·98	2·16
		100·50	99·44

The red clay surrounding the nodules when digested with strong hydrochloric acid leaves a large white residue, and the solution was found to contain, besides iron, V_2O_5 0·17% of the mass of the clay. This determination was made by Hillebrand's volumetric method by Mr. M. H. Hey in the Mineral Department of the British Museum on material collected by Dr. L. J. Spencer from the cliffs west of Budleigh Salterton. The material so tested was taken from a specimen showing a green-black nodule 1½ cm. in diameter surrounded by a pale-green halo 4¾ cm. across. The bleached circular area shows a sharp line of demarcation from the surrounding red clay, the contrast being very striking. The mass of indurated red clay is speckled through with minute pale-green circular areas usually less than 1 mm. in diameter.

Occurrences of vanadiferous impregnations of a closely similar character have been recorded from the Permian shales at Ölsnitz and other localities in Saxony by R. Schreiter.[1] The dark material on analysis gave V_2O_4 14·93, V_2O_3 1·42, FeO 1·60, H_2O 8 – 9 % together

[1] R. Schreiter, Vanadiumoxyde im sächsischen Rotliegenden und ihre Bleichungswirkung. Jahrb. Berg- und Hüttenw. Sachsen, 1927, vol. 101, pp. A 49–A 69. See also Centr. Min., Abt. A, 1925, pp. 143, 214, 242. [Min. Abstr., vol. 3, p. 554.]

with silica, alumina, &c.; and the pale-green bleached aureoles gave V_2O_5 0·1 to 2·4 %; whilst the surrounding red shale contains V_2O_5 traces to 0·1 %.

The bleached patches, often concentrically zoned with the dark material, examined by Schreiter, were attributed by him to the reduction of iron in the presence of the lower oxides of vanadium. Other explanations that have been invoked to account for the concentric banding are rhythmic precipitation in a colloidal medium, and radioactivity effects. In this connexion it should be mentioned that the South Devon nodules are very slightly radioactive, but no thorium or other rare-earths were found on analysis, and the percentage of uranium oxide (U_3O_8) in one nodule examined amounted to only 0·07 per cent. of the whole nodule. The effect on a photographic plate showed a concentric arrangement, and the radioactive portions appeared to be at the margins of the light and dark material.

This occurrence of vanadiferous nodules is of some economic interest, as vanadium minerals are of sparse distribution. A considerable amount of the nodules could no doubt be obtained as a by-product in working the clays in which they occur, which clays are used for brick-making. The occurrence is therefore worth investigating as one of possible emergency value from the economic standpoint as a source of vanadium. In any such investigation that may be carried out, attention should also be given to the Exeter shales, the nodules from which exhibit concentric banding in a still greater degree than those shown by the nodules occurring in the marls.