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A new occurrence of vanadium minerals in Leicestershire

ROBERT J. KING
Department of Geology, The University, Leicester
JOHN A. DIXON
Geological Survey and Mines Department, Entebbe, Uganda

SUMMARY. Two vanadates, tangeïte and volborthite, new to Britain, their association with vanadiferous nodules, and their geological environment are described. A percentage composition graph for vanadium taken across a vanadiferous nodule, by scanning electron probe, is given.

VANADIUM minerals are rare in Britain. Vanadinite, $Pb_5(VO_4)_3Cl$, was first discovered by Johnston (1831) in the Wanlockhead mining district of Dumfriesshire; it was by his account comparatively plentiful and specimens appear in most large mineral collections. Mottramite, $Pb(Cu, Zn)VO_4OH$, first described by Roscoe (1876, p. 111), was so named after its considered origin at Mottram St. Andrews in Cheshire. Though vanadium does occur in the Lower Keuper Sandstone of the Alderley Edge area of Cheshire, of which Mottram St. Andrews is considered to be geologically a part, the minerals present have not yet been specifically identified. It was suggested by Kingsbury (1956) that Roscoe's mottramite probably originated at Pim (or Harmer) Hill in Shropshire where the mineral does occur.

Vanadinite, mottramite, and descloizite, $Pb(Zn, Cu)VO_4OH$, have been described by Kingsbury and Hartley (1956) from the Caldbeck Fells area of Cumberland. Metatyuyamunite ($Ca(UO_2)_2(VO_4)_2 . 5\text{–}7H_2O$) was claimed to form efflorescences on vanadiferous nodules from the Permian of Budleigh Salterton in Devon (Wyley, 1961), but there is some doubt about the identification of the vanadate present and the efflorescence was more probably pascoite, $Ca_2V_6O_{17} . 11(?)H_2O$ (Mr. P. G. Embrey —personal communication).

Apart from the occurrences of vanadiferous nodules in 'red beds', the writers are unaware of any other occurrence of vanadium minerals in this country, and now place on record an occurrence in Leicestershire of tangeïte, $CuCaVO_4OH$, and volborthite, $Cu_3(VO_4)_2 . 3H_2O$, not hitherto described from Britain.

Geology. In the pit worked by the Butterley and Blaby Brick Company Limited at Glen Parva in Leicestershire (SP563987), a maximum thickness of 11 m of Keuper Marl and up to 6 m of Drift deposits (Rice, 1968*a*) is exposed. The Triassic deposits are made up of red flat-lying dolomitic clays, with interbedded greenish-grey 'skerry' bands, and an argillaceous sandstone of varying thickness. The Pleistocene deposit contains much Triassic debris, including blocks of Rhaetic limestone, and is thought by Rice (1968*b*) to be older than the Chalky Boulder Clay. The exact position of the Keuper Marls exposed in the pit within the Upper Triassic succession is unknown. The Tea Green Marls, the highest unit of the Keuper, are not seen but, as the postulated position of the Rhaetic escarpment lies 1·7 km to the east, it is most likely that they occur high in the succession. Following Warrington's recent correlative work on Upper Triassic stratigraphy (1970), it is possible that the marls belong to the Trent Formation of the Keuper Marl Group (Elliott, 1961), formerly the Very Gypsiferous Marls of Bosworth (1912), which are of Upper Keuper age.

A large lens of pink gypsum, 127 m in length and 2·5 m in thickness, appears 1·5 m below the base of the overlying Boulder Clay on the north-east face of the pit. Repeated solution and recrystallization of the gypsum is apparent from the presence of tiny single crystals and veinlets of fibrous gypsum on joint surfaces of the marl below the lens. Vanadiferous nodules, similar in form to those found in the Upper Keuper Marl in Worcestershire (Friend and Vallance, 1939) are abundant in the pit. Their association with the gypsum is of particular significance to the formation of the vanadates described below.

The vanadiferous nodules. The occurrence of black vanadium-bearing nodules is a common feature of red beds of Upper Carboniferous, Permian, and Triassic age in Britain. The presence of vanadium was first detected by Crookes (Barrow *et al.*, 1919, p. 116) in nodules of this type occurring in the Etruria Marls (Upper Coal Measures) of the South Staffordshire Coalfield: other occurrences of vanadiferous nodules in the Midlands have been described by Friend and Vallance (1939) and Ponsford (1954). Carter (1931) proved the presence of uranium in similar vanadiferous nodules in the Permian Marls of South Devon, and this work was amplified by Perutz in 1939.

The nodules, whatever their geological provenance, are usually black and are remarkably similar in form, being characteristically spherical, surrounded by grey-green aureoles, which are probably the product of some reduction process. The size of the nodules varies from 1 mm to 300 mm, and the width of the surrounding spherical aureole is in proportion. The most spectacular occurrence is that of Budleigh Salterton, where the nodules attain their greatest size. The vanadium in the black nodules and in certain of the greyish areas has most commonly been calculated as V_2O_5, and varies somewhat in amount. Carter (1931) published an analysis showing 13·96 % V_2O_5 in the black central portion of a nodule. Friend and Vallance (1939) demonstrated the presence of 5·6 % V_2O_5 in nodules in the Keuper Marl of Worcestershire, and in the grey centres of some of the nodules as much as 8·6 % V_2O_5.

Similar nodules occur in the Keuper Marl of Leicestershire in several localities, especially in the Very Gypsiferous Marls of the Upper Keuper. At Glen Parva the black nodules reach a size of 28 mm. They are characteristically surrounded by a greyish zone, which merges into the more typical green ferrous iron aureole. Analyses by the A.R.L. 29 000B Direct Reading Spectrometer on the grey and black portions of four of these nodules showed a variation of 5·1–6·4 % and 4·0–5·1 % V_2O_5 respectively. No trace of nickel could be found, nor was any radioactivity detected. The form these nodules take at Glen Parva is most commonly almost perfectly spherical, but some, as in fig. 1, are 'double-yolked', and consist of an ellipsoid, outlined with a black rim, containing black sub-spherical hard nodules. Each nodule and the outer ellipsoid are surrounded by greyish zones and the whole is enclosed by a characteristic green reduction aureole.

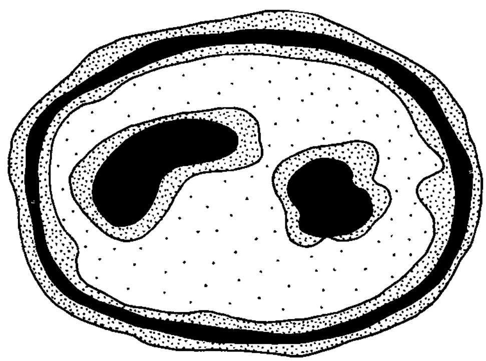

FIG. 1. Section of 'double-yolked' vanadiferous nodule showing inner black kernels and rim, and the distribution of greyish areas (stippled) × 8. The diameter of the surrounding aureole of green reduced marl is 27·5 mm.

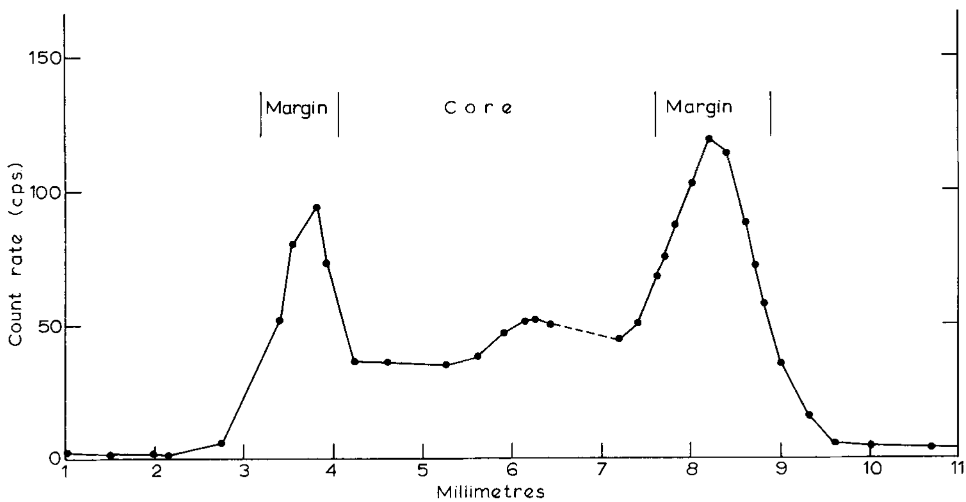

FIG. 2. A.E.I. Scanning Electron Probe traverse for vanadium across a typical nodule.

Fig. 2 shows the result of traversing across a nodule for vanadium with an A.E.I. Scanning Electron Probe Microanalyser. The marly nature of the rock precluded any polishing of the specimen and consequently the results are only qualitative. They are interesting in that a narrow marginal zone of the nodule has a vanadium content two or three times that of the core. To even out the effect of the surface irregularities of the specimen each analysed point is based on the integrated count-rate from an area 0·4 mm square.

The vanadates. Two minerals, tangeïte and volborthite, have been specifically identified from the Butterley and Blaby Pit. During a visit to the pit in 1965 a very small showing of brightly coloured green and yellow encrustations was seen on the northern extremity of the gypsum lens. The intimate associations of the encrustations with the already identified vanadiferous nodules and with the gypsum led the writers to suspect the presence of calcium vanadates. Qualitative analysis by the Scanning Electron Probe confirmed the presence of vanadium and calcium, and also the unsuspected presence of copper. The two distinct differently coloured encrustations were carefully separated and hand concentrated and an X-ray powder photograph taken of each. The two photographs were then compared against material[1] kindly provided by the Department of Mineralogy of the British Museum (Natural History) and the suspected identifications of tangeïte and volborthite confirmed.

Both minerals occur in a variety of associations: as encrustations on the surfaces of vanadiferous nodules; in the form of shell-like, multi-coloured encrustations, obviously the relics of former vanadiferous nodules; on the etched surfaces of gypsum; and on small-scale joints in the marl in the immediate vicinity of a nodule. Macroscopically the vanadium-bearing material, apart from the black nodules, appears to be an indiscriminate mixture of the two minerals, shown by the colour variation. Under the microscope sponge-like reniform masses of pale bluish-green tangeïte are seen to be rimmed by crusts of yellowish-green volborthite. The latter may also form small irregular patches (1 to 2 mm) encrusted on the tangeïte. In both cases the volborthite appears to have been the last to crystallize and is probably the more mobile of the two minerals, or at least stayed in solution the longest.

The critical factor in the genesis of the two vanadates is apparently the association of vanadiferous nodules, lenses and veins of gypsum, and the presence of copper in the Keuper Marls. The presence of the latter was proved by qualitative analysis, but only in the general area in which the nodules were formed. There is a ready source of calcium sulphate in solution from the etching of the primary gypsum by meteoric waters, and leaching of the vanadiferous nodules is obvious from the way they become carious and shell-like, by the same mechanism. There is thus the ready availability of the three essential elements in an environment suitable for the precipitation of the two minerals tangeïte and volborthite.

Specimens from this occurrence showing both tangeïte and volborthite are lodged in the collections of the British Museum (Natural History) and in the geological collections of the University of Leicester (Acc. Nos. 52625–7).

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[1] Volborthite, Paradox Valley, Colorado, B.M. 1909, 681. Tangeïte, Tyuya-muyun, B.M. 1930, 90.

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