# *A galena–wulfenite–uraniferous-asphaltite horizon in the Magnesian Limestone of Nottinghamshire.*

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*Summary.* The top 2 inches of the Lower Magnesian Limestone is feebly but persistently mineralized along its outcrop from Nottingham to Doncaster, predominantly with galena and a little cerussite, frequently with uraniferous asphaltite containing 0·2 to 1 % $U_3O_8$. Wulfenite, both platy and pyramidal in habit, occurs at Bulwell and Kirkby in Ashfield. The mode of formation and the age of these minerals are discussed.

THE Permian rocks of northern England have long been known to contain small amounts of metallic sulphides, principally galena, blende, and pyrite, and while studying these, some ten years ago, a rather persistent galena horizon was recognized in the topmost inch or two of the Lower Magnesian Limestone, immediately below the impervious cover of the Middle Marl. Galena was seen at most of the accessible exposures of this horizon between its commencement at the Zechstein shoreline in Nottingham and the Don Valley near Doncaster, a distance of 40 miles. In 1958, while re-examining specimens of these rocks, two rather unexpected discoveries were made; firstly a black asphaltic mineral that often accompanied the galena was found to be radioactive, and secondly small crystals of wulfenite were recognized in several specimens. A few days' fieldwork in 1959 showed that both these minerals were fairly persistent in the Nottingham area, and the present paper is intended to bring these facts to the attention of those interested in the origin of English metalliferous deposits and in the peculiar geochemistry of Permian rocks. It should be added that the mineralization so far encountered is extremely low grade, nowhere approaching anything of economic interest, and the wulfenite crystals are very small.

## *Distribution and field relationships.*

From the Geological Survey maps (10-mile, 1-inch, and 6-inch scales) the junction between the Lower Magnesian Limestone and the Middle

Permian Marl can be traced with precision from Nottingham northwards for 80 miles to Ripon, but exposures are rather few and often only temporary. Those yielding the minerals discussed here will be described in order from south to north, and defined by National Grid references.

*Bulwell, Nottingham.* At Bulwell Pottery (43/533452) the Middle Marl is worked for the manufacture of flower-pots, and formerly it was the practice to weather the clay by spreading it on the flat-lying surface of the Magnesian Limestone from which the Marl had previously been cleared. In 1950 three of these old weathering floors provided excellent exposures of the mineralized top layer of the Magnesian Limestone, everywhere showing a small percentage of finely disseminated galena. Adjacent to the Pottery, to the north-east, two limestone quarries also exposed its mineralized top surface, and altogether continuous mineralization was indicated over an area of 500 by 200 yards. At present, two of the old floors having been permanently filled over, the galena horizon is seen only in one old floor, north-west of the pottery kilns, and in the top of the Thames Street quarry barely 100 yards east of the kilns. Both exposures yield wulfenite and radioactive asphaltite.

The top layer of the Magnesian Limestone is here a hard, light brown dolomite, from 1 to 3 inches in thickness, which breaks away from the somewhat softer dolomite below at a very thin clay parting. Its upper surface is compact and non-porous, but below this skin the rock is frequently fissured horizontally and composed of a porous mass of dolomite rhombs up to 1 mm. across. Galena occurs thinly disseminated through this granular dolomite, sometimes accompanied by minute crystals of cerussite, sometimes by wulfenite, and very rarely by traces of barytes and specks of malachite. Pyrite and blende are never visible in this layer, although they occur frequently in the deeper parts of the Thames Street quarry about 40 feet below this horizon, and there are no rhombohedral carbonates later than the rock-forming dolomite.

Here and there thin stringers of asphaltite are visible on the top surface of the dolomite, often in an irregular reticulate pattern (see fig. 1), but these extend downwards into the dolomite for only a few millimetres. Isolated specks and blebs of asphaltite also occur sparingly in the top 2 inches of the dolomite, some intimately associated with galena, others apparently free from it. The asphaltite is radioactive to a variable degree, but although hand specimens in a shielded geiger counter show moderate radioactivity, the asphaltite content of the layer is insufficient to allow of its detection with a field ratemeter.

The content of galena varies from mere traces to a few % at points only a few inches apart, and so, to ascertain the average grade at this locality, one of the old weathering floors was sampled systematically to a depth of about 2 inches over an area of 1 500 square yards. Analysis of this average sample indicated 0·65 % Pb, 0·03 % $MoO_3$, 0·01 % Cu, trace Zn, very approximately 0·0005 % $U_3O_8$, and approximately 93 % carbonates (largely dolomite), 5 % quartz as rounded sand grains, a little

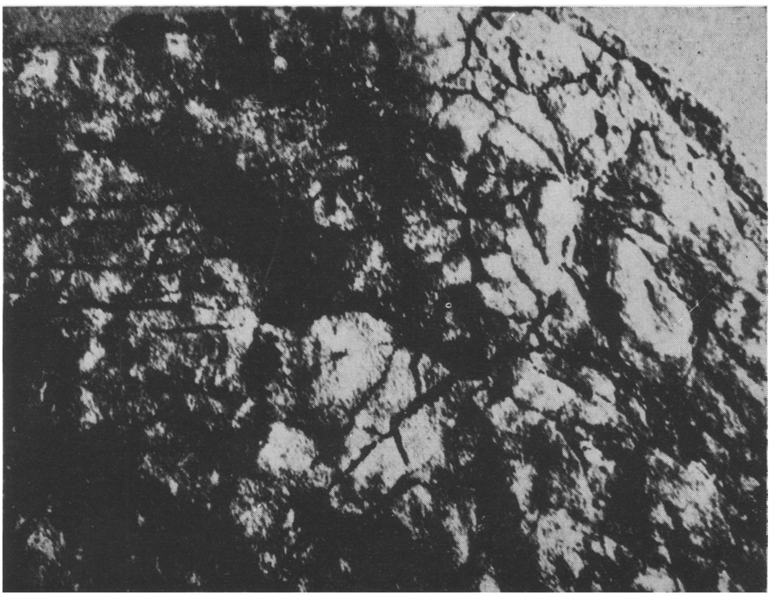

FIG. 1. Stringers of asphaltite on top surface of Lower Magnesian Limestone, Bulwell. Half natural size.

clay, and fractional percentages of asphaltite and barytes. The lead occurs very largely as galena, and cerussite is apparently a little more abundant than wulfenite.

About 1 mile north-east of the pottery the galena horizon was encountered at a depth of 20 feet in a water boring at Springfield (43/545463), and yielded rather coarse galena (up to 4 mm.), cerussite, a little wulfenite, and some asphaltite, all in reddish dolomite in the first 2 inches below the red Middle Marl.

*Papplewick and Newstead.* There are very poor exposures of the dolomite-marl contact in two overgrown quarries in this area, some 4 miles north of Bulwell. The first, a flooded quarry 500 yards north-west of Papplewick Hall (43/545520), has yielded galena, cerussite, chalcopyrite, and traces of malachite. The second, in Limekiln Wood, Newstead (43/536531), yielded galena, traces of wulfenite, and a little asphaltite.

*Kirkby in Ashfield.* At the northern end of Annesley long railway tunnel (43/504550), at the classic Permo-Triassic section described by Sherlock (1911, fig. 2, pp. 80 and 82), the top surface of the Lower Magnesian Limestone is now well exposed for a distance of 400 yards in broad benches along both sides of the cutting. The top layer of the dolomite is a dense fine-grained rock, but contains numerous very small cavities which may possibly be moulds of fossils. Galena is present only in traces, and would pass unnoticed unless carefully sought, but close inspection reveals frequent tiny spherules of malachite, small plates of wulfenite noticeable by their lustre, and occasional asphaltite.

*Mansfield and Shirebrook.* There are good exposures of the top of the Magnesian Limestone in the Mansfield White Stone quarries (43/534601), but usually it is not mineralized. In 1950, however, in one area, the top few inches consisted of a hard impervious dolomite cemented by white barytes and containing grains of black asphaltite, since found to be radioactive. Galena has not been seen here, but was recorded at this horizon 4 miles to the NNE. in Clipstone Colliery sinking at a depth of 385 feet (see Edwards, 1951, p. 157). Farther north, near Shirebrook, there are now few good exposures of this horizon, but in a railway cutting east of Shirebrook Station (43/536678) traces of asphaltite were seen.

*Occurrences farther north.* The occurrences in Yorkshire deserve brief mention here, as they indicate the wide distribution of galena and asphaltite at this horizon. Wulfenite is not yet known in this county. A little galena was seen in the top of the dolomite at a temporary exposure 500 yards ESE. of Woodsetts cross-roads (43/557836). This was the only exposure for many miles, but they become frequent to the south-west of Doncaster. Old workings at New Eddlington brickworks (43/531987) show the top of the dolomite with rather frequent stringers of radioactive asphaltite, rather less radioactive than at Bulwell, and much disseminated galena accompanied by calcite. The overlying marl, seamed with gypsum and containing marl pseudomorphs of halite hopper crystals, is feebly radioactive, but this may be largely due to the fact that it contains 5 % $K_2O$, like the Triassic marls described by Ponsford (1955, p. 40). Railway sections north of Warmsworth (44/543009) and at Sprotbrough (44/534017) as described by Mitchell (1947, p. 115) also show persistent galena below the Marl contact, usually with traces of asphaltite, and in the excavation of the Doncaster Bypass in 1959 similar occurrences were seen in Cusworth Park (44/542035).

*Notes on the minerals.*

*Galena.* The galena is largely disseminated through dolomite and is anhedral, but in cavities it has the common cubo-octahedral forms. Although the majority is unaltered, at several localities some of the crystals are corroded and may then have a sugary coating of cerussite crystals, the latter in a few cases encrusted by wulfenite, clearly indicating the sequence galena, cerussite, wulfenite. In concentrating these minerals it was noted that the galena was diamagnetic. Traces of copper minerals accompany the galena in Nottinghamshire, and in one case mineragraphic study revealed chalcopyrite intergrown with galena and later replacive covelline and chalcocite, but these features have yet to be studied in detail.

Spectrographic analyses of three samples of the galena were made by E. M. El Shazly in 1950 during a comparative study of trace elements in British sphalerites and galenas. These, like others from the Magnesian Limestone, were found to be characterized by much lower contents of antimony and silver than galenas from the Pennine ore deposits, as shown by the following figures recorded by El Shazly, Webb, and Williams (1957, p. 261):

| *Galena sample* | Sb (*p.p.m.*) | Ag (*p.p.m.*) |
|---|---|---|
| Magnesian Limestone/Marl contact: | | |
| Springfield, Bulwell (*a*) | 10 | 10 |
| ,, ,, (*b*) | 30 | 10 |
| New Eddlington | 20 | 15 |
| Pennine Ore Deposits: | | |
| Northern Pennines, average of 9 | 510 | 65 |
| Derbyshire, average* of 4 | 200 | 25 |
| Mill Close Mine, Darley Dale | 100 | 10 |
| Stars Wood, Ashover ... | 10 | 5 |

* Including Mill Close Mine and Stars Wood.

While the contrast with the Pennine averages is very marked, the Derbyshire samples include some, the last two listed above, rather similar to those from the Magnesian Limestone. Of the other trace elements detected, Ba, Sr, Ti, and V are probably largely present in contaminating dolomite and marl, and Cu in sulphides; these do not call for comment, but it is of interest to note that 30 p.p.m. Mo were recorded in Bulwell galena (*a*), presumably from a trace of wulfenite, and that this was the only case in which molybdenum was detected in the seventy-seven British galenas examined.

*Cerussite.* The crystals are very small, colourless, grey, or white, and

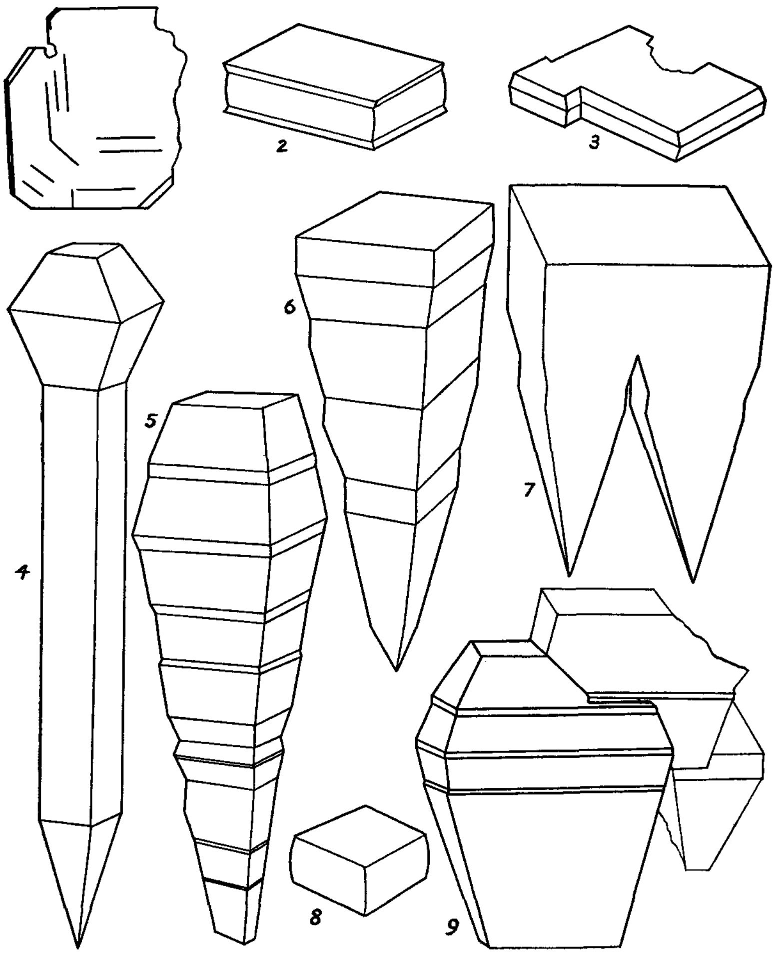


FIG. 2. Sketches of wulfenite crystals from Nottinghamshire. No. 1, Kirkby in Ashfield. Nos. 2–9, Bulwell.

| No. ... ... ... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Size in mm. ... | 1 | 0·3 | 1 | 0·6 | 0·4 | 0·25 | 0·45 | 0·5 | 0·4 |

often twinned. It is nearly always closely associated with galena, whereas the wulfenite frequently occurs quite independently of the sulphide. Rarely wulfenite coats cerussite, and the converse has not been observed.

*Wulfenite*. Although small, the wulfenite crystals display a variety of habits comparable in many ways with those from Struy, Inverness, described by Russell (1946), and from the classic Carinthian localities.

Platy crystals, the only type previously known from English localities, are common, often paper-thin and cream, buff, or pale greenish yellow in colour. Being basal plates they show perfect uniaxial negative optic axis figures. Thicker bevelled plates, up to $1\frac{1}{2}$ mm. across, colourless and transparent with adamantine lustre, occur at Kirkby in Ashfield (fig. 2, no. 1). At Bulwell pyramidal and prismatic forms (usually multiple combinations of both) are plentiful. These crystals are always pale, often of the same cream or buff colour as the dolomite on which they lie, and as they frequently show little lustre they are easily overlooked. A test with a dilute solution of sodium sulphide, which *instantly* stains the wulfenite black, is very effective in revealing these dull crystals. Although too small for angular measurements the forms appear to be the common ones, the prism {010}, pyramids {011} and {021} (in the setting adopted in Dana's System, 7th edn), and base {001}. Many small crystals at first sight appear to be simple pyramids more acute than {021}, but at high magnification are seen to be oscillatory combinations of {021} and {010}. The tapered combinations (fig. 2, nos. 5 and 6) are very reminiscent of Sir Arthur Russell's figured crystals from Struy, and the tooth-like combination (fig. 2, no. 7) of two parallel pyramids {011} terminating in a single prism {010} also matches one he describes from that locality (Russell, 1946, p. 151). The bipyramidal group, fig. 2, no. 9, is pale honey-yellow and transparent. A few squat and slightly curved prismatic crystals occur, and occasionally there are acicular prismatic crystals terminated by pyramids (fig. 2, no. 4) rather similar to some described by Schroll (1950) from Dirstentritt, Tyrol. The wulfenite is clearly the youngest mineral present in these rocks, and from its appearance might well be of very recent formation.

*Uraniferous Asphaltite.* This mineral occurs as small globular granules, or irregular blebs, or as narrow veinlets, dull black when weathered, but shiny black with conchoidal fracture and vitreous lustre when freshly broken. It is brittle, hardness lies between 2 and 3, the streak is black, and its density about 1·7. It is infusible in a Bunsen flame, and insoluble in common organic solvents. In polished section no organic structures are seen and it is clear that it is asphaltic in origin and not coalified plant tissue. The granules in some specimens from Mansfield are deeply cracked, as though by shrinkage.

From specimens from Bulwell Pottery a sample of the asphaltite was gouged out and hand picked as fragments 1 to 5 mm. across. This coarse concentrate was impure, and was therefore crushed to pass a 200-mesh sieve (75 $\mu$ openings) and centrifuged first in ethylene dibromide (sp.gr.

2·18), when galena and dolomite sank and were removed, and secondly in carbon tetrachloride (sp.gr. 1·58) in which the asphaltite sank, except for a mere trace of lighter material. The chemical composition of the inorganic constituents of the asphaltite fraction were first ascertained qualitatively by X-ray fluorescence analysis (kindly made by Dr. A. J. E. Welch), which indicated the presence of Pb, U, and Fe, minor amounts of Cu, Ni, Zn, and Mn, but no evidence of Th, Mo, or V. Mr. R. Pickup then provided the following quantitative chemical analysis: total ash content 18·91 %, including $U_3O_8$ 0·89, PbO 3·90, $Fe_2O_3$,$Al_2O_3$ 1·72, CaO 8·08, MgO 1·32 %. Traces of Cu, Zn, Mn, and Ti were also detected.

Examination of a polished section of the asphaltite showed that in addition to sparse coarse inclusions of dolomite and galena (veined and rimmed with minor amounts of covelline), there are numerous fine inclusions from 1 to 50 $\mu$ across which must have been included in the asphaltite analysed. These inclusions consist of carbonates, galena, and numerous euhedra of pyrite, 2 to 10 $\mu$ across, sometimes replaced by hematite, but as yet no uranium minerals have been detected. X-ray powder photographs of the analysed asphaltite show a broad diffraction band in the region 4·5 Å., characteristic of amorphous hydrocarbons, and also faint lines among which can be recognized the strongest lines of galena and calcite. It is evident, therefore, that the 'ash' is largely derived from calcite, dolomite, and galena, but the manner in which the uranium occurs is still unresolved and needs further study. Provisionally it is suggested that this uraniferous asphaltite is probably akin to the thucholite complexes from older formations, as described by Davidson and Bowie (1951). It differs considerably from the various hydrocarbons and 'carbonites' found in the Derbyshire mineral veins which are far less radioactive and are interpreted by Mueller (1954) as products of hydrothermal distillation.

Radiometric assays show that the uranium content of the asphaltite varies considerably from sample to sample and place to place. Observed values are a range from about 0·5 to 1·1 % $U_3O_8$ at Bulwell, 0·25 % at Mansfield, and 0·3 % at Eddlington, Yorks. As yet there is no evidence of radioactivity in this horizon other than that associated with the asphaltite. Various heavy mineral fractions, for example, showed negligible radioactivity unless contaminated with asphaltite. The overall radioactivity of the horizon appears to be too low to be detected at outcrop with a portable ratemeter, partly because the average uranium content is extremely low, partly because of the relatively high potash content of the overlying marl (around 5 % $K_2O$).

*Comments on the ages and origins of the minerals.*

The location of this varied assemblage of minerals at this contact horizon has presumably resulted from the trapping of metalliferous solutions beneath the semi-permeable Middle Marl. Deposition occurred in at least three stages, firstly galena, then asphaltite, and finally cerussite followed by wulfenite. The galena, introduced into the dolomite after the deposition of the Middle Marl, perhaps very soon after (diagenetically perhaps), or possibly much later, must be late Permian or younger in age, and as the Derbyshire lead mineralization post-dates the dolomitization of the Carboniferous Limestone by solutions descending from the Magnesian Limestone (see Dunham, 1952, p. 415), the geological evidence suggests the possibility of a common age for both types of galena occurrence, despite their stratigraphic separation.

Dr. S. Moorbath of the Department of Geology, Oxford University, has made lead isotope analyses of a sample of the Bulwell galena, and finds it yields a model age of $200\pm60$ million years, which by current time-scales corresponds to a Permo-Triassic origin. This dating is not inconsistent with the geological evidence, but publication of further details regarding this and other British galenas must be awaited before its true significance can be assessed.

Regarding the origin of the galena in this Upper Permian horizon, there appear to be two main alternatives. Firstly, to regard it as derived from the same sources as the galena of the Derbyshire lead deposits, and of similar hydrothermal origin, although presumably deposited at lower temperatures at this higher stratigraphic level. Or secondly, to consider it as resulting from redeposition of some of the syngenetic lead that was precipitated in certain phases of Zechstein sedimentation (see Deans, 1950), but which was subject to redistribution during the complex processes of dolomitization which ensued. In this case, which the writer tends to favour, the source of the lead might either be referred to hydrothermal springs discharging into the Zechstein sea (Dunham, 1952, p. 422), or to the intense cycle of weathering and chemical sedimentation of Zechstein times. A remarkable peculiarity of this horizon is the apparent absence of zinc, for in the Magnesian Limestone as a whole lead and zinc appear to be present in rather similar amounts.

The asphaltite is younger than the galena, which it frequently encloses, but how much younger is not at all clear. Some uraniferous hydrocarbons appear to originate by adsorption of heavy metals (U, V, Cu, Ni, &c.) by the hydrocarbon, whereas others are believed to result from the polymerization of light hydrocarbons (gas or oil) about radioactive particles. The latter process seems the more probable in the present case, for the uranium is not accompanied by comparable amounts of vanadium or other adsorbed metals, and the asphaltite appears to be more akin to thucholite complexes than to the coaly complexes with adsorbed uranium such as Ponsford (1955, p. 40) has described from Gloucestershire. Provisionally it might be suggested that minute quantities of some uranium mineral were deposited in the dolomite at this contact and subsequently polymerized gas or oil as it was impounded beneath the Marl. Oilfields lie only a few miles to the east, so there is no difficulty in invoking migrating oil or gas in the small quantities sufficient to provide this asphaltite. The source of the uranium is obscure, but minor amounts of this element appear to be rather persistent in the Carboniferous rocks of this region, being recorded in phosphatic marine beds in the Nottingham–Derby coalfield, in Millstone Grit shales near Matlock, and in bituminous limestone near Castleton (Ponsford, 1955, pp. 31–34).

The cerussite and wulfenite are clearly secondary minerals, and in considering their origin one can be guided by the extensive literature on the Alpine lead–zinc–molybdenum deposits of Carinthia and the Bavaria–Tyrol border region, especially by the more recent papers of Hegemann (1949), Schroll (1953 *a* and *b*), and Meixner (1956). These classic wulfenite occurrences are widespread in a Middle Triassic dolomite formation (the Wettersteinkalk), but restricted to the oxidation zone of lead–zinc deposits. The primary lead–zinc sulphide ores are free from molybdenum, the latter only appearing later than galena, first as jordisite (colloidal $MoS_2$), which may alter to soluble ilsemannite or be partially transformed to microcrystalline molybdenite. Later, in the oxidation zone, cerussite develops, followed by wulfenite. The formation of wulfenite is ascribed to fixation in the secondary lead deposits of molybdenum derived from overlying bituminous dolomites and shales of the Trias, especially from a bituminous oolitic dolomite in the Cardita beds, which carries 50 to 400 p.p.m. Mo. In some cases wulfenite has formed in mines during the present century. The Nottinghamshire wulfenite occurrences have much in common with those of the Alps, e.g. paragenetic sequence, low silver and antimony contents of the galenas, absence of pyromorphite, &c., which suggests that the wulfenite may well be of similar origin. As yet, however, evidence of an adequate source of molybdenum in the Nottingham area is rather elusive. The Lower Lias of the Vale of Belvoir presumably carries appreciable molybdenum, for it gives rise to teart pastures, and traces of molybdenite in the Mountsorrel granodiorite are well known, but connexions with these occurrences, which are at least 15 to 20 miles distant, seem dubious. Recent analyses of two samples from closer possible source beds, the Middle Marl from Bulwell Pottery and Lower Rhaetic black shales from Owthorpe (south-east of Nottingham), showed only 6 and 11 p.p.m. Mo respectively, which again seem hardly adequate. There remains the possibility, however, that the molybdenum derives from Permian or Triassic sediments, for the Marl Slate of Durham carries high concentrations of that element (Deans, 1950, p. 348); the recent formation of ilsemannite in the Magnesian Limestone at Billingham described by Raymond (1959), and the extent of the present wulfenite occurrences, also point to such an association. Some of the Bulwell wulfenite crystals appear as though they might be of very recent origin, and this possibility is strengthened by the evidence that molybdenum is still mobile in the Magnesian Limestone at Billingham, and in the Triassic dolomites of the Alps.

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