Baryte-bearing nodules from the Middle Lias of the English east midlands.[1]

(With Plate I.)

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[Read November 25, 1948.]

Introduction.

THE Middle Lias of Rutland, east Leicestershire, and north-west Northamptonshire was described by Judd[2] in 1875 as comprising an upper ferruginous member—the Marlstone Rock Bed—and a lower argillaceous division of blue clays, often micaceous or sandy, and carrying bands of 'septaria' and of 'ironstone balls'. In the septaria he recorded the occurrence of 'specular-iron, zinc-blende and pyrites'.

During the six-inch survey of one-inch New Series sheets 157 (Stamford) and 171 (Kettering) together with the adjacent parts of sheets 156 (Leicester) and 170 (Market Harborough) a considerable area of the lower argillaceous division was mapped. These beds, about 50–80 feet in thickness, and belonging to the *margaritatus* zone can be broadly separated into an upper series of fine micaceous blue-grey silts and silty clays and a lower series of blue-grey clays. In both members the nodules described by Judd are of common occurrence. In the northern and central parts of the area under consideration the upper subdivision of silts and silty clays is succeeded by the ferruginous limestones and oolitic ironstones of the Marlstone Rock Bed (*spinatum* zone): over much of the southern part, however, the Rock Bed is absent.

Exposures in the Middle Lias silts and clays are poor. Sections described by Judd at a few small brickyards, such as those near Whissendine in Rutland and Owston and Billesdon in Leicestershire, are now almost completely obscured. Exposures are to-day almost wholly confined to small sections on the banks of the brooks and streams tributary to the rivers Welland and Eye.

[1] Published with the permission of the Director of H.M. Geological Survey.

[2] J. W. Judd, The Geology of Rutland. Mem. Geol. Surv., 1875.

Nature and occurrence of the nodules.

Fine-grained carbonate nodules occur throughout the *margaritatus* zone both as discontinuous bands and as apparently isolated nodules. The horizontal spacing between individual nodules is very variable from less than a foot up to several yards. In the limited exposures available it is not possible to establish any relation between horizontal spacing of the nodules within a band and the vertical spacing of successive bands, as has been done for the Lower Lias of the Dorset coast by Lang, Spath, and Richardson.[1]

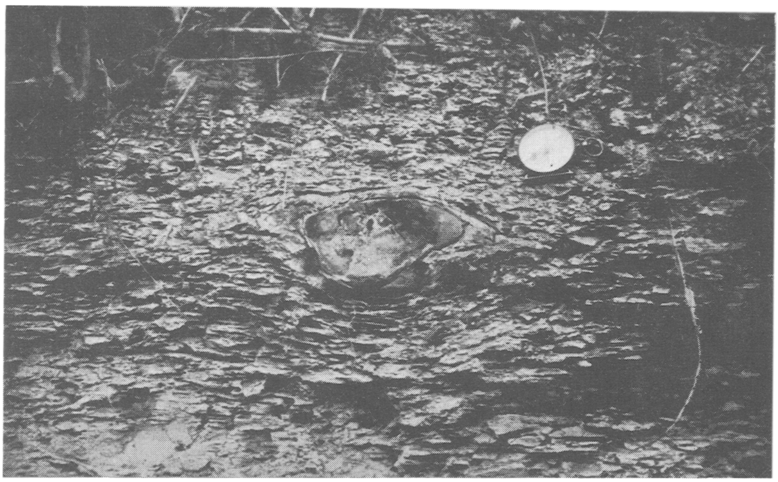
The nodules have a more or less flattened ellipsoidal shape. The ratio of the horizontal diameter to the vertical diameter is commonly between 2:1 and 3:1. Exceptionally it is as high as 4:1. As recorded by Tomkeieff[2] in the case of clay-ironstone nodules from the Coal Measures, the degree of flatness is greater in the larger nodules and the tendency is for small nodules to approach the spheroidal. The largest of the *margaritatus* zone nodules to be observed had maximum and minimum diameters of 16 inches and 4 inches respectively. In many exposures bedding planes and laminations in the Liassic silts and clays are not sufficiently obvious for their relation to the nodules to be determined. Wherever such planes are clearly distinguishable they are conformable to both the upper and lower surfaces of the nodules (text-fig. 1).

Two types of nodules are readily recognizable. The majority are of 'cementstone' type, fine-grained, pale to medium grey calcite mudstones reacting freely with cold dilute acid. Others confined largely to bands in the lower part of the zone are of 'clay-ironstone' type and consist of fine-grained iron carbonate. They are readily distinguishable from the cementstone nodules by reason of their darker grey to grey-brown colour, higher specific gravity, and resistance to dilute acid. Apart from such differences, due to the character of the carbonate present, the structure of the nodules both in hand-specimen and thin section appears to be identical. The majority of the nodules show a partially weathered and exfoliated outer skin and a central portion in which irregular septarian cracks are developed. No traces of lamination within the nodules are visible. In thin section they are seen to consist of turbid carbonate of average grain-size 0·005–0·015 mm. Through this

[1] W. D. Lang, L. F. Spath, and W. A. Richardson, Shales with "beef", a sequence in the Lower Lias of the Dorset coast. Quart. Journ. Geol. Soc. London, 1923, vol. 79, pp. 47–99. [M.A. 2–535.]

[2] S. I. Tomkeieff, On the occurrence and mode of origin of certain kaolinite-bearing nodules in the Coal Measures. Proc. Geol. Assoc. London, 1927, vol. 38, pp. 518–547. [M.A. 3–555.]

discoloured and often nearly opaque groundmass are scattered quartz grains, 0·05–0·1 mm. across and often marginally replaced by the carbonate, granular pyrite, a few flakes of white mica, occasional grains of alkali-felspar, and a varying amount of interstitial pale yellow-brown clay. Digestion of two nodules, one clay-ironstone, the other cementstone, in hot 10 % hydrochloric acid yielded insoluble residues of 10·7 %



TEXT-FIG. 1. Chalybite mudstone nodule from *margaritatus* zone clays, bank of river Welland, 1200 yards NE. by N. of church at Rockingham, Northants. Nodule shows some exfoliation consequent upon weathering. Deformation of the bedding of the Lias clays both above and below the nodule is visible.

and 28·0 % respectively. The extremely fine-grained clay constituents of these residues are difficult to identify optically. Some kaolinite appears to be present associated with material of higher birefringence (approx. 0·011). X-ray examination of one of the residues by Dr. G. W. Brindley suggested the presence of both a kaolin-type and a mica-type clay, probably in comparable proportions.

An analysis of one of the iron carbonate nodules from an exposure in the banks of a brook, 1150 yards ESE. of Whissendine station, Rutland, was carried out by Mr. C. O. Harvey in the Geological Survey laboratories (1948) and is given opposite.

Calculation of the mineral content of the rock from the analysis shows that 83·6 % of the nodule consists of carbonate of the composition indicated. No calcite or dolomite was recognized in the rock and the carbonate appears to be wholly chalybite with values of ω ranging from

1·792 to 1·832. As compared with the carbonate of a similar rock-type (chalybite mudstone) from the Northampton Sand Ironstone[1] it is richer in $MgCO_3$ and $MnCO_3$ and poorer in $CaCO_3$: the content of $FeCO_3$ and the values of ω in the two cases do not differ greatly.

TABLE I. Analysis of iron carbonate nodule from Middle Lias.

Analyst, C. O. Harvey, Geological Survey Lab. no. 1518, Microsection no. E. 22355.

SiO_2	4·72
Al_2O_3	2·45
Fe_2O_3	1·64
FeO	41·68
MgO	4·34
CaO	6·13
Na_2O	0·22
K_2O	0·27
$H_2O > 105°$ C. ...	2·11
$H_2O < 105°$ C. ...	0·38
TiO_2	0·10
P_2O_5	1·77
MnO	0·60
CO_2	33·37
SO_3	0·07
Cl	trace
F	0·03
S	0·35
Cr_2O_3	nil
Li_2O	nil
BaO*	0·01
SrO*	0·05
	100·29
O for S and F ...	0·14
	100·15

Calculated mineral composition.

Collophane ...	$Ca_3(PO_4)_2$	3·9	
Gypsum	$CaSO_4.2H_2O$ ...	0·1	
Pyrite	FeS_2	0·7	
Carbonates ...	$FeCO_3$	66·6	83·6
	$MgCO_3$	9·1	
	$CaCO_3$	7·0	
	$MnCO_3$	0·9	
Quartz	SiO_2	1·3	
Goethite	$Fe_2O_3.H_2O$ ...	1·8	
Rutile	TiO_2	0·1	
Clay residue†	... ...	8·5	
		100·0	

† Including little white mica and felspar.

Composition of carbonate.

$FeCO_3$ ...	79·7	Range of ω 1·792–1·832.
$MgCO_3$ ...	10·8	
$CaCO_3$ ...	8·4	
$MnCO_3$ ...	1·1	
	100·0	

*Semi-quantitative spectrographic determinations by Dr. J. A. C. McClelland.

The figure of 1·3 % of quartz in the Middle Lias nodule is based upon a grain count. After satisfying the P_2O_5, SO_3, S, Fe_2O_3, and TiO_2 to give collophane, gypsum, pyrite, goethite, and rutile respectively, a residue of 8·5 % is left representing clay together with small amounts of white mica and felspar. While no very accurate significance can be attached to the percentages of the remaining oxides in this residue, the occurrence of appreciable amounts of Na_2O and K_2O may be indicative of the presence of an alkali clay, possibly corresponding to the mica-type mineral suggested by X-ray examination.

[1] J. H. Taylor, Petrology of the Northampton Sand Ironstone formation. Mem. Geol. Surv.. 1949, pp. 48–50.

Minerals in the septarian cracks.

The septarian cracks range up to 15 mm. across, but the majority are less than 6 mm. wide. They are infilled, partially or completely, by one or more of the minerals calcite, baryte, pyrite, and zinc-blende. No trace of the 'specular-iron' recorded by Judd (loc. cit., p. 69) has been noted. Not infrequently successive deposition of material lining the walls of the fissure has given a banded structure to the resulting veinlet.

The commonest mineral of the septarian cracks is calcite. Many are occupied solely by this material, or by it in association with pyrite. In some cases the result is a veinlet in which finely disseminated pyrite is scattered irregularly through calcite (22356).[1] More commonly the veinlet is margined by pyrite and filled centrally by platy calcite (22357, 22362 C, 22363, pl. I, fig. 1). The pyrite margins, which range in width from 0·05 to 0·4 mm., often show good crystalline form with crystals projecting into the central calcite. Locally the margins join and for a short distance the veinlet may consist wholly of pyrite. Commonly the wall-rock on either side of the fissure is stained brown for a distance of up to 0·4 mm. away from the pyrite. The continuity of the pyrite margins to the main fissure is here and there broken by small veinlets of calcite cutting across them (22362 B, 22363, pl. I, fig. 1). No trace of marcasite is visible in polished section.

Another type of infilling consists wholly of calcite much of which has a spherulitic habit (22360–1). This consists of sheaf-like aggregates radiating from the walls of the fissure towards its centre and occupying in some cases a zone up to 3 mm. wide on either side of the veinlet. The central portion is commonly filled with clear platy calcite (pl. I, fig. 2). In some cases this central zone is absent and the two sets of radiating sheaves meet along the median line of the veinlet. In another type of infilling calcite has a prominent bladed habit developed roughly parallel to the walls of the fissure (22362 C, 22466).

Baryte[2] as an infilling to the septarian cracks, though less abundant than calcite, is widespread. Commonly it develops the typical bladed or radiating habit: occasionally it projects as euhedral crystals into cracks only partially filled. None of these varieties exhibits any trace of fluorescence. A section of a typical baryte-filled veinlet (22464, pl. I, fig. 3) shows tabular crystals projecting across the vein at right angles

[1] These numbers refer in all cases to the Geological Survey's English series of microscope slides.

[2] Spectrographic analysis by Dr. J. A. C. McClelland shows a strontium content in the baryte of approximately 2·5 %.

or obliquely. In other parts of the same septarian nodule the disposition of the laths is parallel to the walls of the fissure. In some cases (22464, 22466) single large baryte crystals occupy the full width of a veinlet. Marginal bands of pyrite are as common in the case of the baryte-filled cracks (22362, 22362 B, 22362 C) as with the calcite-filled ones.

Many septarian cracks contain both calcite and baryte. Commonly the junction between the two minerals is a sharp crystal boundary (22362 C, 22466, pl. I, fig. 4), so that a vein filled with calcite passes suddenly into one filled with baryte. In other cases (22362 B, 22362 C) a thin impersistent zone of calcite 0·01–0·05 mm. across separates marginal pyrite from central baryte. Locally the calcite cuts through the pyrite and extends into the wall-rock (pl. I, figs. 5–6). Occasionally the calcite zones on the two sides are linked by thin stringers (0·03–0·04 mm. wide) extending completely across the baryte. In 22466 calcite has infiltrated along cleavages of baryte and along junctions between individual crystals of baryte. Such examples provide clear evidence of replacement of baryte by calcite. The radiating or bladed habit exhibited by calcite in certain specimens (22360–1, 22362 C) is reminiscent of baryte, but there is no evidence to show that, in these cases, the calcite is, in fact, pseudomorphous after baryte.

Blende is also commonly present in the septarian cracks though in smaller quantity than calcite, baryte, or pyrite. Frequently it occurs as small triangular crystals or in aggregates of crystals growing like the teeth of a saw on one side of a common base line. These bodies are enclosed either in calcite (22358, 22364, 22465, 22467) or in baryte (22362 B, 22464). In one case (22362 B) some of the blende is clearly following cleavages in the baryte and locally blende is separated from baryte by a thin zone of calcite in exactly similar manner to that in which pyrite is separated from blende in the same specimen. No trace of blende following cleavages in the calcite was ever seen and it appears that none of the blende post-dates the calcite.

Origin of the septarian nodules and associated minerals.

The conformability of the bedding planes of the Lias to both upper and lower surfaces of the nodules, the flattened form of the nodules and their repeated arrangement in well-marked layers are suggestive of an origin subsequent to the deposition of the enclosing sediments.[1] They may well, however, have been formed at an early stage in the compaction

[1] W. A. Richardson, The relative age of concretions. Geol. Mag. London, 1921, vol. 58, pp. 114–124. [M.A. 1-399.]

of the Lias clays and silts by some form of colloidal segregation in the manner suggested for the clay-ironstone nodules from the Coal Measures by Tomkeieff (*loc. cit.*) and by North and Howarth.[1] Presumably the formation of calcite or chalybite in the nodules was controlled by the relative abundance of the hydrosols of Fe, Ca, and Mg at different horizons in the sediments. Gradual recrystallization of the nodules from outside with desiccation of the centre in the manner postulated by Richardson[2] would give rise to the system of septarian cracks.

The infilling of the septarian cracks was evidently a consequence of waters circulating through the nodules and depositing in cavities any substances present in a state of supersaturation. There seems little reason to doubt that these substances were derived from the surrounding sediments. The Middle Lias silts and silty clays are both calcareous and pyritic. Spectrographic examination of three samples from the *margaritatus* zone by Dr. J. A. C. McClelland have given the following semi-quantitative results:

Sample no.	Locality.	Percentages. Ba.	Zn.	Pb.
644	Ashwell railway cutting, 1150 yards NE. by N. of Westfield House, Rutland. Silty clay ...	0·02	0·05	0·03
673	Ashwell railway cutting, 1260 yards NNE. by N. of Westfield House, Rutland. Clay ...	0·02	trace	0·04
684	Bank of river Welland, 1200 yards NE. by N. of Rockingham church, Northants. Clay ...	0·02	trace	0·04

The figures for Ba are actually less than Goldschmidt's average for the earth's crust[3] of 390 gm. per ton (= 0·038 %) or Clarke's average for 78 shales[4] of 0·05 % BaO (= 0·045 % Ba). The Zn percentage of 0·05 from sample 644 (silty clay) is well above the figure of 40 gm. per ton (= 0·004 %) given by Goldschmidt for the average of the earth's crust,[3] and also that of 0·01 % for sedimentary rocks in general recently quoted by Guimaraes.[5] Many sediments are, however, considerably richer in

[1] F. J. North and W. E. Howarth, On the occurrence of millerite and associated minerals in the Coal Measures of South Wales. Proc. S. Wales Inst. Eng., 1928, vol. 44, pp. 325–348. [M.A. **4**–84.]

[2] W. A. Richardson, On the origin of septarian structure. Min. Mag., 1919, vol. 18, pp. 327–338.

[3] V. M. Goldschmidt, The principles of distribution of chemical elements in minerals and rocks. Journ. Chem. Soc. London, 1937, pp. 655–673. [M.A. **7**–165.]

[4] F. W. Clarke, The data of geochemistry. 5th edit., Bull. U.S. Geol. Surv., 1924, no. 770, p. 30.

[5] D. Guimarães, Mineral deposits of magmatic origin. Econ. Geol., 1947, vol. 42, p. 733.

zinc than this figure indicates, as has been made clear by Goldschmidt.[1] The Pb percentages from the Middle Lias sediments (considerably in excess of Guimarães's average for sediments of 0·0016 %) are of interest in view of the fact that no trace of galena has been found in any of the nodules examined.

From the observed relations of the minerals in the septarian cracks it is evident that pyrite, which so commonly lines the walls of the fissures, was the earliest to be formed. It seems probable that there was considerable overlap in the periods of deposition of the other constituents. In some specimens blende is enveloped by and appears to have preceded baryte; elsewhere it follows cleavages in this mineral and is clearly later. Calcite also has in some cases infiltrated along cleavages in the earlier formed baryte; in others where calcite and baryte meet in sharp crystal boundaries they appear to be broadly contemporaneous. While there is locally evidence that calcite is later than the other three constituents of the vein there is nowhere any trace of these other minerals postdating a part of the calcite. The paragenesis of the four constituents of the septarian cracks can therefore be represented diagrammatically as follows:

Pyrite

Blende

Baryte

Calcite

EXPLANATION OF PLATE I.

Photomicrographs of infillings of septarian cracks in Middle Lias nodules from Leicestershire and Rutland. (E numbers refer to microscope slides and M numbers to photographs in the Geological Survey collection.)

FIG. 1. Calcite mudstone nodule, bank of brook 850 yards W. by S. of church at Great Easton, Leicestershire. (E. 22363, M. 2316.) Septarian crack margined by pyrite and infilled centrally with platy calcite which at one point cuts across marginal pyrite. Crossed nicols. × 19.

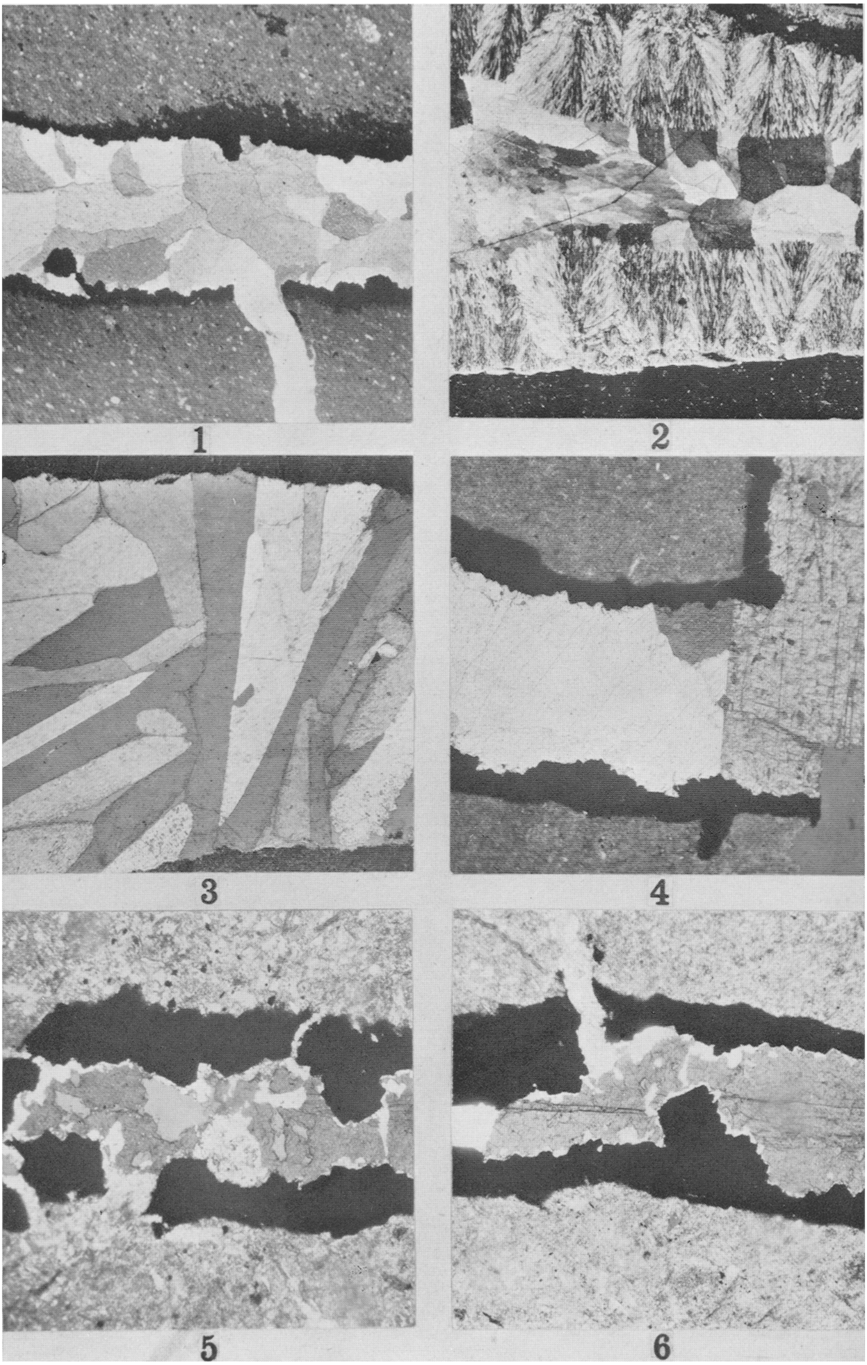
FIG. 2. Calcite mudstone nodule, bank of river Gwash 860 yards ESE. of church at Braunston, Rutland. (E. 22361, M. 2320.) Septarian crack infilled with marginal radiating calcite and central platy calcite. Crossed nicols. × 7.

FIG. 3. Chalybite mudstone nodule, bank of brook 1150 yards ESE. of railway station at Whissendine, Rutland. (E. 22464, M. 2317.) Septarian crack infilled with tabular baryte. Crossed nicols. × 16.

[1] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente. IX. Die Mengenverhältnisse der Elemente und der Atom-Arten. Skrifter Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Kl., 1938, for 1937, no. 4, pp. 81–82. [M.A. 7-166.]

FIG. 4. Calcite mudstone nodule, bank of river Gwash 770 yards ESE. of church at Braunston, Rutland. (E. 22362 C, M. 2314.) Junction of two septarian cracks margined by pyrite and infilled centrally by calcite (on left) and baryte (on right). Crossed nicols. $\times 19$.

FIGS. 5–6. Calcite mudstone nodule, bank of river Gwash 770 yards ESE. of church at Braunston, Rutland. (E. 22362 B, M. 2321–2.) Septarian cracks margined by pyrite and infilled centrally with baryte (dark): calcite (pale) replacing baryte and locally cutting through marginal pyrite. Crossed nicols. $\times 33$.



J. H. TAYLOR: BARYTE, ETC., IN SEPTARIAN NODULES FROM THE LIAS