The habit of pyrite in some sedimentary rocks.

(With Plate XI.)

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Summary.—Authigenic pyrite crystals or their pseudomorphs found in heavy residues from sedimentary rocks are cubes, octahedra, or pyritohedra. Combinations of these forms are common; trapezohedron and rhombic dodecahedron faces are rare. The cube is most often recorded in the literature, but the octahedron is dominant in some districts and may be favoured by calcareous environment. X-ray tests have been applied and goethite and hematite detected as alteration products.

IN the writer's collection of mineral grains from sedimentary rocks the commonest crystal form shown by pyrite is the octahedron, a form given in textbooks of mineralogy, but not found in textbooks of sedimentary petrology. A search of readily available papers on sedimentary petrology has shown that octahedra occurring in sediments and having the appearance of pyrite were observed under the microscope at least as early as 1911, when Travis and Greenwood[1] reported them in the Trias. Bannister,[2] examining large nodules from the chalk, which had well-developed octahedra on their surfaces, employed X-ray methods and showed them to be pyrite; but those who have examined microscopic particles appear to have relied on visual methods. In 24 papers recording crystals of pyrite or pseudomorphs after pyrite with a statement of the forms present, the cube was reported in 18, the octahedron in 11, and the pentagonal dodecahedron (pyritohedron) in 9. Only the paper by Travis and Greenwood reported the rhombic dodecahedron.

[1] C. B. Travis and H. W. Greenwood, Proc. Liverpool Geol. Soc., 1911, vol. 11, p. 116.
[2] F. A. Bannister, Min. Mag., 1932, vol. 23, p. 179.

Treatment and microscopical methods.

The present work is based on a collection formed mainly during heavy mineral work in Yorkshire[1] and North Wales. Pyrite crystals of recognizable habit or unmistakable pseudomorphs after pyrite were found in 143 rock specimens (chiefly sandstones, limestones, and calcareous shales) representing nine British counties and six geological systems. Calcareous rocks were treated with cold dilute hydrochloric acid and some ferruginous rocks with hot acid.

Microscopic examination and photomicrography were carried out with Canada balsam mounts, using a top light directed by means of a bull's-eye condenser and a separate lamp for background illumination. Photographs were taken on plates 16 mm. square placed in the microscope tube to receive the primary image.[2] In photographing the crystals singly the depth of the subject is not much less than the diameter and it is more important to get definition tolerable throughout than perfect at one level. Trials showed that objectives $\times 10$ to $\times 15$ fitted with stops would ensure negatives sharp enough for enlargement by $\times 10$ to $\times 20$, giving prints of the size shown in plate XI.

General description of crystals.

Octahedral types. Many of the impure limestones contain minute brassy pellets or clusters of pellets. Careful inspection may show their surfaces to be smooth (pl. XI A) or faceted, generally with equilateral triangles indicative of the octahedron (pl. XI B), the latter type being common in parts of the Yorkshire Jurassic, e.g. Lias, Grey Limestone, and Cornbrash. Sometimes the octahedra are larger and particles may consist of a few or of single crystals (pl. XI C–E). One example of smooth pellets and one of good octahedra were selected for X-ray examination which showed both to be essentially pyrite.

Octahedra sometimes have their solid angles blunted. In one Anglesey sample this is produced by the pyritohedron and cube (pl. XI F–H). More commonly cube faces of various sizes are developed, giving a range of types leading to blunted cubes (pl. XI I–L).

Cubical types. The cube commonly occurs uncombined, usually as single crystals with faces striated (pl. XI M) or smooth. Floods of brown cubes are found in yellow Triassic sandstones in Yorkshire; and similar

[1] F. Smithson, Proc. Geol. Assoc., 1931, vol. 42, p. 125; Proc. Yorks. Geol. Soc., 1934, vol. 22, p. 188; Quart. Journ. Geol. Soc., 1942, vol. 98, p. 27.

[2] F. Smithson, Nature, 1954, vol. 173, p. 1047.

crystals occur in Lower Carboniferous sandstones near Bangor, some showing blunting as in plate XI L.

The only specimen of Wenlock Limestone examined showed the cube blunted by the octahedron and the cube-octahedron edge bevelled by the trapezohedron (pl. XI N–P). In the Coniston Grit crystals similar to plate XI L, but with the cube edges bevelled by narrow pyritohedral facets, have been observed though they are too small to be photographed satisfactorily. Another cubical type (pl. XI Q) is discussed in the section on X-ray examination.

Pyritohedral types. These were found in only three samples, all from the Dogger formation at one locality in Yorkshire, where they occur both simple and in combination with small octahedron and cube faces (pl. XI R–T).

Twins. Although joined crystals are common, the only examples of definite twinning were interpenetrating cubes in the Millstone Grit of Anglesey.

Alteration. Many of the examples appeared to be 'pseudomorphs of so-called limonite after pyrite' which according to the revised Dana[1] 'probably consist for the most part of goethite'. Examples obtained by dissolving limestones in cold hydrochloric acid were not corroded. The mineral is brown and opaque and exhibits none of the optical peculiarities of goethite even where X-ray examination shows it to be the major constituent.

Frequency and distribution.

Nearly half the calcareous rock specimens examined yielded crystals of fresh or altered pyrite (81 out of 171), but for the non-calcareous the proportion was low (62 out of 893). Single residues normally showed a single habit, but though in some districts most of them also showed uniformity one with another (e.g. a preponderance of octahedra in the Jurassic of Yorkshire), in other districts there was much diversity (e.g. octahedra, cubes, and combinations in the Carboniferous of Caernarvonshire and Anglesey).

Mr. Greig-Smith of the University College of North Wales has tested the data statistically in relation to the supposition that calcareous rocks favour octahedral habit. Taking all the cases where octahedral or cubical types preponderate (135 in all), he found a significant association of the kind suspected ($P < 0{\cdot}05$).[2] Taking data for the Yorkshire Jurassic

[1] The System of Mineralogy, 7th edn, vol. 1, 1944, p. 683.

[2] P is the probability that the observed association is due to chance.

alone (88 cases) *no association* was *observed*, the recorded figures having the nearest integral values to chance expectation; in the remainder (47 cases) the association was present with enhanced statistical significance ($P = c.\ 0{\cdot}01$). One explanation of these results is that the statistical association represents a generalization valid in most regions and that, as P. G. H. Boswell[1] has written, 'the Jurassic system in Yorkshire includes mineralogically "abnormal" formations'.

X-ray examination (G. B.).

Particulars of the four samples selected for X-ray examination are included in the key to plate XI. Preliminary treatments included hand-picking, crushing, and dilution with gum arabic. A 9·0-cm. diameter evacuated powder camera with filtered Co-$K\alpha$ radiation was used and the observed spacings compared with those calculated from the cell constant for pyrite,[2] $a = 5{\cdot}40$ Å.

By this means the brassy material in samples i–iii was shown to be mainly pyrite. In sample ii there were weak reflections, $d = 4{\cdot}87$ Å. and $d = 3{\cdot}76$ Å., possibly due to melanterite for which the A.S.T.M. index gives $d = 4{\cdot}90$ Å. and $d = 3{\cdot}78$ Å. as the two strongest reflections; and a reflection $d = 4{\cdot}13$ Å. corresponded to the strongest goethite reflection. Marcasite was proved in none of the samples, although two very weak lines observed in sample iii at $d = 2{\cdot}31$ Å. and $d = 1{\cdot}76$ Å. might indicate a trace, since they correspond to two strong, though not the strongest, lines of this mineral.

Sample iv consisted of pseudomorphs and was selected because the cubo-octahedral crystals showed striations and occasional pyritohedron faces that left little doubt as to the original composition. As the crystals varied from warm to blackish-brown, colour types were separated for examination. Using the powder patterns given by Rooksby[3] as reference, goethite was shown to be the chief constituent, with 10–20 % of hematite in the warm brown variety and 30–40 % in the blackish-brown. A trace of pyrite, suspected on account of a very weak discontinuous line at $d = 1{\cdot}627$ Å., was confirmed by taking a rotation photograph of a

[1] P. G. H. Boswell, Quart. Journ. Geol. Soc. (Proceedings), 1941, vol. 97, p. lxviii.

[2] W. L. Bragg, Atomic Structure of Minerals, p. 71, New York, 1937. The disparities amongst the four cards for pyrite in the 'Index of X-ray Diffraction Data', A.S.T.M., Philadelphia, 1953, are sufficient to preclude their use where recognition of impurities is desired.

[3] H. P. Rooksby, in X-ray Identification and Crystal Structure of Clay Minerals, chap. x, Min. Soc., London, 1951.

single brown grain rotated about the cube axis. The photograph showed superposed powder patterns of goethite (80–90 %) and hematite (10–20 %) with no preferred orientation. In addition several spots, weak and extending over several degrees, could be indexed as 022, 111, 113, and 202 reflections from a near-parallel aggregate of pyrite crystallites rotating about a cube axis. These are the only pyrite reflections of more than moderate intensity which would not coincide with the powder haloes of goethite and hematite.

KEY TO PLATE XI (A–T) AND X-RAY SAMPLES I–IV.

Except where stated the material is apparently unaltered pyrite. The line drawings are idealized representations of the correspondingly lettered photomicrographs. On the line drawings, the letters are *a*{100}, *o*{111}, *e*{210}, and *n*{*hll*} (probably {211}).

A. Pellet and pellet-cluster. From calcareous shale, Lower Carboniferous, Menai Strait, Caernarvonshire. ×210. X-ray sample i.

B. Pellet showing small octahedra. From the Grey Limestone, Jurassic, Hundale Point, Yorkshire. ×160.

C, D, E. Octahedral types. From the Grey Limestone, Jurassic, Gate Holme Beck near Whitby, Yorkshire. ×140, ×170, ×210. X-ray sample ii.

F, G, H. Octahedral types blunted by cube and pyritohedron. G and H are the same crystal giving reflections from *a* and *e* respectively. From sandstone, Lower Carboniferous, Lligwy Bay, Anglesey. ×200, ×160, ×160.

I, J, K. Combinations of octahedron and cube. From limestone, Devonian, Dulas coast, Anglesey. ×120, ×105, ×115. X-ray sample iii.

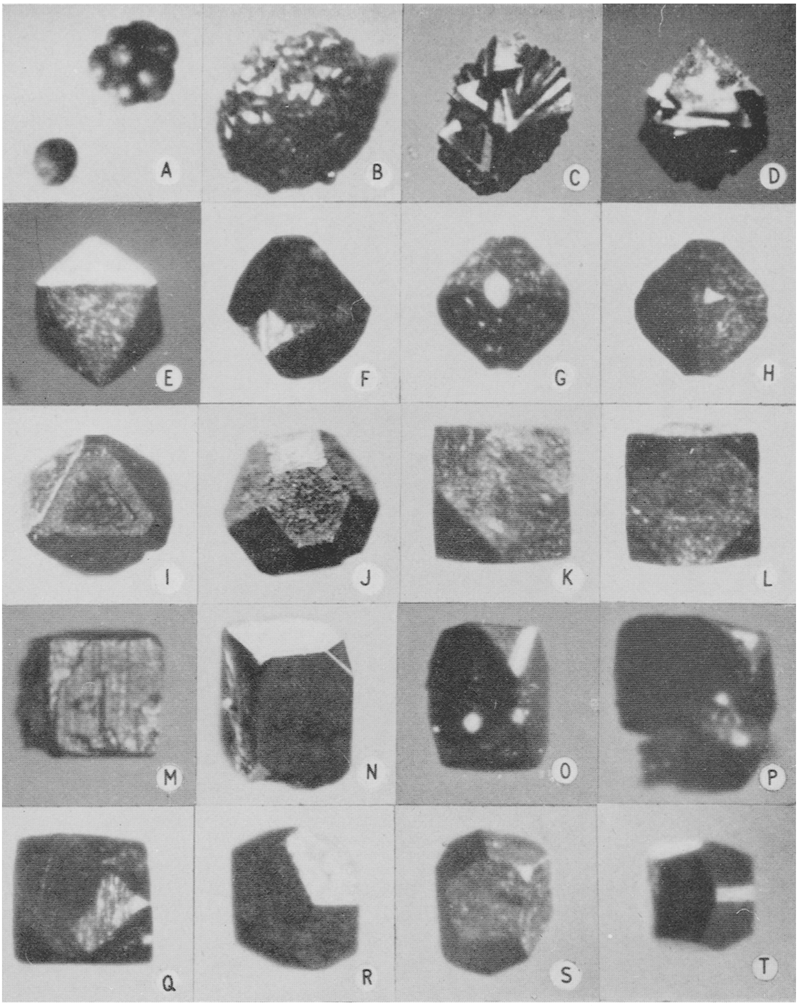
L. Cube blunted by octahedron. 'Limonitic' pseudomorph from sandstone. Lower Carboniferous, Menai Strait, Caernarvonshire. ×185.

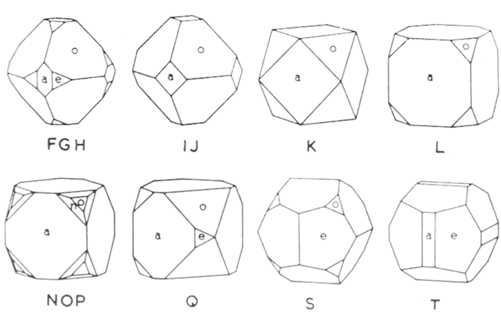
M. Striated cube. From boulder beds, Lower Carboniferous, Lligwy Bay, Anglesey. ×175.

N, O, P. Combinations of cube, octahedron, and trapezohedron. From Wenlock Limestone, Shropshire. ×135, ×185, ×270.

Q. Combination of cube, octahedron, and pyritohedron. Goethitic pseudomorph from soil on Carboniferous Limestone, Bwrdd Arthur, Anglesey. ×125. X-ray sample iv.

R, S, T. Pyritohedral types. From ferruginous calcareous beds, Dogger, Jurassic, The Wainstones, Cleveland Hills, Yorkshire. ×270, ×235, ×270.





F. SMITHSON: PYRITE