The distinction of pyrite from marcasite in nodular growths.

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RECENT account of pseudo-meteorites by Dr. L. J. Spencer¹ A RECENT account of pseudo-increasing and includes a description of nodules of pyrite 'popularly thought to be "thunderbolts"'. Dr. Spencer himself collected in 1931 a large number from the Lower Chalk outcropping on the foreshore below 'The Warren' at Folkestone, Kent. Some of these show welldeveloped octahedra 5 to 10 mm. across on the outer surface, undoubtedly to be referred to pyrite. More commonly the nodules exhibit small distorted octahedra which might easily be mistaken for marcasite. Indeed, in the past, many of these nodules from the Chalk at Folkestone and elsewhere, have been named marcasite, and they were so labelled in the British Museum collection. Dr. Spencer, therefore, suggested that modern methods should be applied to those cases where the crystalline form is distorted or not sufficiently developed to serve as a means of distinction between pyrite and The methods suggested in his paper are (1) X-rays, (2) marcasite. polarized light reflected from polished sections of nodules.

Before passing to an account of the technique employed and the results obtained by the present investigations, a short review will be given of the methods employed by previous workers in this field. The crystallographic distinction based on the difference in forms exhibited by well-formed crystals of cubic pyrite and orthorhombic marcasite is dealt with adequately in text-books, and need not be dwelt upon here. The following table shows that all observers are agreed that marcasite is lower in density than pyrite (p. 180). If we place most reliance on recent measurements the probable difference in density of the two minerals is over 0.10, but certainly less than

¹ L. J. Spencer, Nat. Hist. Mag. British Museum (Natural History), 1931, vol. 3, p. 56.

0.20. It is clear that density measurements on nodular growths cannot be conclusive, and are quite useless if we are looking for a mixture of the two minerals in the same specimen.

				Density of			
Autho	rity.			Marcasite.	Pyrite.		
Dana ¹				4.85 - 4.90	4.95 - 5.10		
Spencer ²				4.609 - 4.887	4.970 - 5.169		
Stokes 3				4.88 - 4.90	5.02 - 5.04		
Allen ⁴				4.887	5.027		
Bannister	: (X-r	ay)	• •••	4 ·90	5.03		

The case for colour distinction has been put very clearly by H. N. Stokes (loc. cit.), and my own observations are in agreement with his conclusions. Text-book descriptions of colour are based in most instances on tarnished specimens. Freshly fractured or polished surfaces of pyrite and marcasite are pale brass-yellow and tin-white respectively; the latter colour is not restricted to arsenical marcasite. The comparison of fresh surfaces in ordinary white light is the most simple test that can be applied. More elaborate methods are only justified in the study of fine-grained intergrowths, or where we suspect the presence of small quantities of pyrite in marcasite, or vice versa.

Chemical methods of distinguishing pyrite from marcasite have been described, but they are not reliable unless the exact conditions of the original experiments are repeated. Surface effects more especially influence the success of such qualitative tests. The studies of Stokes and later those of E. T. Allen, J. L. Crenshaw, J. Johnston, and E. S. Larsen (loc. cit.), are, however, on a different footing, and the quantitative results obtained merit closer attention. In Stokes's method an excess of finely powdered mineral is boiled with an aqueous solution of a ferric salt in an atmosphere of carbon dioxide. The oxidation is supposed to take place in two stages :

(1) $\text{FeS}_2 + \text{Fe}_2(\text{SO}_4)_3 = 3\text{FeSO}_4 + 2\text{S},$

(2) $2S + 6Fe_2(SO_4)_3 + 8H_2O = 12FeSO_4 + 8H_2SO_4$.

It was found that in the case of marcasite about 18% of the total

1 E. S. Dana, System of Mineralogy, 6th edition, 1892, pp. 85, 94.

- ² L. J. Spencer, Min. Mag., 1927, vol. 21, pp. 363-364.
- ³ H. N. Stokes, Bull. United States Geol. Survey, 1901, no. 186, p. 12.

⁴ E. T. Allen, J. L. Crenshaw, J. Johnston, and E. S. Larsen, Amer. Journ. Sci., 1912, ser. 4, vol. 33, p. 170.

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sulphur was oxidized according to the second equation above. whereas 60 % was the figure for pyrite. Apparently these figures are not affected by varying the grain of the material used, and so the difference in the oxidation figures cannot be accounted for by surface differences. Only the speed of the reaction, not the equilibrium state, is affected by the fineness of powdering. Upon these experiments Stokes bases the determination of the amounts of marcasite and pyrite in mixtures of known proportions, and then applies the method to various specimens including nodular growths. He probably claimed too high an accuracy for his results. The later work of Allen, Crenshaw, Johnston, and Larsen, does, however, confirm, with certain exceptions of detail, the main features of the method. Since Stokes's work in 1901 new methods of investigation have arisen, and the results now obtained on specimens similar to those he used should be in complete agreement.

The application of X-ray methods to this type of problem is generally straightforward and some freedom of choice is in this case possible. The powder method though, perhaps, the most obvious method is subject to at least two disadvantages: (1) any orientation of crystalline matter in the original specimen is lost by powdering; (2) the time of exposure is longer than for single crystal photographs. When single crystal fragments, or fibrous or platy aggregates, can be isolated, the rotation method should be employed. Even when a specimen appears to be compact and very fine-grained it is better to use a chip than to powder a fragment for investigation. It was first necessary to take single crystal photographs of known material for comparison, not only for marcasite about the three axes a, b, and c, but also for pyrite about a cube axis. The published data for pyrite comprise W. L. Bragg's original X-ray spectrometer results¹ (pyrite was one of the first minerals to be examined in this classical work). Ewald's Laue photographs,² and data from powder photographs of various other authors.³ The rotation photographs constitute valuable identifications of the minerals and are superior to powder photographs since complete coincidence in the positions and intensities of spots must occur in two dimensions, not merely in one. Rotation photographs

¹ W. L. Bragg, Proc. Roy. Soc. London, Ser. A, 1914, vol. 89, p. 468.

² P. P. Ewald, Physikal. Zeits., 1914, vol. 15, p. 299.

³ M. J. Buerger (Amer. Min., 1931, vol. 16, p. 361) in his work on the structure of marcasite used molybdenum radiation. The indices and intensities of spots on marcasite photographs obtained in the present work using $Cu - K_{\alpha}$ radiation are in substantial agreement with his data.

of marcasite about the a and b axes are at once distinguishable from a photograph of pyrite about a cube axis, simply by the difference in the spacing of the layer-lines. In a cylindrical camera of



FIG. 1. Diagrams of rotation photographs of pyrite (about a cube axis) and of marcasite (about the c-axis). The width of each diffraction line represents the visually estimated intensity on the original photograph. Camera diameter 6.04 cm.; $Cu-K_{\alpha}$ radiation, $\lambda-1.539$ Å., using a nickel filter.

diameter 6.04 cm., and using $Cu - K_{\alpha}$ radiation, the distances 2r between the various layer-lines above and below the equator are:

			Distances 2 r.			
			lst layer- line.	2nd layer- line.	3rd layer- line.	Spacing.
Marcasite	abou	t [100]	 3.08 cm.	*	*	3.38 Å.
,,		[010]	 2.23	5.80 cm.	*	•4·44
,,	,,	[001]	 1.80	4.20	10.07 cm.	5.39
	۰,	[110]	 1.77	3.97	8.90	5.58
Pyrite ab	out	[100]	 1.80	4.19	9.96	5.40

* These layer-lines do not fall upon the film.

In order to distinguish photographs of marcasite about the [001] and [110] axes from pyrite [100] photographs, it is necessary to study also the distribution of spots along the layer-lines. This has been done very carefully and fig. 1 shows the rotation diagrams for photographs of marcasite and pyrite about the [001] axis. The layer-line spacing is practically identical and certain spots along the equator



FIG. 2. Diagram of powder photographs of pyrite and marcasite. The heights of the ordinates represent the visually estimated intensities of the lines on the original photographs. Camera diameter 6.04 cm.; $Cu - K_{\alpha}$ radiation, $\lambda = 1.539$ Å., using a nickel filter.

coincide, but the two diagrams are not superposable and are readily distinguished. Although the rotation diagram for marcasite about the [110] axis differs from pyrite a little in its layer-line spacing, the equatorial spots are nearly coincident, and it is only when the first and second layer-lines are compared that striking differences are found. It is generally possible to set a crystal fragment of pyrite or marcasite with a face parallel to the axis of rotation, so that it is highly necessary to have a knowledge of photographs about important zone-axes of the minerals concerned.

Having obtained the rotation photographs and indexed them carefully it is possible to index the powder photograph of marcasite with certainty. Fig. 2 shows a comparison of the powder photographs of pyrite and marcasite. They are reproductions to scale of the distribution of the lines, and the intensities are represented by the lengths of the ordinates. The important conclusions to be drawn from the comparison are: (1) the number of coincident lines when the two photographs are superposed; (2) the possibility of ensuring freedom of each specimen from its polymorph by considering certain important lines. The powder photographs serve as standards for comparison only when they have been studied in this way. It is best to take these standard powder photographs on large films using a circular aperture as Debye originally did and not a parallel-jawed slit system. If a crystal fragment set in chance orientation be rotated, the resulting photograph cannot always be associated with one of the rotation photographs about a zone-axis. It is always possible to superpose it upon an 'extended' powder photograph of the same substance.

The three X-ray methods employed may thus be summarized :

(1) Rotation photograph of crystal fragment about any important zone-axis.

(2) Rotation photograph of crystal fragment about an axis in chance orientation.

(3) Powder photographs.

The nodules of iron disulphide, so abundant in the Chalk of the south of England, show a considerable variation in shape and size, and all possible gradations between a smooth outer limonitized surface and a surface made up of quite large crystals. If a nodule be broken open the bulk of the material is seen to be made up of compact radiating blade-like aggregates, pale brass-yellow in colour, terminating at the surface in large or small crystal faces. The blades do not, however, generally terminate at the centre ; a fine granular material occupies the central space, which varies from a few millimetres to a centimetre in diameter. There is no appearance in any nodule I have examined of concentric layers and the colour of a freshly fractured nodule is always the pale brass-yellow typical of pyrite.

X-ray rotation photographs have been taken of blade aggregates from the interior of several nodules, and also of crystal fragments from the surface. Powder photographs have also been taken of the granular material from the centre. The granular material sometimes contains gypsum crystals which were picked out before taking a photograph. All the nodules from Folkestone, Kent, and Oxted, Surrey (nos. 1, 2, and 3) yield pyrite photographs whichever part of the nodule is tested. Long exposures failed to detect any weak marcasite lines. The blade aggregates yield photographs which show that the blades are elongated along a cubic axis and flattened parallel to a cube face. Small ellipsoidal nodules showing no internal radial structure from a pebble of calcareous shale collected on the beach at Newhaven, Sussex (no. 4), also proved to be pyrite, and not marcasite as labelled.

The only aggregated specimens of true marcasite examined were the elongated cylindrical stalactites from Mineral Point, Wisconsin, U.S.A. (no. 7). These break perpendicular to the axis of elongation and are radiating structures terminating on the surface in large or small crystals with the form of marcasite. The colour on a fresh surface is tin-white, and crystals from the surface and also fragments from the interior yield marcasite photographs. No pyrite lines could be detected.

The following table summarizes these results :

No.	Locality.	B.M. No.	X-ray result.	
1.	Folkestone, Kent	unregistered	pyrite	
		duplicate		
2.	ditto	$\overline{\mathrm{ditto}}$	ditto	
3.	Oxted, Surrey	1931,141	\mathbf{pyrite}	
4.	Newhaven, Sussex	88316	pyrite	
5.	Sparta, Illinois, U.S.A. (disk in shale)	84424	pyrite	
6.	Bordean chalk pit, Langrish, Petersfield,	1910,364	pyrite	
	Hampshire			
7	Mineral Point, Wisconsin, U.S.A.	35744	marcasite	

X-ray methods afford the most certain means of distinction between marcasite and pyrite. Only a small quantity of material, however, can be photographed at any one time. Polished sections of nodules have therefore been examined by reflected polarized light in order to discover any intergrowth of marcasite with pyrite. This second method permits a comparatively rapid survey of an area 1-2sq. cm., and its success depends upon a ready distinction between marcasite and pyrite. Schneiderhöhn's data¹ show that this should be easily achieved. I used as standards of comparison polished sections of spear-head marcasite twins from the Chalk of Folkestone, and fresh plane surfaces on large pyrite crystals from Morro Velho, Brazil. Between crossed nicols, marcasite shows characteristic and vivid yellow, plum, and pale-green polarization colours. The pyrite crystals are completely isotropic. The trace of the twin-plane (110)

¹ H. Schneiderhöhn and P. Ramdohr, Lehrbuch der Erzmikroskopie, 1931 Berlin, vol. 2, pp. 157, 192; see also coloured plate, no. 2. in marcasite is a further aid to discrimination. The nodules from the Chalk examined by X-ray methods yield isotropic sections made up of radiating crystals weathered on the surface to limonite, which appears a grey to brown finely grained mineral between crossed nicols.

Further sections of nodules from the Chalk give the same result. In certain cases where weathering has been severe, the limonite appears to reach down in dendritic growths between the blades of pyrite. Not a single nodule from the Chalk so far examined has revealed an intergrowth of marcasite. The true marcasite stalactites from Wisconsin, U.S.A., possess an outer zone of large marcasite crystals showing twinning and therefore giving alternate bands of the polarization colours described above. The inner portion of the stalactite is far more compact than a pyrite nodule and between crossed nicols shows pale yellow and mauve blotches which change colour on rotating the section. The anisotropy is manifest throughout the whole nodule.

A closer examination of two sections of pyrite nodules from the Chalk revealed very weak anisotropy. These sections possessed a higher polish than the others and neighbouring blades showed very faint pink and blue polarization colours which changed on rotating the section. This effect may easily be overlooked, and it is sharply distinguished from the anisotropy of marcasite. Moreover, one of the sections showing this effect had already been examined thoroughly by X-ray methods and shown to be typical pyrite. The polarization colours though very faint can be followed over the whole section so that it cannot be attributed to any local effect or inclusion. It is a property of the nodule as a whole. Several writers have referred to anisotropic pyrite and Schneiderhöhn states that it can always be distinguished from true marcasite. He attributes the anisotropy in certain cases to arsenic content. Ehrenberg¹ claims that powder photographs of banded pyrite from Aachen show small differences in the positions of the lines from those of a normal pyrite photograph, and he attributes this to the excess of iron found by chemical analysis. His polished sections, however, are isotropic. Any replacement of sulphur by arsenic atoms in the pyrite structure would affect the intensities of diffracted spots on a rotation photograph. Ehrenberg does not give any X-ray data to support his contention that additional iron atoms are present in the structure of the Aachen pyrite. Any such addition would certainly reveal itself more clearly in changes

¹ H. Ehrenberg, Neues Jahrb. Min., Abt. A, 1928, vol. 57, p. 1303.

of intensity than cell-size. The X-ray rotation photographs of blades from the anisotropic nodules of pyrite from the Chalk at Folkestone appear to be normal in intensity and in the positions of the spots. There is no X-ray evidence of departure from the normal pyrite structure. I would attribute the anisotropy of these nodules to a condition of strain. The final appeal in any doubtful case that may arise should be to X-ray methods.

It is now necessary to see how the present results agree with Stokes's work. The later work of Allen, Crenshaw, Johnston, and Larsen shows that the determination of any one component in a mixture of pyrite and marcasite is accurate to +5% and probably less accurate for mixtures near to pure pyrite or marcasite. Stokes examined one nodule, 'No. 25', from Folkestone, Kent, evidently similar to those studied in the present work, in which he found 3% of marcasite, but this result must be regarded as very doubtful. He also states 'I have received several supposed marcasite concretions from Folkestone all of which are clearly pyrite'. Some specimens he examined were undoubtedly mixtures, and contained about 30 % pyrite; but these were not nodular growths, and a fractured surface revealed the two minerals by colour difference. Intergrowths of pyrite and marcasite have been recorded by other writers. Interesting cases, in particular, are those of parallel growths of marcasite twins on cubes of pyrite cited by Sadebeck¹ and Trechmann.² The spear-head marcasite twins from Folkestone, Kent, show warty excrescences of pyrite and in some cases a regular parallel growth of pyrite cubes, the cube axes being arranged parallel to the twin-plane (110). In these cases, parallel growth occurs when the [001] and the [110] axes of marcasite are coincident with the cube axes of pyrite, the spacings being 5.39, 5.58, 5.40 Å. respectively. These examples of intergrowth are quite obvious from an examination of the crystal forms and colour. The nodules from the Chalk, however, are from all methods definitely pyrite and no case has yet been found among them of intimate intergrowth of the two minerals.

In conclusion I should like to thank Dr. W. R. Jones of the Imperial College of Science and Technology who has assisted me personally throughout the course of the metallographic work and who placed additional sections, made under his supervision, at my disposal.

A. Sadebeck, Ann. Chem. Phys. (Poggendorff), 1878, Erg.-band 8, p. 625.
C. O. Trechmann, Min. Mag., 1892, vol. 9, p. 209.