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New data on woodwardite

WOODWARDITE was originally reported from Cornwall, and has subsequently also been identified in material from Klausen in Italy (Meixner, 1940). The formula is given as 'probably $Cu_4Al_2(SO_4)(OH)_{12}.2-4H_2O$' by Palache *et al.* (1951). The X-ray powder-diffraction data for alleged woodwardite from Carnarvonshire, Wales, is given in the JCPDS file under the number 17–132, but there are major discrepancies between these powder data and those published by Meixner.

Four samples labelled 'Woodwardite, Cornwall' were obtained from the British Museum through the kindness of Mr. P. G. Embrey; sample numbers were BM 40035, BM 40077, BM 40079, and BM 40083. All four samples produced similar X-ray powder-diffraction patterns, which consist of only a few broad, diffuse lines. Measurements made on one of the Debye-Scherrer patterns are tabulated in Table I; X-ray diffractometer tracings gave equivalent results.

Comparison of these X-ray diffraction data with those given by Meixner (also included in Table 1) shows several apparent discrepancies. The chief one is the absence of the 9·1 Å line in the latter's data. Since Meixner did not report his camera size it is possible that he employed a small-diameter camera in which the beam stop blocked the imprint of this line. The single 4·43 Å line observed in this study is very broad and diffuse; it is quite possibly made up of the two lines at 5·30 Å and 3·91 Å reported by Meixner, and presumably better resolved in his pattern. Finally, Meixner's weak 1·297 Å line is matched approximately by a very faint shadow on the writer's patterns,

although it is too weak for accurate measurement. There is, however, quite good agreement between intensities in the two sets of data relating to the Cornish woodwardite. Taking the various factors into consideration, the diffraction data appear to be comparable.

The diffraction pattern of the Carnarvonshire sample, on the other hand, is significantly different. Particularly notable is the large basal spacing of 10·9 Å versus the

TABLE I. *X-ray powder-diffraction data*

Cornwall no. BM 40035 (this paper)		Cornwall and Klausen (Meixner, 1940)		Carnarvonshire. JCPDS File no. 17–132	
d(Å)	I	d(Å)	I	d(Å)	I
9·1	vs	—	—	10·9	100
*4·43	w	{ 5·30	w	5·46	60
		{ 3·91	w	3·66	50
2·58	m	2·61	s	2·613	40
—	—	—	—	2·454	20B
1·50	m	1·525	m	1·535	5B
—	—	1·297	w	—	—

* Very broad, diffuse.

TABLE II. *Effect of increasing temperature on the basal spacings of woodwardite and of the Carnarvonshire mineral*

	Room temp.	30 °C	60	90	120
Cornwall, woodwardite	9·1 Å	8·8	8·5	8·3	8·1
Carnarvonshire mineral	10·9 Å	10·9	10·4*	—	—

* Weak, broad.

9·1 Å basal spacing of the Cornish samples. Mr. D. E. Evans of the National Museum of Wales kindly sent the author a sample labelled 'Woodwardite, coating grass, Simdde, Dallhuan, Drws-y-coed, Nantlle, Carnarvonshire', with the number 27111-GR463. The diffraction pattern produced by this sample corresponds with the data for the Carnarvonshire woodwardite given on JCPDS card no. 17–132.

On the expectation that the Carnarvonshire material represented a hydrated equivalent of the Cornish woodwardite, both samples were submitted to moderate heating on a diffractometer stage, followed by X-ray diffraction at temperature intervals of 30 °C. The results (Table II) show that the behaviour of the two samples is quite different. The basal spacing of the Cornish sample decreased progressively to 8·1 Å at 120 °C, whereas the basal spacing of the Carnarvonshire material decreased

only slightly from 10·9 Å to 10·4 Å at 60 °C, after which all diffraction lines disappear. It is therefore apparent that the Carnarvonshire material is not simply a hydrated version of the Cornish woodwardite.

Infra-red spectra for the two minerals, kindly obtained by Dr. L. H. Little, Department of Chemistry, University of Western Australia, are very similar (see illustration), except at low frequencies where interpretation is difficult. The absorption peaks at 3400 cm^{-1} and 1600 cm^{-1} can be assigned to H_2O stretching and bending frequencies, respectively. The weak deflection at 1400 cm^{-1} is probably due to CO_3, and the strong absorption at 1100 cm^{-1} can be attributed to SO_4.

Electron-microprobe analyses were attempted on samples from both localities, but it was evident that the minerals in question decomposed under the electron beam. Consequently probe analyses cannot be regarded as being reliable. However, since the analyses were made under similar conditions, it is probably valid to compare cation ratios.
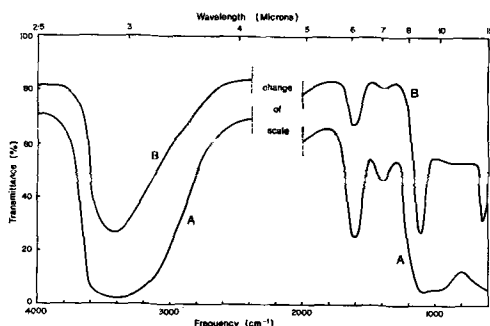

FIG. 1. Infra-red absorption spectra of woodwardite from Cornwall (A) and the mineral from Carnarvonshire (B). Spectral assignments are given in the text.

The principal elements in both samples are copper and aluminium. The Cu : Al atomic ratio in the Cornish woodwardite was found to vary, in five out of six spots analysed, between 1·73 and 2·03; the sixth gave an anomalously low value of 1·21. Apart from the latter, the Cu : Al ratios correspond reasonably well with the formula proposed by Meixner (1940) and accepted by mineralogical reference sources. The material from Carnarvonshire, on the other hand, gave Cu : Al ratios between 0·62 and 0·82 (four spots analysed), which is much lower than in the Cornish woodwardite. Appreciable sulphur and small amounts of iron were detected in both samples, but the Carnarvonshire material gave appreciably high silicon counts. The silicon is probably due to siliceous impurities, perhaps amorphous silica.

In conclusion, although the samples labelled as woodwardite from Cornwall and Carnarvonshire both appear to be hydrated sulphates of copper and aluminium, their different Cu : Al ratios, X-ray diffraction patterns, and behaviour on heating indicate that they do not represent the same mineral. Since the type locality for woodwardite is Cornwall, only the Cornish material can be regarded as being the true woodwardite.

The Welsh sample labelled as woodwardite, and whose X-ray diffraction data have made their way into the JCPDS files must be regarded as a different mineral, having a substantially lower Cu : Al ratio than woodwardite and a lower degree of structural stability under increasing temperature. Unfortunately the writer does not have sufficient amounts of pure material from Carnarvonshire to undertake a complete chemical analysis, but this is clearly what needs to be done to characterize the mineral. In the meantime, the X-ray powder diffraction data for woodwardite from Cornwall

given in this paper, should supplant the Carnarvonshire data now in the JCPDS data file.

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Sample preparation for fluid inclusion studies

AN increasing interest in fluid inclusion studies has created the need for a routine method of sample preparation. For normal thermometric analysis, using an air-conduction heating stage, the specimens are examined in the form of thin mineral plates polished on both sides to ensure maximum optical definition and minimal thermal lag. Various oil-immersion stages have been tried but these are more difficult to operate and are limited by the stability of the circulating medium (Roedder, 1962). Since most inclusions are less than $100 \mu m$ in diameter the scattering of transmitted light by surface irregularities becomes quite critical. The development of a high polish can therefore be regarded as a prerequisite for this particular technique, and in addition the specimen must neither be mechanically nor thermally stressed.

Disregard of these conditions may destroy or permanently damage the inclusions in low temperature or easily cleaved minerals, particularly those containing liquid carbon dioxide (Larson *et al.*, 1973). The method described below has been developed to meet these requirements.

Method. The specimens to be examined are blocked with cold-setting Araldite resin (MY750/HY956) in 1-in. diameter silicone-rubber moulds. When set, the blocks are secured in a specially designed clamping jig (fig. 1), which is attached to the magnetic chuck of a diamond saw by a vertical steel pillar. This affords firm support and reduces surface shattering of the specimens by the saw blade. Parallel-sided slices 2 to 3 mm in thickness are then removed and lapped on both sides to the required optical thickness