

Kidwellite from Cornwall

KIDWELLITE, $\text{NaFe}^{3+}(\text{OH})_{10}(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, is a 5 Å fibre axis phosphate, recently described (Moore and Ito, 1978) from several localities in the USA and West Germany, where it forms greenish-yellow silky needles in radiating aggregates pseudomorphous after rockbridgeite and other phosphates.

In 1968 one of us (H.C.) collected a specimen from the dumps of Wheal Phoenix, Linkinhorne, Cornwall (near SX 265 722) showing a pale greenish-yellow radiating mineral, which was found to be a hydrated iron(III) phosphate, with a characteristic infrared absorption spectrum which could not be matched with that of any mineral available to the authors at that time. In 1978 Dr A. L. Kidwell of Houston, Texas, sent R.S.W.B. a sample of kidwellite from Coon Creek mine, Polk County, Arkansas, which yielded an infrared spectrum identical with that of the Wheal Phoenix material described above, and which was also identical in specific gravity with it.

The Wheal Phoenix kidwellite consists of greenish-yellow fibres grouped in radiating globular aggregates less than 1 mm in diameter investing small cavities in a cellular quartz-goethite gozzan, and apparently pseudomorphous after a radiating globular mineral, probably the dufrenite well known from the locality (Kinch and Butler, 1886; Kinch, 1888; Frondel, 1949). This dufrenite is dark green when unaltered, and normally alters to brown goethite, many specimens labelled 'dufrenite' from this locality in collections being actually of goethite. Kidwellite is rare here, and probably does not represent an intermediate in the 'normal' oxidative alteration of dufrenite to goethite for this locality, but is formed under localized special conditions, or from a starting material other than dufrenite, perhaps rockbridgeite (Kingsbury, 1957) or even the rare andrewsite (Maskelyne, 1871, 1875; Frondel, 1949). Small amounts of unaltered chalcosiderite occur on top of the kidwellite spherules and in other nearby parts of the matrix, but no trace of the original dufrenite or other starting material was detected.

Infrared absorption spectra. The infrared spectra of the kidwellites from Wheal Phoenix (RSWB 68-401) and from Coon Creek mine (RSWB 78-69) were measured in 'Nujol' mulls, in the 670-4000 cm^{-1} region, using a Perkin-Elmer 137 spectrophotometer with sodium chloride optics,

calibrated against polystyrene, and were virtually identical. The spectrum of the Coon Creek kidwellite was also measured over a wider wave-number range, 380-4000 cm^{-1} , in Nujol mull, between KBr plates, using a Perkin-Elmer 397 grating spectrophotometer, to give greater accuracy in wave-number, higher resolution, and to include the regions of the ν_2 and ν_4 absorptions of the phosphate anion.

The wave-numbers and assignments of absorptions are given in Table I, and parts of the spectrum are reproduced in fig. 1.

The sharp absorption at 3570 cm^{-1} indicates an

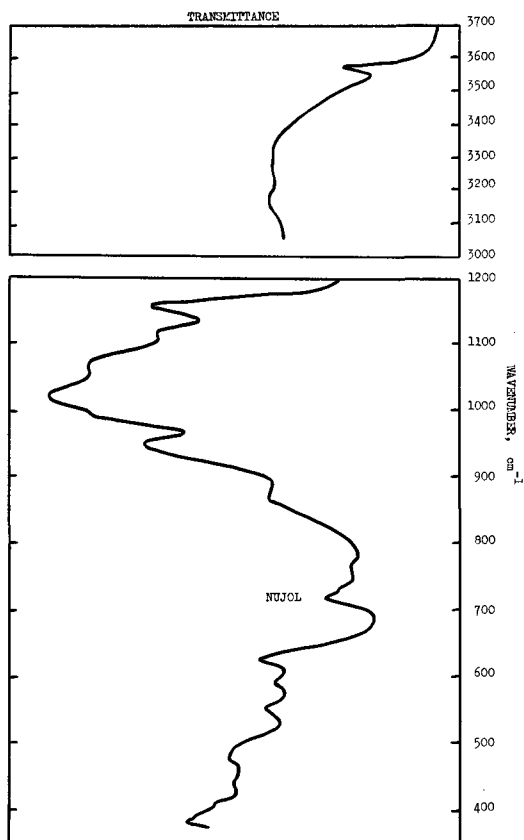


FIG. 1. Infrared absorption spectrum of kidwellite from Coon Creek mine, Polk County, Arkansas (Off RSWB 78-69).

O-H stretching absorption not modified by hydrogen bonding. Hydrogen bonding broadens this absorption and shifts it to lower wave-numbers, as is shown by the broad bands at 3300 and 3170 cm^{-1} . The broad band at 1635 cm^{-1} is the 'scissor' bending mode of the H_2O molecules in the lattice.

The presence of the phosphate ν_1 (symmetrical

stretch) and ν_2 (symmetrical bend) absorption bands near 950 and 500 cm^{-1} respectively indicates phosphate anion distortion, site symmetry being less than T_d , these symmetrical vibrations being inactive in the infrared for T_d symmetry. This is confirmed by removal of spectroscopic degeneracy from the ν_3 and ν_4 modes. These are triply degenerate, and all three maxima appear in both modes, indicating a site symmetry of C_{2v} , C_2 or C_s for the phosphate anion. The doubly degenerate ν_2 mode shows as a rather broad absorption at 485 cm^{-1} , with a hint of a shoulder near 492 cm^{-1} . If this is a single absorption, the phosphate site symmetry would be C_{2v} , but if the shoulder is due to splitting of the degeneracy, the site symmetry would be C_2 or C_s . Assignment and interpretation of absorption bands in this part of the spectrum are made uncertain by the possibility of plurality of phosphate site symmetries, and of the presence of metal-oxygen absorptions.

TABLE I. Wavelengths and probable assignments of infrared absorption maxima of kidwellite from Coon Creek mine, Polk County, Arkansas (Off RSWB 78-69)

Absorption maxima cm^{-1}	Assignments
485 ms (492) ?	} $\text{PO}_4^{3-} \nu_2$ bend
558 ms	
593 ms	} $\text{PO}_4^{3-} \nu_4$ bend
632 ms	
770 w, br	} Fe-O-H bend?
875 m, br	
950 s, sh (995)	$\text{PO}_4^{3-} \nu_1$ symmetrical stretch
1025 vs (1073) s	} $\text{PO}_4^{3-} \nu_3$ stretch
1120 s	
1160 s, sh	} $\text{PO}_4^{3-} \nu_3$ stretch, or P-OH in-plane bend?
1635 m, br	
3170 s, br	} H-bonded O-H stretch
c.3300 s, br	
3570 ms, vsh	O-H stretch, not H-bonded

w = weak, m = medium, s = strong, v = very, br = broad, sh = sharp. Values in brackets are of shoulders.

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