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Philipsburgite from the Caldbeck Fells and kipushite from Montana, and their infrared spectra

THE material forming the main subject of this paper was collected in 1965 from the dumps around the then recently abandoned mine buildings of Potts Gill or Ghyll baryte mine, Caldbeck, Cumbria, which were situated at NY 320 367. No sign of these workings can be seen today, as the land has been completely reclaimed for agricultural use. All the material collected came from one small boulder of vein quartz and white cleavable massive baryte containing drusy cavities lined with quartz terminations about 2 mm across, partly coated with black wad and iron staining, and with minor pale green fibrous chrysocolla (identified by infrared spectroscopy), presumably pseudomorphous after a fibrous mineral. On the wad and quartz crystals in some of these cavities are sparse to rich coatings of green globular aggregates to about 2 mm in diameter. Many of these spherules are of dark green compact fibrous radiating malachite, in which only traces of zinc could be detected by a microchemical test using diammonium tetrathiocyanatomercurate(II) solution. Other spherules are more spiky than fibrous in appearance, more translucent, and of a paler green colour. These latter gave an infrared spectrum which did not match that of any material available to the authors at the time, and which indicated that the material contained hydroxide, phosphate and arsenate, and was distinct from phosphatian cornwallite, known from the same mine. Microchemical tests indicated the presence of Cu and Zn, and an energy dispersive SEM scan confirmed the presence of major Cu, Zn, As and P.

An X-ray powder diffraction photograph (X 12696) of a sample was taken by Miss E. E. Fejer at the British Museum (Natural History), and shown to match that of a sample submitted previously by Mr W. F. Davidson, but which was otherwise unknown at the time, though related to those of the adelite group.

The discovery of philipsburgite, $(Cu,Zn)_6(AsO_4,PO_4)_2(OH)_6 \cdot H_2O$, from Montana by Peacor *et al.* (1985) suggested a possible comparison, and a sample of the type material in the Smithsonian Institution, off NMNH 161201, was sent to one of us (R.S.W.B.). The infrared spectrum of this sample was found to be similar to that of the Potts Gill unknown, apart from a small difference in the intensity ratios of the phosphate and arsenate absorption maxima arising from solid solution compositional difference.

The habit of the Potts Gill philipsburgite in the globular aggregates is not unlike that of the Montana material, as shown in the SEM photograph (Fig. 1). This is the first record of philipsburgite from the British Isles.

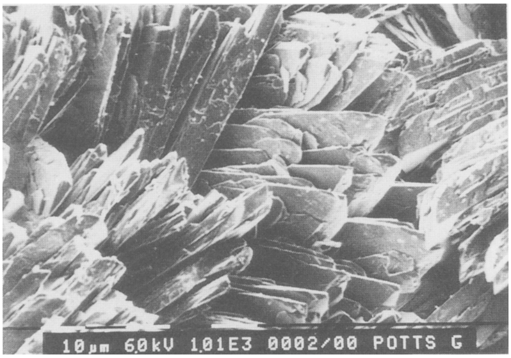

FIG. 1. SEM photograph of philipsburgite from Potts Gill mine, Cumbria. White bar = 10 μm.

Chemical composition. A sample of the Potts Gill philipsburgite was analysed by Mr D. A. Plant in the Geology Department, University of Manchester, using a modified Cambridge Geoscan electron microprobe with Link Systems 290 electronics, utilizing an operating voltage of 15 kV and a sample current of 3 nA, measured on cobalt. The averages of three analyses with good reproducibility gave the results shown and compared with other analyses in Table 1. The formula of the Potts Gill philipsburgite is near $(Cu_{0.82}Zn_{0.18})_6(As_{0.74}P_{0.26}O_4)_2(OH)_6.H_2O$, with a somewhat higher Cu/Zn ratio than in that of the analysed Montana and Neubulach specimens, whereas its As/P ratio is close to that of the Neubulach material, and higher than that of the Montana type specimen.

Infrared spectroscopy. The infrared spectra of samples of the Potts Gill and type Montana philipsburgites, carefully picked under the microscope, were measured in Nujol mulls between KBr plates over the 400–4000 cm^{-1} range using a Perkin-Elmer PE 397 spectrophotometer. These spectra, reproduced in Fig. 2, are very similar, but the higher As/P ratio of the Potts Gill material over that of the Montana sample is clearly shown by comparing the relative intensities of the $AsO_4\nu_3$ bands in the 800–900 cm^{-1} region with those of the $PO_4\nu_3$ bands at 1030 cm^{-1}. No absorptions due to contamination, e.g. with bayldonite (Peacor *et al.*, 1985) or quartz are evident in either spectrum.

We have recently identified two more specimens of philipsburgite from the Caldbeck Falls, from samples collected by Mr M. P. Cooper from an old trial on Low Pike, associated with bayldonite, phosphatian cornwallite and phosphatian mimetite, on quartz. From the relative intensities of their AsO_4 and $PO_4\nu_3$ infrared absorption bands, one has an As/P ratio somewhat lower, and the other somewhat higher, than that of the Potts Gill material studied, the former possibly being a highly arsenatian kipushite, a quantitative analysis being required to determine whether As/P < 1.

The infrared spectra of some samples labelled 'philipsburgite' from Black Pine mine, Philipsburg,

TABLE 1. Analyses of philipsburgites and kipushite.

	1	2	3	4	5
CuO %	51.7	51.4	46.3	49.0	43.0
ZnO %	11.6	11.8	18.2	13.2	24.4
As_2O_5 %	22.5	23.3	16.3	23.1	-
P_2O_5 %	4.9	5.2	8.7	5.1	20.9
Cu/Zn, atom	4.55	4.5	2.6	3.8	1.1 to 2.6
As/P, atom	2.85	2.8	1.2	2.8	-

1. Theoretical values for $(Cu_{0.82}Zn_{0.18})_6(As_{0.74}P_{0.26}O_4)_2(OH)_6.H_2O$.
2. Philipsburgite, Potts Gill mine, Cumbria. Off RSWB 65-534.
3. Philipsburgite, Black Pine mine, Montana (Peacor et al, 1985) NMNH 161201.
4. Philipsburgite, Neubulach, Black Forest, Germany (Walenta et al., 1985).
5. Kipushite, Kipushi, Zaire (Piret et al., 1985).

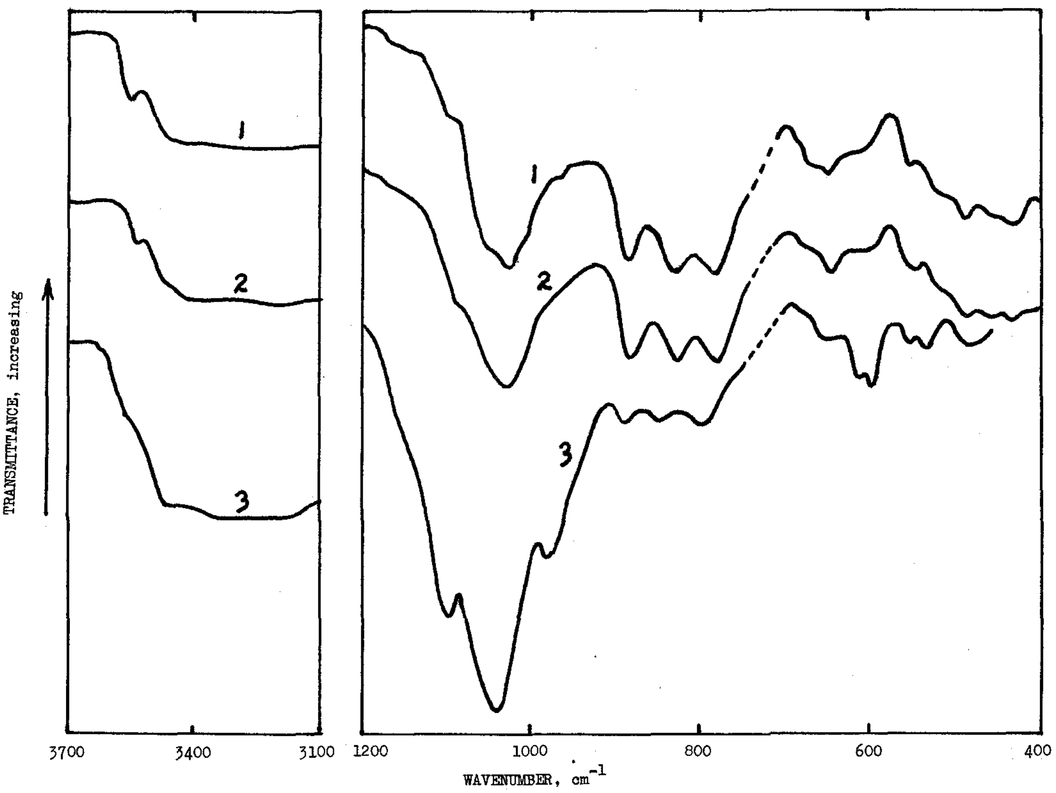

FIG. 2. Infrared spectra of philipsburgites and kipushite. 1. Philipsburgite, Potts Gill mine, Cumbria. Off RSWB 65-346. 2. Philipsburgite, Black Pine mine, Philipsburg, Montana. Off NMNH 161201. 3. Kipushite, Black Pine mine, Philipsburg, Montana. Off specimen supplied by Richard Tayler.

Montana, the type locality, were measured in Nujol mulls over the 200–4000 cm^{-1} range using a Perkin-Elmer PE 684 spectrophotometer. These samples, obtained recently from a mineral dealer, consist of typical bright green spherules of tiny clear crystals on quartz crystals, and are associated with colourless tapering prismatic phosphatian mimetite, yellow earthy bindheimite, and an unidentified blue-green translucent botryoidal phase giving a distinctive infrared spectrum. These 'philipsburgites' gave spectra similar to those of the others, but with very weak arsenate absorptions and correspondingly strong phosphate absorptions (Fig. 2). This pattern suggests that the specimens are slightly arsenatian kipushite, which should be added to the list of minerals from the Black Pine mine, and which, with the Low Pike specimens, are evidence of the extent of the expected solid solution series between kipushite and philipsburgite. More analyses and X-ray diffraction studies of Black Pine mine 'philipsburgites' are desirable, as it seems that a wide range of compositions may occur there, which might well provide further evidence of the extent of this solid solution series.

The wavenumbers of the infrared absorption maxima for these samples are listed in Table 2, along with probable assignments, based on the known positions of absorption bands for isolated ions (Hertzberg, 1945; Nakamoto, 1978) and on comparison with published assignments for chemically related minerals.

A notable feature of the spectra is the very strong splitting of the triple degeneracy of the arsenate ν_3 absorption compared with that of the corresponding phosphate absorption. The three well separated absorptions indicate that the symmetry of the distorted anion is lower than any with a threefold axis, and the coordination must be through at least two of the arsenate oxygens, probably bidentate, possibly bridging. This stronger splitting also suggests that the arsenate coordinates more strongly to the metal ions than does the phosphate; perhaps the bite-size of the arsenate fits the lattice packing better than that of the phosphate ion.

TABLE 2. Absorption maxima in the infrared spectra of philipsburgite and kipushite

Absorption maxima, cm^{-1}, intensities		Assignments
Philipsburgite, Potts Gill. Off RSWB 65-534.	Arsenatian Kipushite, Montana.	
3550 wm, sp	3550 sh	O-H stretch, not appreciably H-bonded.
~3000 to 3480 m, vbr	3480 sh	O-H stretch, H-bonded.
	~3120 to 3360 m, vbr	
~1640 vw, br	~1620 vvw	H-O-H "scissor" deformation, H-bonded. Extremely weak, possibly absent (moisture).
1100 sh	1098 sp	Phosphate ν_3 unsymmetrical stretch. Note 1.
1058 sh	1060 sh (?)	
1030 vs	1032 vs, sp	
965 vvw	975 m	PO_4 ν_1 symmetrical stretch. Note 2.
888 vs	882 w	AsO_4 ν_3 unsymmetrical stretch. Note 3.
835 vs	840 w	
650 wm	653 sh	
	615 wm	O-H deformation and/or Cu-O stretch? Note 4.
600 sh	600 m	
550 wm	553 w	PO_4 ν_4 unsymmetrical bend. Note 5.
520 sh	532 w, sp	
483 m	480 w, br	Metal-OH stretch? Note 6.
460 w		AsO_4 ν_4 unsymmetrical bend, PO_4 ν_2 symmetrical bend, metal-O stretch? Note 7.
435 m	430 sh	

s = strong, m = medium, w = weak, v = very, br = broad, sp = sharp, sh = shoulder.

NOTES TO TABLE 2.

1. Triply degenerate. At 1050 cm^{-1} in libethenite (Braithwaite, 1983).
2. Forbidden, and therefore weak. At 980 cm^{-1} for the isolated ion (Hertzberg, 1945) and at 960 cm^{-1} for cornetite (Moenke, 1962, 1966).
3. The triply degenerate AsO_4 ν_3 is near 878 cm^{-1}, and the weak, forbidden AsO_4 ν_1 symmetrical stretch is near 850 cm^{-1} for the free ion (Nakamoto, 1978). The ν_3 absorption is between 800 - 900 cm^{-1} for most arsenates (Moenke, 1962, 1966). The ν_1 absorption is usually hidden under this.
4. A band at 610 cm^{-1} in libethenite, shifted on deuteration, is ascribed to an O-H deformation (Braithwaite, 1983). CuO absorbs at 610 cm^{-1} and Cu_2O at 615 cm^{-1} (Ferraro, 1971).
5. Triply degenerate. At 543, 575 cm^{-1} in pyromorphite (Levitt and Condrate, 1970). Absorptions due to Cu-O are also found in this region for copper arsenates (Sumin de Portilla, 1974; Sumin de Portilla et al., 1981), as are those of hydroxy-bridged complexes of copper(II) (Ferraro, 1971).
6. A Cu-OH stretch in malachite is at 485 cm^{-1} (Goldsmith and Ross, 1968).
7. The triply degenerate AsO_4 ν_4 bend is near 420 cm^{-1} (Nakamoto, 1978), in olivenite at 452 cm^{-1} (Moenke, 1962, 1966). The PO_4 ν_2 forbidden, and therefore weak symmetrical bending vibration is at 436 cm^{-1} in pyromorphite (Levitt and Condrate, 1970), and at 415 and 464 cm^{-1} in cornetite according to Moenke (1962, 1966). However, Cu-O stretching vibrations are also found in this region, e.g. between 400 - 425 cm^{-1} in malachite and azurite (Goldsmith and Ross, 1968; see also Braithwaite, 1983).

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