



# Post-mining amorphous Cu-Al hydroxyphosphate from West Caradon Mine, Liskeard, UK

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With 4 figures and 2 tables

**Abstract:** Amorphous post-mining matter with the simplified formula  $\text{CuAl}_5(\text{PO}_4, \text{SiO}_4, \text{SO}_4, \text{AsO}_4)\text{F}(\text{OH})_{11-13} \cdot n\text{H}_2\text{O}$  ( $n = 5-6$ ) was discovered in the West Caradon Mine, Liskeard District, Cornwall, England and characterized by means of electron microprobe analyses, direct determination of  $\text{H}_2\text{O}$ , IR spectroscopy, powder X-ray diffraction and optical data. Origin of the Cu-Al hydroxyphosphate and its relationships with amorphous phosphate minerals are discussed.

**Key words:** copper aluminium hydroxyphosphate; amorphous mineral; infrared spectroscopy; post-mining mineralization; West Caradon Mine; England

## Introduction

The West Caradon Mine situated at the western slope of Caradon Hill, near the village of St Cleer and 250 m SSE of Gonamena settlement, Liskeard District, Cornwall, England (50° 30' 18" N, 4° 27' 4" W), was exploited for copper from 1837 to 1886. Mining was focused on a set of near-vertical Cu ore veins trending E-W for about 400 m in granitic host rock at the SE margin of the Bodmin Moor granite (Dines 1956). The site apparently remained undisturbed till 1983/84 when local collectors took samples of

a blue mineral substance from the underground workings, marketing it as presumed woodwardite.

In August 1985 similar samples were collected by one of the authors (S.W.) and Mike Merry (Camborne) in a small area 6–7 m above the partially flooded West Caradon Adit during a survey of the old mine workings. A dark-blue glassy substance forms botryoidal crusts covering an only m<sup>2</sup>-sized area of a fluorite bearing vein trending N–S. This mineralization is apparently of post-mining

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formation. The brecciated quartz-rich vein rock contains fragments of the host rock (silicified, chloritized and hydrothermally altered pelitic schist).

Semi-quantitative WDS analyses of the blue Caradon mineral indicated the presence of Cu, Al and P. X-ray diffractometry of a powdered sample showed that the mineral is amorphous with minor reflections pointing to traces of fluorite impurity. An IR spectrum obtained by B. Suhner (Herisau, CH) in 1986 showed that the Caradon mineral is very rich in H<sub>2</sub>O. The results of a quantitative wet chemical analysis on some main components of a powdered sample performed by T. Dorfner (Mineralogical-Petrographical Institute, Munich University) in 1987 are (wt.%): Al<sub>2</sub>O<sub>3</sub> 37.31, P<sub>2</sub>O<sub>5</sub> 10.99, H<sub>2</sub>O 33.81, -O = F 2.03, total 84.14 (Cu and As were not measured).

A preliminary short note and a photo of this unnamed CuAl-phosphate has been published by Weiß (1987). The study of this mineral was resumed only in 2016, and in this paper we report its results.

## Occurrence, morphology and associated minerals

The discussed X-ray amorphous Cu-Al hydroxyphosphate forms deep blue botryoidal crusts up to 5 mm thick (Figs. 1a, b) on brecciated vein rock that contains, besides quartz and chlorite, primary fluorite and chalcopyrite. The crusts are sporadically covered by woodwardite which was confirmed by IR spectroscopy.

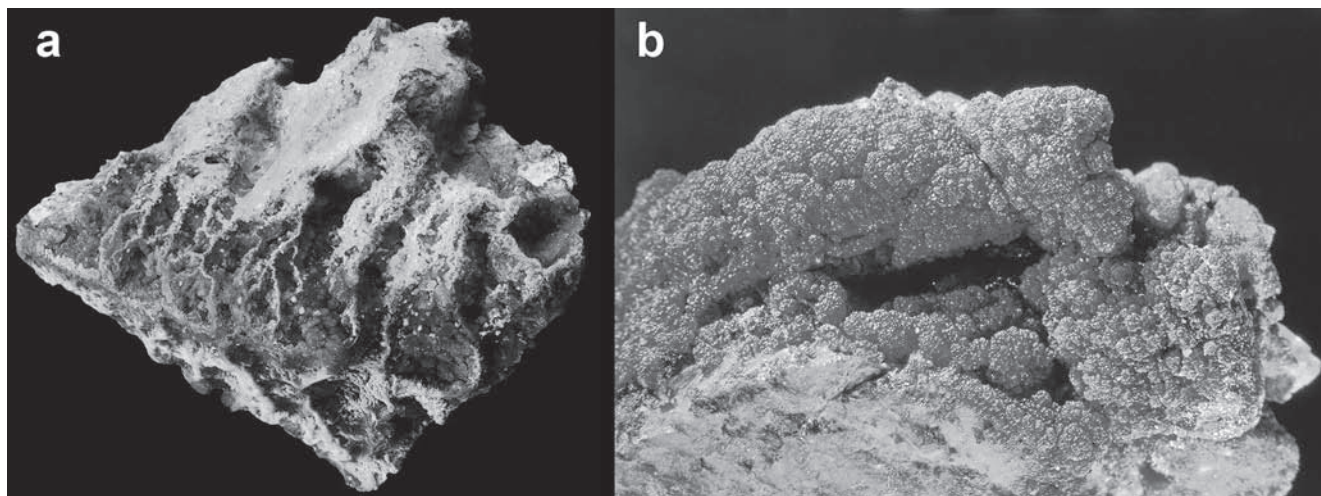
## Analytical techniques

In order to obtain IR absorption spectrum, hand-picked grains were ground in an agate mortar, mixed with anhydrous KBr, pelletized, and analysed using an ALPHA FTIR spectrometer (Bruker Optics) in the range of wavenumbers from 360 to 3800 cm<sup>-1</sup>, with a spectral resolution of 4 cm<sup>-1</sup>. The IR spectrum of a pure KBr disk was used as a reference.

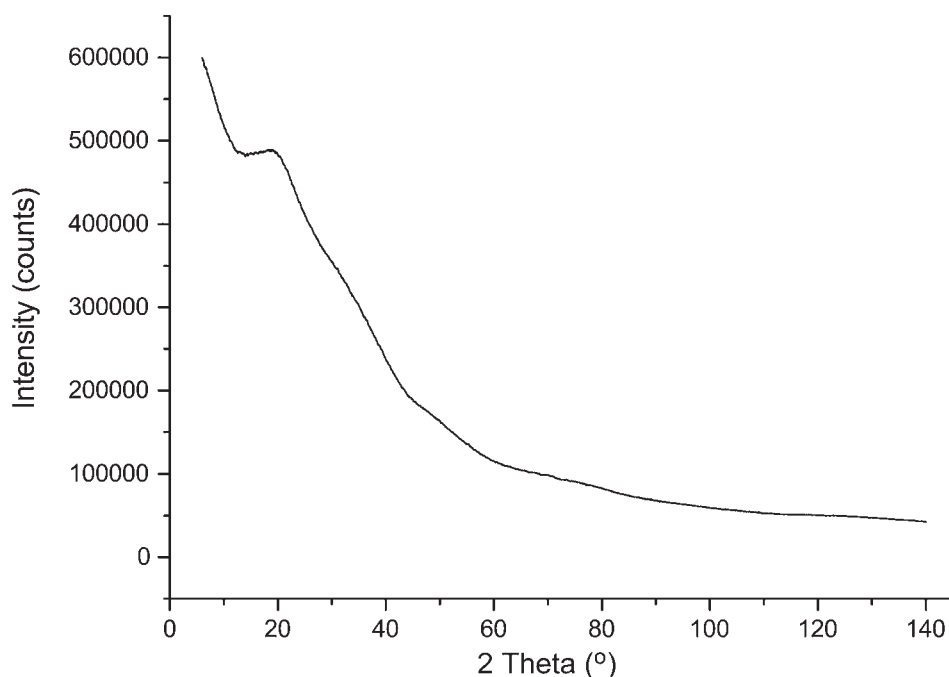
The density was measured by the flotation method using mixtures of bromoform with ethanol. Optical properties have been determined in immersion liquids. Electron microprobe analyses were carried out using a Tescan VEGA-II XMU INCA scanning electron microprobe with an Energy 450 digital electronic microscope (20 kV, 190 pA, 180 nm beam diameter). The standards used for micro-analysis were MgF<sub>2</sub> for F, MgO for Mg, Al<sub>2</sub>O<sub>3</sub> for Al, SiO<sub>2</sub> for Si, LaPO<sub>4</sub> for P, BaSO<sub>4</sub> for S, wollastonite for Ca, InAs for As, and pure Cu and Zn for corresponding elements.

H<sub>2</sub>O was determined by the Alimarin method, a modified Penfield method based on selective sorption of H<sub>2</sub>O on Mg(ClO<sub>4</sub>)<sub>2</sub> from gaseous products obtained by heating the mineral at 1080 °C in oxygen at 1 atm.

Powder X-ray diffraction data were obtained using a Rigaku RAXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector, in Debye-Scherrer geometry. The following conditions were applied: CoK $\alpha$  radiation (rotating anode with microfocus optics), 40 kV, 15 mA,  $d=127.4$  mm, exposure time



**Fig. 1.** Amorphous Cu-Al hydroxyphosphate forming deep blue botryoidal crusts (a) partially overgrown by woodwardite (light turquoise-blue), on brecciated vein rock (field width 4.4 cm, photographer R. Appiani) and (b) on a vein rock containing quartz and fluorite (field width 3.5 cm).



**Fig. 2.** Powder X-ray diffraction pattern of amorphous Cu-Al hydroxyphosphate.

15 minutes. The primary image plate data were processed using the *osc2×rd* program (Britvin et al. 2017) and Stoe WinXPOW 2.08 software.

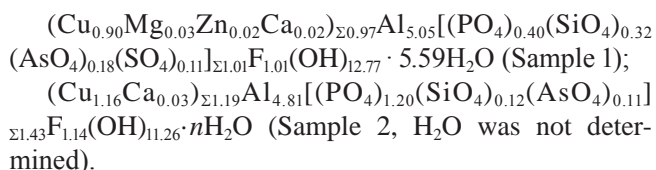
### Powder X-ray diffraction data

The powder X-ray diffraction pattern of the amorphous Cu-Al hydroxyphosphate is given in Fig. 2. No reflections of crystalline phases have been observed. The wide halo observed in the  $2\theta$  region of about  $20^\circ$  corresponds to the scattering of the glass fibre used for sample mounting.

### Chemical data

Analytical data (mean of 5 point analyses for Sample 1 and mean of 3 point analyses for Sample 2) are given in Table 2. Contents of other elements with atomic numbers  $> 8$  are below their detection limits.

The charge-balanced empirical formulae based on 6 metal cations are:

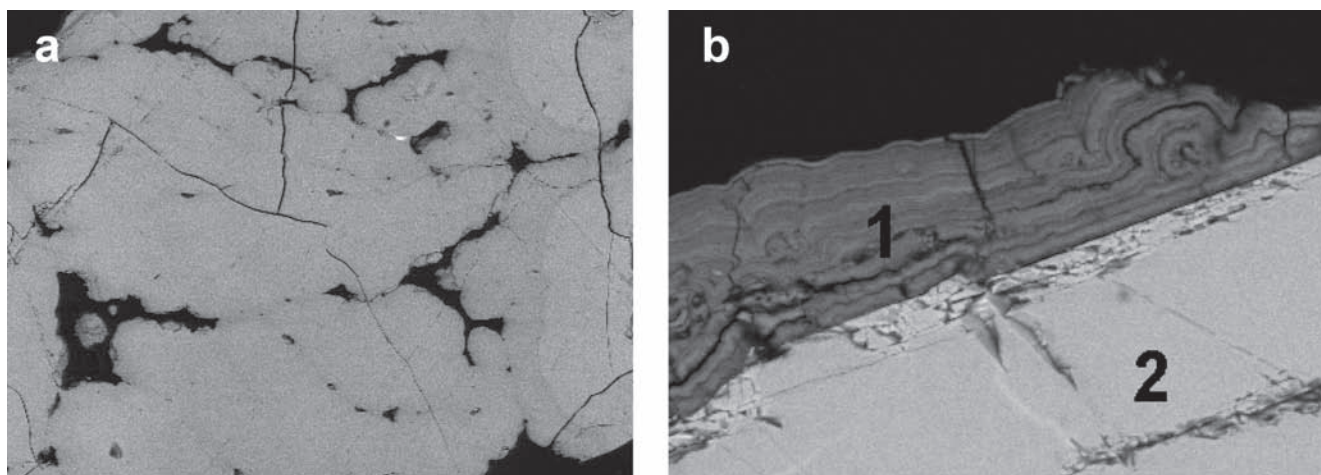


As one can see from Table 1 and Figs. 3a,b, Sample 1 is rather uniform in composition, whereas Sample 2

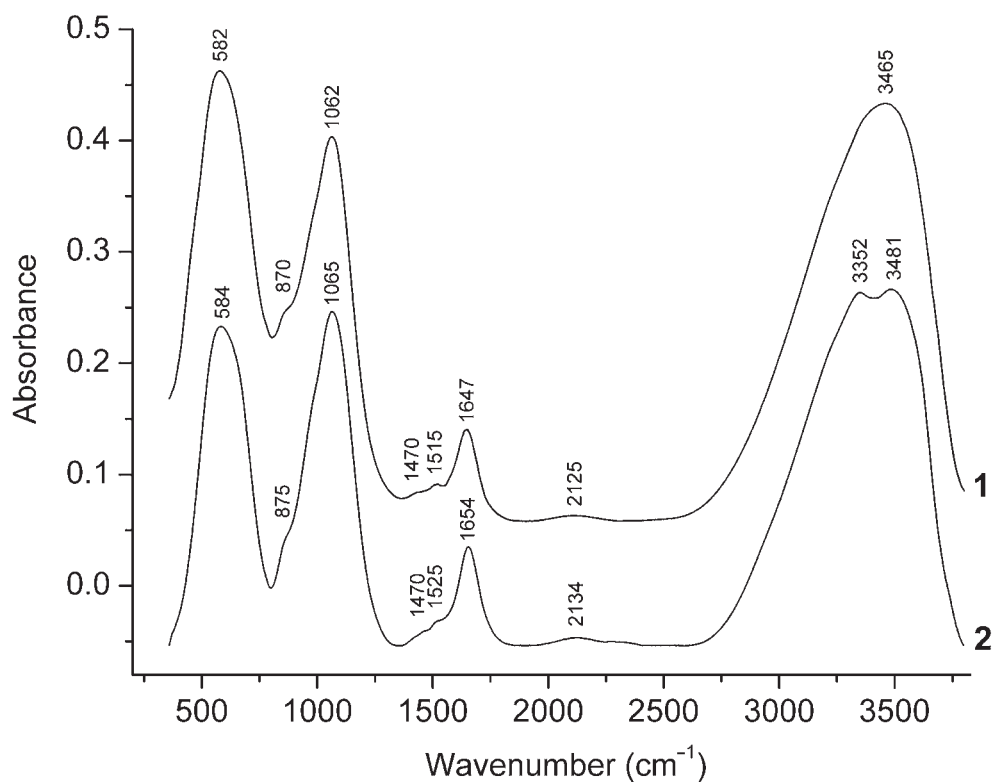
**Table 1.** Chemical composition (in wt%) of amorphous Cu-Al hydroxyphosphate. Upper and lower values correspond to Sample 1 and Sample 2, respectively.

Constituent	Content	Range	Standard deviation
MgO	0.21 n.d.	0.17–0.26 –	0.03 –
CaO	0.20 0.26	0.18–0.25 0.16–0.43	0.03 0.12
CuO	11.04 14.49	10.79–11.30 12.59–16.50	0.16 1.60
ZnO	0.27 n.d.	0.17–0.35 –	0.06 –
Al <sub>2</sub> O <sub>3</sub>	39.79 38.42	39.70–40.23 36.55–40.04	0.24 1.44
SiO <sub>2</sub>	2.97 1.16	2.52–3.41 1.01–1.34	0.28 0.14
P <sub>2</sub> O <sub>5</sub>	4.41 13.33	4.12–4.68 12.73–13.87	0.22 0.47
As <sub>2</sub> O <sub>5</sub>	3.29 1.97	3.04–3.72 1.29–2.56	0.24 0.44
SO <sub>3</sub>	1.42 n.d.	1.21–1.63 –	0.17 –
F	2.99 3.39	2.43–3.47 2.76–4.10	0.33 0.60
H <sub>2</sub> O	33.5 ± 0.5 No data		
–O = F	–1.26 –1.43		
Total	98.82 71.59		

Note: n.d. means that the component was not detected by electron microprobe analyses.



**Fig. 3.** Amorphous Cu-Al hydroxyphosphate: (a) Sample 1, field width 200  $\mu\text{m}$  and (b) zonal crust of Sample 2 (1) on fluorite (2), field width 150  $\mu\text{m}$ . Light zones are enriched in As and Cu. Polished sections. SEM (BSE) images.



**Fig. 4.** Infrared spectra of amorphous Cu-Al hydroxyphosphate: (1) Sample 1 and (2) Sample 2. The spectra have been offset for comparison.

shows wide variations of Cu, Al, P, As and F. The simplified formula of the amorphous Cu-Al hydroxyphosphate can be written as follows:  $\text{CuAl}_5(\text{PO}_4, \text{SiO}_4, \text{SO}_4, \text{AsO}_4)\text{F}(\text{OH})_{11-13} \cdot n\text{H}_2\text{O}$  ( $n = 5-6$ ).

### Physical properties

Two samples (Sample 1 and Sample 2) have been investigated. Cu-Al hydroxyphosphate from the West Caradon Mine is semitransparent, deep blue to greenish-blue. The

**Table 2.** Comparative data for amorphous Cu-Al hydroxyphosphate from West Caradon Mine and some other amorphous hydrous supergene phosphate minerals.

Mineral	Cu-Al hydroxyphosphate (Sample 1)	Evansite	Rosièresite	Santabarbaraite	Delvauxite
Simplified formula	$\text{CuAl}_5(\text{PO}_4)\text{F}(\text{OH})_{13} \cdot n\text{H}_2\text{O}$ ( $n = 5-6$ )	$\text{Al}_3(\text{PO}_4)(\text{OH})_6 \cdot 8\text{H}_2\text{O}$	$\text{Pb}_x\text{Cu}_y\text{Al}_z(\text{PO}_4)_m \cdot n\text{H}_2\text{O} ?$	$\text{Fe}^{3+}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$	$\text{CaFe}^{3+}_4(\text{PO}_4)_2(\text{OH})_8 \cdot 4-5\text{H}_2\text{O}$
Density, g/cm <sup>3</sup>	2.08	2.0	2.2	2.42	2.38–2.53
Refractive index	1.500	1.445–1.485	1.50	1.695	1.57–1.73
Strongest bands of the IR spectrum (cm <sup>-1</sup> )	3465, 1654, 1062, 582	3470, 1645, 1073s, 597, 567	No data	3250, 3100, 1634, 1018, 585, 541, 470	3380, 1640, 1020, 580, 472
Sources	This study	García-Guinea et al. (1995), Chukanov (2014)	Palache et al. (1951)	Pratesi et al. (2003), Chukanov (2014)	Palache et al. (1951), Čech & Povondra (1979), Chukanov (2014)

streak is light blue. The lustre is vitreous. It is brittle, with an estimated Mohs' hardness of 2½ to 3. Its powder is slightly soluble in warm (30–40 °C) water. The measured density is equal to 2.08(1) g/cm<sup>3</sup> (for Sample 1).

The assignment of absorption bands in the IR spectra (Fig. 4) made in accordance with Chukanov and Chervonnyi (2016) is as follows.

3000 to 3800 cm<sup>-1</sup>: O–H stretching vibrations;

2125–2134 cm<sup>-1</sup> (broad bands): overlapping overtones of asymmetric stretching modes of PO<sub>4</sub> and SO<sub>4</sub> tetrahedra;

1647–1654 cm<sup>-1</sup>: bending vibrations of H<sub>2</sub>O molecules;

1470 to 1525 cm<sup>-1</sup>: possibly, combination modes or stretching bands of trace amounts of CO<sub>3</sub><sup>2-</sup>;

1062–1065 cm<sup>-1</sup>: overlapping bands of symmetric stretching vibrations of PO<sub>4</sub> and SO<sub>4</sub> tetrahedra);

582–584 cm<sup>-1</sup>: combination of Al–O-stretching vibrations, bending vibrations of PO<sub>4</sub> and SO<sub>4</sub> tetrahedra and librational vibrations of H<sub>2</sub>O molecules.

The assignment of the shoulder observed in the range of 870–875 cm<sup>-1</sup> is ambiguous because of low contents of As and Si. This absorption may be due to Al···O–H bending and Si–O-stretching vibrations. The strongest bands of the AsO<sub>4</sub> tetrahedra are typically observed in the range from 780 to 880 cm<sup>-1</sup>.

The bands of O–H stretching vibrations correspond to medium-strengths hydrogen bonds. The mean distances  $d(\text{O} \cdots \text{O})$  (in Å) between the oxygen atoms of the hydrogen bond donor and acceptor can be estimated using the following correlation (Libowitzky 1999):  $\nu_{\text{O-H}} (\text{cm}^{-1}) = 3592 - 304 \cdot 10^9 \cdot \exp[-d(\text{O} \cdots \text{O})/0.1321]$ . The values  $\nu_{\text{O-H}}$  of 3352, 3465 and 3481 cm<sup>-1</sup> correspond to the  $d(\text{O} \cdots \text{O})$  distances equal to 2.77, 2.85 and 2.87 Å, respectively. The splitting of the band of O–H stretching vibrations in the IR spectrum of Sample 2 may be due to its compositional inhomogeneity (Fig. 3, Table 1).

Despite the Cu-Al hydroxyphosphate and evansite have different stoichiometry, positions of the strongest bands in their IR spectra are close, but differ significantly from those of Fe<sup>3+</sup>-bearing amorphous phosphates (Table 2). Most likely, these differences are due to the different polarizing ability of Al and Fe<sup>3+</sup> towards the PO<sub>4</sub><sup>3-</sup> and OH<sup>-</sup> groups.

Under the microscope, the Cu-Al hydroxyphosphate is pale blue. The mineral is optically isotropic with  $n = 1.500(2)$  ( $\lambda = 589 \text{ nm}$ ). The low value of the Gladstone-Dale compatibility index (Mandarino 1981)  $1 - (K_p/K_c) = -0.006$  calculated for Sample 1 confirms correctness of determination of its chemical composition, refractive index and density.

## Discussion

Among supergene hydrous phosphate minerals, numerous amorphous species are known. Their comparative data are given in Table 2. In terms of chemical composition and chemical properties, the amorphous Cu-Al hydroxyphosphate from the West Caradon Mine shows the most close relationships to evansite and rosièresite.

In ore deposits located in Cornwall, supergene alteration of copper ores commonly leads to the formation of sulphates (like brochantite or langite) which do not contain fluorine as a main component. Only locally, always with pelitic schists as a host rock, late-hydrothermal formation of hydrous Al-bearing phosphates like childrenite may be observed (*e.g.* within the contact metamorphic aureole of the St. Austell granite (Braithwaite & Cooper 1982)). The formation of the late-stage F-bearing phosphate mineral is uncommon for ore deposits of the Cornish mining district.

The post-mining formation of this amorphous Cu-Al hydroxyphosphate was obviously favoured by adjoining

Al-rich and P-bearing pelitic country rocks, while the chalcopyrite-containing fluorite vein served as a source of Cu and F. Hypothetically, Cu-Al hydroxyphosphate may be a product of sorption of  $\text{Cu}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$  and subordinate anions on  $\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  gel (Pa Ho Hsu & Bates 1964) or  $\text{Al}(\text{OH})_3$  nanoparticles (Al'myasheva et al. 2005) formed as a result of exposure of aluminosilicates to sulfuric acid (a product of chalcopyrite oxidation). In this reference, it is worth to note that sorption of  $\text{Cu}^{2+}$  and  $\text{F}^-$  on microcrystalline  $\text{Al}(\text{OH})_3$  are well-known processes (see Dubbin & Sposito 2005, Valdivieso et al. 2006).

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