

Pseudomalachite–cornwallite and kipushite–philipsburgite solid solutions: chemical composition and Raman spectroscopy

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Abstract: A suite of 60 mineral samples with compositions intermediate between pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$, and its arsenate analogue cornwallite, and between kipushite, $(\text{Cu,Zn})_6(\text{PO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$, and its arsenate analogue philipsburgite was investigated by electron-probe microanalysis, scanning electron microscopy, powder X-ray diffraction and micro-Raman spectroscopy. A wide range of compositions was found, covering 77.5 mol% and 75 mol% of the cornwallite–pseudomalachite and kipushite–philipsburgite solid solutions, respectively, demonstrating an extended $\text{P} \leftrightarrow \text{As}$ substitution in these minerals. The analyses also reveal a Zn deficiency in the tetrahedral site of the kipushite–philipsburgite structure, leading to the crystal-chemical formula $^{[4]}(\text{Zn,Cu})^{[6]}\text{Cu}_5(\text{P}_{1-x}\text{As}_x\text{O}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$ for this series. Raman spectra of the pseudomalachite–cornwallite solid solution are sensitive to the $\text{P}/(\text{As} + \text{P})$ ratio. The up-shift of a band assigned to the symmetric stretching vibrations of (AsO_4) group recorded in Raman spectra of the arsenate pseudomalachite is indicative of shortening As–O bonds and of bond-angle adjustment to accommodate the large As ions in the pseudomalachite structure. This feature is less evident in the arsenate kipushite, perhaps due its larger cell volume, where larger ions can be more easily accommodated in the anionic sublattice. Raman imaging and cluster analysis were applied to reveal chemical heterogeneity and structural disorder in the kipushite–philipsburgite solid solution.

Key-words: cornwallite; kipushite; philipsburgite; pseudomalachite; solid solution; arsenate; phosphate; Raman spectroscopy; Miedzianka.

1. Introduction

Base-metal arsenates and phosphates in the oxide zone of ore deposits often form solid solutions. The mimetite–pyromorphite series may be the best known example of a complete arsenate–phosphate solid solution (Markl *et al.*, 2014). Unlimited miscibility between phosphate and arsenate anions results from the same charge (–3) and similar size of the $[\text{AsO}_4]$ (248 pm) and $[\text{PO}_4]$ (238 pm) tetrahedra (Williams, 1990).

Cornwallite, $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$, and particularly pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$, are among the most commonly encountered secondary minerals in oxidized copper deposits. Their stability fields are similar regarding pH range and Cu^{2+} activity, though cornwallite has a much narrower stability field (Magalhães *et al.*, 1986, 1988). Both minerals are isostructural (space group $P2_1/c$); hence the existence of an anionic complete solid-solution series has been postulated based on X-ray powder diffraction data (Berry, 1951) and single-crystal structure refinement (Artl & Armbruster, 1999). However, published chemical analyses of both minerals cover a limited compositional range with the $\text{As}/(\text{As} + \text{P})$ ratio in pseudomalachite not exceeding 0.23 (Plášil *et al.*, 2009) and the $\text{P}/(\text{As} + \text{P})$ ratio in cornwallite up to

0.12 (Williams, 1990). The limited number of analyzed samples may not have been sufficient to cover the entire compositional range between cornwallite and pseudomalachite.

Philipsburgite, $(\text{Cu,Zn})_6(\text{AsO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$, and kipushite, $(\text{Cu,Zn})_6(\text{PO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$ (Peacor *et al.*, 1985; Piret *et al.*, 1985) provide an example of more complex solid solution with cationic and anionic substitutions. Complete miscibility between the isostructural ($P2_1/c$) end-members is expected on the ground of crystal chemistry. However, no philipsburgite end-member has been found. The $\text{As}/(\text{As} + \text{P})$ ratio in philipsburgite ranges from the highest value of 0.815 reported recently (Shirose & Uehara, 2011) to 0.54 in the specimen from the type locality (Peacor *et al.*, 1985). Similarly, a limited substitution between Cu and Zn has been reported for philipsburgite, with the Zn/Cu ratio in the range 0.22–0.38. The highest Zn/Cu ratio (0.55) was reported in kipushite (Piret *et al.*, 1985). Philipsburgite and kipushite are relatively rare and only few chemical analyses of those minerals are available in the literature (Peacor *et al.*, 1985; Piret *et al.*, 1985; Walenta *et al.*, 1985; Braithwaite & Ryback, 1988; Shirose & Uehara, 2011; Siuda & Gołębiewska, 2011).

In this paper we provide direct evidence for the existence of extended solid solutions between cornwallite and

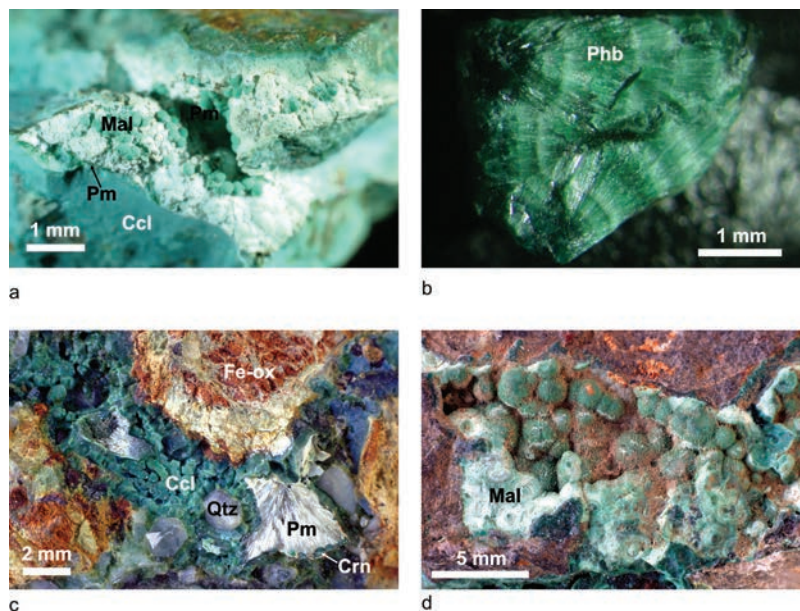


Fig. 1. Examples of samples from Miedzianka investigated in this study: (a) a crust of chrysocolla (Ccl) overgrown by pseudomalachite (Pm) and malachite (Mal) in sample M1; (b) radial aggregates of kipushite–philipsburgite (Phb) crystals with pronounced banding, sample M2; (c) highly weathered amphibolite altered to Fe-oxides and hydroxides (Fe-ox) with chrysocolla (Ccl), whitish pseudomalachite (Pm), and cornubite (Crn), Qtz – quartz, sample M3; (d) chain of malachite spheroidal aggregates (Mal) on chrysocolla in a highly weathered amphibolite, sample M4. (online version in colour)

pseudomalachite and between philipsburgite and kipushite, on the basis of electron-microprobe analyses and Raman spectroscopy of samples collected from old dumps around the Miedzianka (former Kupferberg) historic mining town (N 50°52'41.06"; E 15°56'34.91"; 504 m a.s.l.) in the Sudety Mtns., SW Poland.

Polymetallic orebodies in Miedzianka were almost uninterruptedly mined for copper, silver, lead, pyrite, and arsenic from the beginning of the 14th century till 1925. Between 1948 and 1952 uranium ore was mined in Miedzianka, producing some 15 tons of uranium metal (Siuda & Borzęcki, 2014). Miedzianka is a type locality for uranophane.

The Miedzianka ore deposit occurs within diopside amphibolite and amphibolite schists, mica schists, hornfelses, and calc-silicate rocks of the eastern metamorphic cover of the Karkonosze granitic pluton (328–304 Ma) (Mochacka *et al.*, 2015). There are three types of ore mineralization: (a) magnetite (+ sulfides) related to skarns developed at the contact with the Karkonosze granite; (b) polymetallic veins with Cu-sulfides (bornite, chalcocite) as major ore minerals associated with sulfides and sulfosalts of Ag, As, Bi, Co, Ni, Fe, and Pb; (c) polymetallic veins with uraninite (variety pitchblende) (Mochacka *et al.*, 2015). Gangue minerals are calcite, barite, fluorite, and quartz. A suite of 37 secondary supergene minerals including cornwallite, pseudomalachite, and philipsburgite have been observed in old dumps and in museum specimens (Ciesielczuk & Bzowski, 2003; Siuda & Gołębiewska, 2011 and references therein). They occur as veinlets, crusts, and well-developed crystals in small vugs.

2. Samples

Sixty samples of amphibolites and heavily weathered amphibolites with green and blue oxy-minerals were investigated. The following paragenetic sequence was determined based on spatial relationships between the observed secondary Cu,Zn-minerals: chrysocolla → cornubite → pseudomalachite–cornwallite → philipsburgite–kipushite → malachite. Chrysocolla is the most common secondary copper mineral in all of the samples (Fig. 1a, c and 2d). It occurs as chemically homogeneous sky-blue, greenish blue or green botryoidal crusts, coatings and vein fillings.

Pseudomalachite–cornwallite most commonly occur as dark green, pale-green to yellowish-green massive, botryoidal or radial aggregates of lath-shaped crystals up to 2 mm long (Fig. 1 and 2). They can also occur as well-developed crystals in vugs. Single crystals are translucent and show vitreous luster on crystal faces and greasy luster on fracture surfaces.

Kipushite–philipsburgite occurs as emerald-green botryoidal or spheroidal aggregates composed of lath-shaped crystals (Fig. 1b and 2b). Individual crystals are transparent and have a light-green streak and vitreous luster. A distinct banding due to alternating dark and bright zones is seen in cross-sectioned hand specimens (Fig. 1b).

Botryoidal and spheroidal malachite overgrows all other secondary minerals in the samples (Fig. 1a, d and 2a).

3. Analytical methods

Samples were investigated by optical microscopy, scanning electron microscopy (SEM), X-ray powder

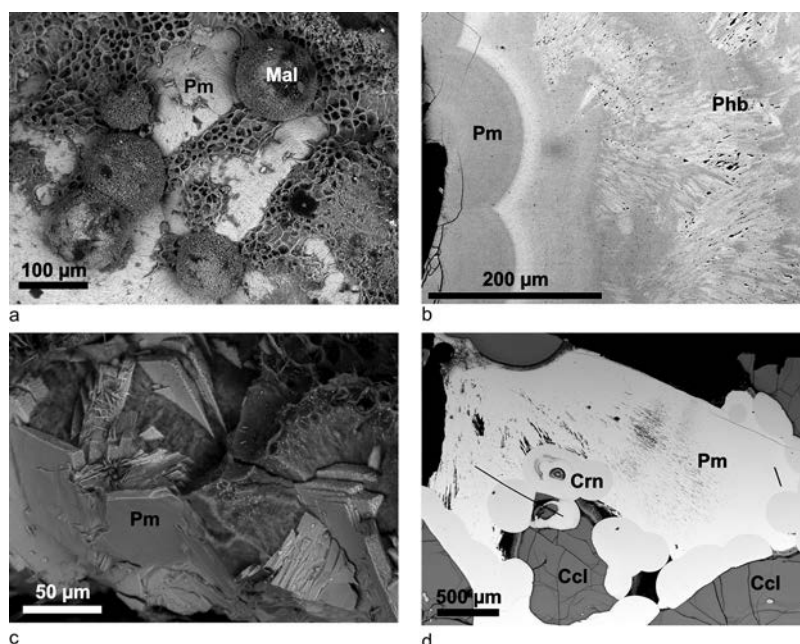


Fig. 2. (a) Scanning electron microscope (SEM) image of a cellular silica-rich crust overgrown by pseudomalachite (Pm) and malachite (Mal), sample M5; (b) BSE image of a cross section through botryoidal pseudomalachite (Pm) overgrown by radial aggregates of kipushite–philipsburgite (Phb), sample M2; (c) SEM image of a cluster of tabular pseudomalachite crystals, sample M1; (d) BSE image showing the paragenetic sequence: chrysocolla (Ccl) – cornubite (Crn) – pseudomalachite (Pm); note the mottled contrast in pseudomalachite due to variations in P/As ratio; fractures in chrysocolla most probably originated from dehydration; sample M3.

diffraction (XRD), electron-probe microanalysis (EPMA), and Raman spectroscopy.

Eleven powdered samples were examined using a fully automated X-ray Philips PW 3710 diffractometer operated at 45 kV and 30 mA. Graphite-monochromated $\text{CuK}\alpha$ radiation was applied. Two samples were analysed by microdiffraction technique with the aid of mono-capillary optics (Panalytical 135x0.1 mm prefix collimator). Small amounts of powders were placed on the surface of a silicon plate (zero-background holder) and analysed using a Panalytical X'Pert PRO-PW 3040/60 X-ray diffractometer equipped with $\text{CuK}\alpha 1$ source radiation ($\lambda = 1.540598 \text{ \AA}$), Ni-filter to reduce the $K\beta$ radiation and an X'Celerator detector at the Faculty of Earth Sciences, University of Silesia. Measurement parameters were: $10\text{--}70^\circ$ or $5\text{--}65^\circ$ 2θ range, time limit 2500 or 3000 s, step size 0.02° 2θ . Quantitative analysis of the collected data was carried out by means of the X'PERT HighScore Plus + software using the newest PDF4+ database. The quantitative analysis was performed using the Rietveld method.

Mineral morphology and spatial relationships between observed minerals were examined using a Philips XL 30 ESEM/TMP scanning electron microscope coupled to an energy-dispersive spectrometer (EDS; EDAX type Sapphire) at the Faculty of Earth Sciences, University of Silesia. Operating conditions were: accelerating voltage 15 kV; working distance *ca.* 10 mm; counting time 40 s. The same conditions were applied for back-scattered electron (BSE) imaging.

The chemical composition of samples was determined at the Inter-Institute Laboratory of the Microanalysis of Minerals and Synthetic Materials (Faculty of Geology, University of Warsaw) using a CAMECA SX-100 microprobe operated in the wavelength-dispersive (WDS) mode at an accelerating voltage of 15 kV and a beam current of 10–20 nA. Counting time for each element was 40 s at peak position and 20 s for background. The beam diameter was 10 μm whenever it was possible to find a homogeneous grain with suitable size. Otherwise, 3 μm beam size was used as a compromise between the precision and accuracy of the measurements and the availability of suitable spots for analysis. Numerous test analyses with varying beam current, probe diameter and counting times were performed to optimize the analytical conditions. Smaller beam diameter caused too much beam damage in the sample and larger beam diameter in most cases was too broad to collect X-rays from a single homogeneous grain. Analyses obtained with 10 or 3 μm beam diameter are reported in Tables 1 and 3. The $L\alpha$ and Ma lines were measured for As, Cd and Pb, Bi, respectively; $K\alpha$ lines were measured for other elements. The following standards were used: GaAs for As, synthetic YPO_4 for P, chalcopryrite for Cu, sphalerite for Zn, synthetic V_2O_5 for V, crocoite for Pb, Bi_2Te_3 for Bi; diopside for Si, Ca, and Mg. Aluminum, Ca, Cd, Cl, Mg, Fe, and Mn were below the detection limit of the electron microprobe.

Raman spectra were recorded in the range $120\text{--}4000 \text{ cm}^{-1}$ using WITec alpha300 R system equipped with a Nd:YAG laser (532 nm) at 40 mW power and a high-sensitivity back-illuminated Newton-CCD camera

Table 1. Electron microprobe analyses (wt.%) members of the pseudomalachite–cornwallite series from Miedzianka.

Sample M5	M2	M5	M7	M7	M4	M9	M4	M4	M4	M10
Analysis 1	2	3	4	5	6	7	8	9	10	12
SiO ₂	0.44	0.28	0.46	0.39	0.61	0.16	0.21	0.15	0.22	0.42
CuO	68.08	65.05	66.27	63.05	64.30	65.58	63.28	64.08	62.98	61.83
ZnO	0.05	1.17	0.00	1.18	0.92	0.39	0.20	0.22	0.10	0.10
PbO	0.08	0.16	0.03	0.11	0.21	0.14	0.39	0.23	0.14	0.24
P ₂ O ₅	18.55	17.62	17.27	14.50	14.51	11.63	9.97	9.39	8.95	6.11
As ₂ O ₅	5.20	6.82	7.34	11.02	9.78	15.79	17.74	18.88	19.81	23.04
V ₂ O ₅	0.64	0.69	0.00	0.93	0.95	0.13	0.23	0.28	0.15	0.23
Total	93.04	91.79	91.37	91.18	91.28	93.82	92.02	93.23	92.35	91.97
Number of atoms per formula unit on a 7 cation basis										
Cu	5.09	4.97	5.08	4.94	5.01	5.08	5.06	5.07	5.05	5.06
Zn	0.00	0.09	0.00	0.09	0.07	0.03	0.02	0.02	0.01	0.01
Pb	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.01
ΣM	5.09	5.06	5.08	5.03	5.09	5.11	5.09	5.10	5.06	5.08
P	1.55	1.51	1.48	1.27	1.27	1.01	0.89	0.83	0.80	0.56
As	0.27	0.36	0.39	0.60	0.53	0.85	0.98	1.04	1.10	1.31
V	0.04	0.05	0.00	0.06	0.06	0.01	0.02	0.02	0.01	0.02
Si	0.04	0.03	0.05	0.04	0.06	0.02	0.02	0.02	0.02	0.04
ΣT	1.90	1.95	1.92	1.97	1.92	1.89	1.91	1.91	1.93	1.93

Note: Al, Bi, Ca, Cd, Cl, Fe, Mg, and Mn below the detection limit.

(Institute of Material Sciences, University of Silesia). The excitation laser radiation was coupled into a microscope through a single-mode optical fiber with a 50 mm diameter. An air Olympus MPLAN (50 $\times$ /0.76NA) objective was used. Raman scattered light was focused onto a multi-mode fiber (50 mm diameter) and monochromator with a 600 line/mm grating. Single Raman spectra were accumulated by 5 scans with an integration time of 10–15 s and a resolution of 3 cm⁻¹. Moreover, Raman imaging of philipsburgite was performed in a 470 μ m $\times$ 420 μ m area using 235 $\times$ 210 pixels (= 49 350 spectra) with an integration time of 50 ms per spectrum, a precision of $\pm$ 1 cm⁻¹ and a resolution of 3 cm⁻¹. All spectra were accumulated in the range between 120 and 4000 cm⁻¹. The spectrometer monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm⁻¹). The data were manipulated by performing a baseline correction and cosmic-ray removal. Additionally, based on the Raman imaging data the *K-means* Cluster Analysis was done to find all phases. Finally, band fitting analysis for each spectrum using a Lorentz-Gauss function with the minimum number of components was done using the GRAMS software package.

4. Results and discussion

4.1. Pseudomalachite–cornwallite solid solution

4.1.1. Chemical composition

Representative EPMA data for minerals identified by X-ray powder diffraction as belonging to the pseudomalachite–cornwallite series are given in Table 1. Low

analytical totals and low sums of As + P in the analyses most probably resulted from analytical problems related to the matrix effect (inappropriate standards for As and Cu; arsenide and sulfide instead of oxy-compounds) and the H₂O content in the analyzed minerals. The amount of H₂O in Cu₅(AsO₄)₂(OH)₄ and in Cu₅(PO₄)₂(OH)₄ is 5.43 wt.% and 6.26 wt. %, respectively. Calculation of H₂O from charge balance (not shown in Table 1) improved the analytical totals, however not to the entirely satisfactory level. Similar problems with low analytical totals in EPM analyses of cornwallite and pseudomalachite were reported by other researchers (Plášil *et al.*, 2009; Števkó *et al.*, 2011).

None of the analyses represents an end-member of the cornwallite–pseudomalachite solid solution. The only specimens with the Cu₅(AsO₄)₂(OH)₄ stoichiometry encountered during this study were identified by X-ray powder micro-diffraction and Raman spectroscopy as cornubite – a triclinic dimorph of cornwallite (Fig. 1c and 2d). The P content in the investigated samples ranges from 0.15 to 1.55 atoms per formula unit (*apfu*) and As ranges from 0.27 to 1.84 *apfu*, V and Si remaining subordinate. Therefore, the maximum occupancy of the tetrahedral sites by P and As in the structure of these minerals is 77.5 % and 92 %, respectively. Almost all analyses plot linearly and continuously within analytical error along the 2.00 *apfu* tie-line in the As against P diagram (Fig. 3), covering 77.5 mol% of the expected solid solution. The compositional gap of 22.5 mol% is asymmetrical, being wider towards the pseudomalachite end-member (15 mol%). Published analyses of cornwallite and pseudomalachite included in Fig. 3 do not narrow the compositional gap as they cluster around end-member

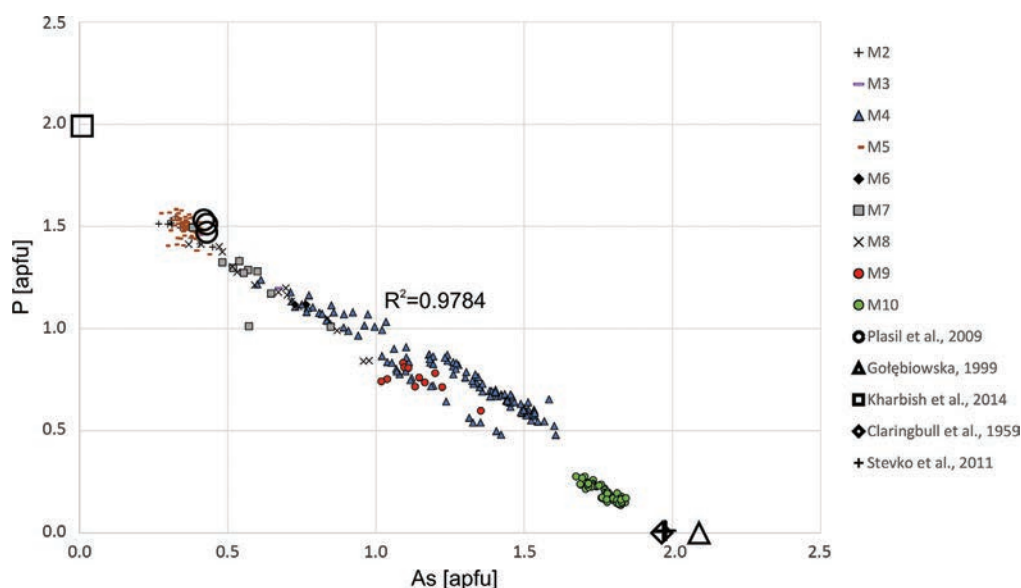


Fig. 3. Summary plot of As vs. P in atoms formula unit (*apfu*) in the pseudomalachite–cornwallite solid solution. Symbols refer to nine samples from Miedzianka, in which 334 EPM analyses were performed. (online version in colour)

compositions (2.00 *apfu*). Most probably, the compositional gap reflects the lack of data rather than crystallochemical constraints on the solid solution. In the case of samples from Miedzianka, the lack of chemical compositions closer to end-members suggests high activities of P and particularly of As in solution preventing crystallization of pure pseudomalachite and cornwallite. There are samples with P/As ratio of unity or very close to that value (Fig. 3 and M7–9 in Table 1). The existence of intermediate composition between end-members is reflected in the unit-cell dimensions of a mineral with 52 mol.% cornwallite (Table 2), which plot (not shown) on the line tying the unit-cell dimensions of pseudomalachite and cornwallite.

Further in this article we will use the terms arsenian pseudomalachite (As-pseudomalachite) and phosphatian cornwallite (P-cornwallite) for minerals with compositions between 1 and 2 *apfu* of P and As, respectively.

The P/(P + As) ratio of samples from Miedzianka varies not only between samples but also within a single specimen. The results of an EPMA traverse across oscillatory zoned pseudomalachite and adjacent philipsburgite are shown in

Fig. 4. Alternating dark and light bands seen in BSE reflect differences in the amount of As and P in pseudomalachite. Light bands are enriched in As relative to P. Broad bands with a width of 20–40 μm show fine zoning with individual zones less than 1 μm wide. Changes in the chemical composition within sub-micrometer zones could not be measured because their width is smaller than the electron-beam diameter of 3 μm used in analyses. The P/(P + As) ratio in pseudomalachite scatters between the extreme values of 0.45 and 0.8. Close to the boundary with philipsburgite (analyses 13 and 14 in Fig. 4), the amount of As increases in pseudomalachite to the level measured in philipsburgite. Philipsburgite is enriched in As relative to pseudomalachite in Fig. 4, particularly towards the termination of crystals (analyses 24 to 30 in Fig. 4), though some zones are enriched in P. Combining BSE image with X-ray element-distribution maps reveals a rather patchy zoning of P (darker laths within the philipsburgite aggregate in Fig. 4). There is a general trend in increasing As from the early stages of pseudomalachite crystallization to the late stages of philipsburgite crystallization. The transition from pseudomalachite to philipsburgite is marked by an abrupt drop in the Cu/(Cu

Table 2. Unit-cell dimensions of pseudomalachite (Shoemaker *et al.*, 1977), cornwallite (Artl & Armbruster, 1999) and a mineral with 52.5 mol.% cornwallite and 47.5 mol.% pseudomalachite.

	Pseudomalachite	Sample M9 52.5 % cornwallite, 47.5 % pseudomalachite	Cornwallite
<i>a</i> , Å	4.4728(4)	4.5388(6)	4.600(2)
<i>b</i> , Å	5.7469(5)	5.7581(5)	5.757(3)
<i>c</i> , Å	17.032(3)	17.217(1)	17.380(6)
β°	91.043(7)	91.540(5)	91.87(3)
<i>V</i> , Å ³	437.73	449.80	460.02

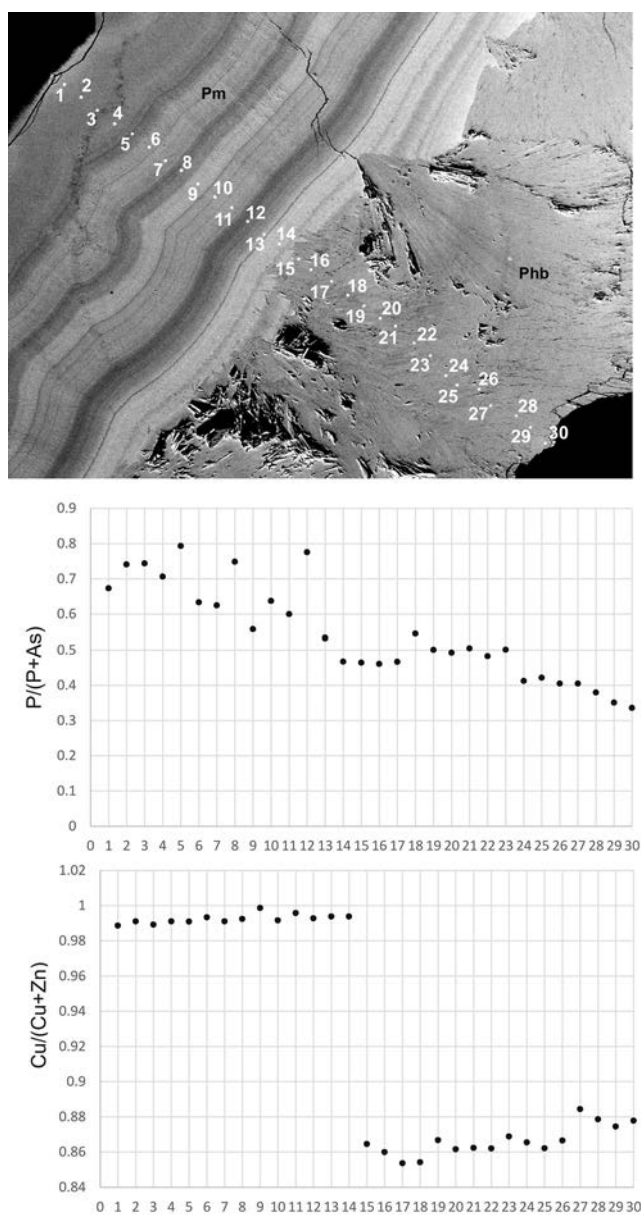


Fig. 4. BSE image of pseudomalachite (Pm) and philipsburgite (Phb) showing the distribution of P, As, Cu, and Zn expressed by their ratios across zoned pseudomalachite and radial aggregates of philipsburgite. The path of electron microprobe analyses is shown by a line of light dots. Numbers refer to analyses shown in the plots. The length of the microprobe traverse is 575 μm .

+ Zn) ratio from almost 1.0 to 0.87. The concentration of Zn increases towards termination of philipsburgite crystals. The embayed boundary between pseudomalachite and philipsburgite (Fig. 4) suggests a period of pseudomalachite dissolution prior to the crystallization of philipsburgite.

4.1.2. Raman spectroscopy

Raman spectra of samples with the P/(P + As) ratio of 0.83, 0.48 and 0.30 are reproduced in Fig. 5. Analysis of Raman-active vibrational modes in isolated tetrahedral XO_4^{3-} (X = As, P) molecular groups with ideal T_d

symmetry is the starting point for the assignment of Raman bands in arsenates and phosphates. According to Farmer (1974), the following types of vibrations and respective Raman band positions are characteristic of $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ (values in brackets) molecular groups: symmetric stretching mode (ν_1) at $\sim 980\text{ cm}^{-1}$ ($\sim 820\text{ cm}^{-1}$), anti-symmetric stretching mode (ν_3) at $\sim 1040\text{ cm}^{-1}$ ($\sim 840\text{ cm}^{-1}$), bending mode (ν_2) at $\sim 450\text{ cm}^{-1}$ ($\sim 340\text{ cm}^{-1}$) and (ν_4) at $\sim 570\text{ cm}^{-1}$ ($\sim 390\text{ cm}^{-1}$). Isomorphic substitutions of the type $\text{P} \leftrightarrow \text{As}$ cause deviation from the ideal T_d symmetry of XO_4 tetrahedra inducing new Raman bands and shifts of bands compared to the ideal tetrahedra. That may explain differences in band positions and in number of bands reported by various authors, especially for pseudomalachite (Frost *et al.*, 2002a and b; Kharbush *et al.*, 2014). Those differences may also result from crystal orientation effects as experimentally shown by Kharbush *et al.* (2014).

In the deconvoluted Raman spectrum of a sample (M2 in Fig. 5) with the highest amount of P ($\text{P}/(\text{P} + \text{As}) = 0.83$) almost all bands can be attributed to pseudomalachite except for two strong and broad bands at 881 and 872 cm^{-1} (Fig. 5). Those bands are problematic because there are only weak Raman bands at 876, 820, and 807 cm^{-1} (Frost *et al.*, 2002a and b) or at 844 and 822 cm^{-1} (Kharbush *et al.*, 2014) reported for pseudomalachite in the spectral region of 900–800 cm^{-1} . There are, however, strong bands in that region observed in the Raman spectra of hydroxy copper arsenates, including cornwallite, assigned to the ν_1 , $\nu_3(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$ stretching modes (Frost *et al.*, 2002c, 2014a, Martens *et al.*, 2003; 2015). There may be some contribution from the POH symmetric stretching mode to the band at 881 cm^{-1} and from the hydroxyl deformation mode of CuOH to the band at 872 cm^{-1} (Frost *et al.*, 2002a and b, 2003, 2014b). However, taking into account that 17 % of tetrahedral cationic sites in sample M2 are occupied by As, the assignment of the strong Raman bands in the region of 900–800 cm^{-1} to vibrations of $(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$ groups is justified. This is further confirmed by the increasing intensity of the most intense band in the 900–800 cm^{-1} region and its shift towards lower wavenumbers typical of cornwallite with increasing As content in the investigated samples (Fig. 5).

Similar intensity but different full width at half-maximum (FWHM) of the bands at 881 (FWHM $\sim 40\text{ cm}^{-1}$) and 872 cm^{-1} (FWHM $\sim 100\text{ cm}^{-1}$) suggest two different positions of the arsenate ion in the As-pseudomalachite structure due to the difference in local symmetry of AsO_4 tetrahedra. By analogy, two bands at 950 and 975 cm^{-1} assigned to $\nu_1(\text{PO}_4)^{3-}$ vibrations suggest two different positions of the phosphate ion and local distortion of PO_4 tetrahedra.

The distortion of XO_4 tetrahedra in As-pseudomalachite is most probably caused by the partial substitution of P^{5+} ions (38 pm) by larger As^{5+} ions (58 pm). The average As–O distance in cornwallite (1.674 Å) (Artl & Armbruster, 1999) is longer than the average P–O distance (1.538 Å) in pseudomalachite (Shoemaker *et al.*, 1977). Therefore, the

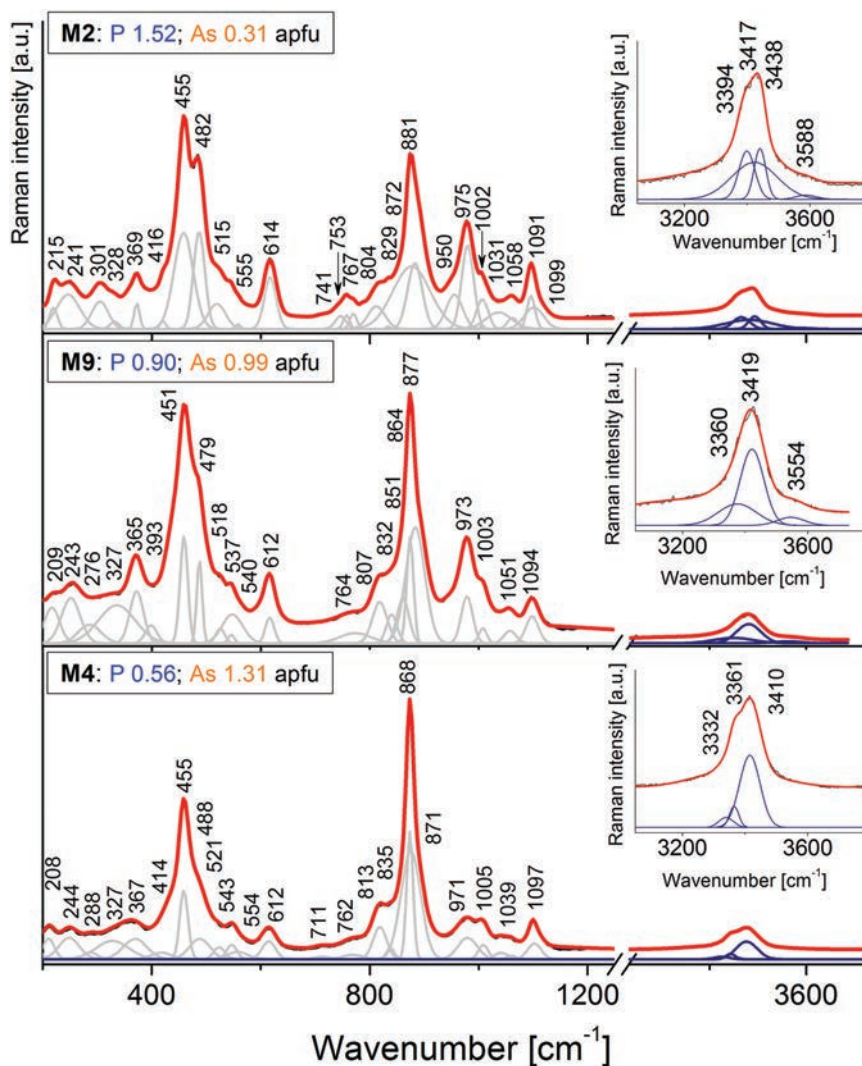


Fig. 5. Raman spectra of the pseudomalachite–cornwallite solid solution (samples: M2, M9, M4). The hydroxyl region in all spectra was enlarged to better visualize components of the bands. (online version in colour)

substitution of As^{5+} ions for P^{5+} ions in the tetrahedral sites of pseudomalachite requires the adjustment of relatively large AsO_4 tetrahedra by shortening As–O bond lengths and adjusting O–As–O angles. Interstitial or Schottky defects originate during that kind of structural adjustment (Dulski *et al.*, 2015). Possibly, the local disorder in the structure of pseudomalachite caused by the random replacement of PO_4 by distorted AsO_4 tetrahedra brings about the enhancement of the AsO_4 vibrations. The observed band splitting (Fig. 5) may also result from the hydroxyl groups in non-equilibrated position due to local non-symmetric ion environment. This effect is well seen in the Raman bands at 767, 753, and 741 cm^{-1} (spectrum M2 in Fig. 5). The Raman band at 753 cm^{-1} is assigned to the hydroxyl deformation mode in CuOH , whereas the two other bands may have resulted from the symmetry reduction due to isomorphic substitution of P by As (Frost *et al.*, 2002b, 2003).

Five low intensity bands observed at 1002, 1031, 1058, 1091, and 1099 cm^{-1} (Fig. 5) may result from a combination of two types of vibrational modes, namely the ν_3 anti-symmetric stretching vibrations of $(\text{PO}_4)^{3-}$ and $(\text{HOPO}_3)^{2-}$ groups (Frost *et al.*, 2014b).

The Raman spectrum of sample M2 in the 750–350 cm^{-1} spectral range is dominated by bands at 614 and 555 cm^{-1} assigned to the $\nu_2(\text{PO}_4)^{3-}$ vibrations, and a series of bands at 515, 482, 455, 416, and 369 cm^{-1} attributed to the ν_4 bending modes. The region of the Raman spectrum in the range 800–350 cm^{-1} represents the combination of modes originating from the overlapping vibrations of $(\text{PO}_4)^{3-}$ + $(\text{HOPO}_3)^{2-}$ groups as well as of $(\text{AsO}_4)^{3-}$ + $(\text{HOAsO}_3)^{2-}$ groups (Frost *et al.*, 2002b, 2014b). The band at 455 cm^{-1} related to tetrahedral P is characteristic of pseudomalachite, whereas bands at 515 and 482 cm^{-1} are assigned to the ν_4 $(\text{AsO}_4)^{3-}$ and those at 416 and 369 cm^{-1} are attributed to the

ν_2 (AsO_4)³⁻ bending modes (Frost *et al.*, 2002b, 2014b). In the low-wavenumber region, bands at 328 and 301 cm⁻¹ are assigned to the Cu–O stretching vibration and those at 241 and 215 cm⁻¹ may be related to metal–oxygen stretching vibrations and lattice mode (Frost *et al.*, 2002c).

All bands in the deconvoluted Raman spectrum of a sample (M9 in Fig. 5) intermediate between cornwallite and pseudomalachite ($\text{P}/(\text{P} + \text{As}) = 0.48$) are narrower and shifted towards lower wavenumbers compared to the spectrum of As-pseudomalachite (M2). The shift is due to smaller amount of P, which has a strong impact on the structural ordering. Three bands at 1094, 1051, and 1003 cm⁻¹ are assigned to the ν_3 vibration of (PO_4)³⁻ and (HOPO_4)²⁻ groups. The single band at 973 cm⁻¹ suggests a single position of P in the structure of sample M9 and higher symmetry of PO_4 tetrahedra compared to sample M2. Therefore, the band at 973 cm⁻¹ can be assigned to the ν_1 symmetric vibration of (PO_4)³⁻.

Two strong bands at 877 and 864 cm⁻¹ are assigned to the ν_1 , ν_3 vibrations of (AsO_4)³⁻ and (HOAsO_4)²⁻ groups, respectively (Frost *et al.*, 2014a), whereas the weak band at 764 cm⁻¹ is attributed to the hydroxyl deformation modes and is indicative of higher local symmetry of the tetrahedrally coordinated ions. Other band assignments in the spectrum of sample M9 are the same as for sample M2.

In the deconvoluted Raman spectrum of a sample (M4 in Fig. 5) with the highest amount of As ($\text{P}/(\text{P} + \text{As}) = 0.30$), a group of bands attributed to pseudomalachite still persist, though their intensity is much lower than in the spectra of samples with lower amount of As. This is well illustrated by the decrease in intensity of the $\nu_1(\text{PO}_4)$ band at 455 cm⁻¹ and bands at 1097, 1039, 1005 cm⁻¹, and 971 cm⁻¹ attributed to the ν_3 and ν_1 stretching modes of the (PO_4)³⁻ and (HOPO_3)²⁻ groups (Fig. 5).

The most intense bands at 871 and 868 cm⁻¹ are assigned to the stretching mode of (AsO_4)³⁻ and (HOAsO_3)²⁻ groups (Frost *et al.*, 2014a). The band position of the strongest band at 868 cm⁻¹ is exactly half-way (± 13 cm⁻¹) between the band at 881 cm⁻¹ in the spectrum of As-pseudomalachite (M2 in Fig. 5) and the major band at 859 cm⁻¹ in the Raman spectrum of P-free cornwallite (Frost *et al.*, 2014a, RRUFF Cornwallite R110146).

The intensity of the ν_1 mode for arsenate (868 cm⁻¹) and phosphate (455 cm⁻¹) ions depends on the $\text{P}/(\text{P} + \text{As})$ ratio. The $\nu_1(\text{PO}_4)^{3-}/\nu_1(\text{AsO}_4)^{3-}$ intensity ratio decreases from 1.26 in sample M2 ($\text{P}/(\text{P} + \text{As}) = 0.83$), through 0.4 in M9 ($\text{P}/(\text{P} + \text{As}) = 0.48$) to 0.16 in M4 ($\text{P}/(\text{P} + \text{As}) = 0.30$).

The low-wavenumber region of the P-cornwallite spectrum is dominated by bands at 612, 554, 543, 521, 518, 488, 455, 414 and 367 cm⁻¹ (Fig. 5). Those bands are attributed to the combination modes of ν_2 , ν_4 vibrations of (PO_4)³⁻ + (HOPO_3)²⁻ and (AsO_4)³⁻ + (HOAsO_3)²⁻ groups. Bands at 367 and 327 cm⁻¹ can be assigned to the Cu–O stretching vibration whereas weak bands at 288, 244, and 208 cm⁻¹ are attributed to metal–oxygen stretching vibrations and lattice mode (Frost *et al.*, 2002c).

Comparison of the Raman spectra in the hydroxyl stretching region (3050–3800 cm⁻¹) reveals smaller differences

between samples than in the case of the stretching and bending vibrations of XO_4 tetrahedra (Fig. 5). In the spectrum of As-pseudomalachite (M2 in Fig. 5) the fitting analysis revealed bands at 3588, 3438, 3417, and 3394 cm⁻¹. In the compositionally intermediate sample M9 there are bands at 3554, 3419 and 3360 cm⁻¹. In the spectrum of P-cornwallite there are partially separated bands at 3410, 3361 and 3332 cm⁻¹. Their positions are in good agreement with bands at 3411 and 3350 cm⁻¹ observed for pure cornwallite (Frost *et al.*, 2014a). Those bands are considered to be indicative of the OH-vibration modes assigned to the AsOH group if the protons are delocalized, and their positions suggest relatively weak H-bonds (Libowitzky, 1999).

The Raman spectra obtained in this study do not consist of simply superimposed spectra of end-members of the cornwallite–pseudomalachite solid solution. Substitution of P by relatively small amount of As results in the occurrence of unique Raman bands that reflect the adjustment of AsO_4 tetrahedra to the pseudomalachite structure. With chemical composition approaching the cornwallite stoichiometry, the Raman bands assigned to (AsO_4)³⁻ and (HOAsO_4)²⁻ groups shift towards wavenumbers characteristic for P-free cornwallite. Unfortunately, due to lack of samples with appropriate chemical composition we could not obtain Raman spectra of samples with less than 30 mol% pseudomalachite and less than 17 mol% cornwallite to further inspect changes in Raman spectra of the cornwallite–pseudomalachite solid solution.

4.2. Kipushite–philipsburgite

4.2.1. Chemical composition

Table 3 lists representative chemical compositions of the kipushite–philipsburgite series from Miedzianka. The amount of ions in formula unit calculated from EPM analyses and supplemented by published data is plotted on the regression line tying extreme compositions as a result of extended cationic and anionic substitutions (Fig. 6). Compositional gaps seen in Fig. 6 most probably reflect the lack of data to cover the entire compositional range of the kipushite–philipsburgite solid solution.

While published data (Peacor *et al.*, 1985; Piret *et al.*, 1985; Walenta *et al.*, 1985; Braithwaite & Ryback, 1988; Shirose & Uehara, 2011) show the amount of Zn in the philipsburgite–kipushite series to be higher than 1 *apfu*, most samples analyzed during this study have Zn contents less than 1 *apfu* (Fig. 6). This observation implies some problems with the cationic site distribution in the Zn-deficient kipushites and philipsburgites. According to Piret *et al.* (1985) there are five octahedrally coordinated cationic sites and one tetrahedrally coordinated site occupied exclusively by Zn in the unit cell of kipushite ($Z = 4$). Two octahedra are highly distorted due to the Jahn–Teller effect and can accommodate only Cu. The other three more regular octahedra host Cu and the remaining Zn. Therefore, there are structural constraints on the substitution in the cationic sublattice of the type: $^{[4]}\text{Zn}(\text{Cu}_{5-x}\text{Zn}_x)$.

Table 3. Electron-microprobe analyses (wt.%) of members of the kipushite–philipsburgite series from Miedzianka.

Sample	M2	M7	M2	M7	M2	M8	M8	M10	M10	M8	M2	M8
Analysis	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	0.27	0.41	0.23	0.65	0.12	0.12	0.13	0.51	0.14	0.12	0.05	0.10
CuO	54.44	54.73	53.41	54.07	53.31	54.65	53.69	57.63	53.61	52.87	50.40	52.57
ZnO	11.13	10.16	11.36	9.24	11.19	8.47	8.71	7.50	7.49	8.37	9.65	8.24
P ₂ O ₅	11.77	11.08	10.02	9.41	9.06	7.86	5.53	4.68	3.76	3.55	2.78	1.87
As ₂ O ₅	10.49	11.59	13.78	13.99	15.72	17.01	21.02	21.77	23.65	24.13	24.97	26.33
V ₂ O ₅	0.83	0.79	0.57	0.62	0.49	0.49	0.33	0.05	0.00	0.10	0.08	0.03
Total	89.03	88.76	89.37	87.98	89.89	88.60	89.41	92.14	88.65	89.14	87.93	89.14

Number of atoms per formula unit on an 8 cation basis

Cu	5.02	5.08	4.96	5.11	4.97	5.20	5.15	5.36	5.25	5.16	5.02	5.19
Zn	1.00	0.92	1.03	0.85	1.02	0.79	0.82	0.68	0.72	0.80	0.94	0.79
ΣM	6.02	6.00	5.99	5.96	5.99	5.99	5.97	6.04	5.97	5.96	5.96	5.98
P	1.21	1.15	1.04	1.00	0.95	0.84	0.59	0.49	0.41	0.39	0.31	0.21
As	0.67	0.74	0.89	0.92	1.01	1.12	1.40	1.40	1.60	1.63	1.72	1.80
V	0.07	0.05	0.05	0.04	0.04	0.03	0.02	0.00	0.00	0.01	0.00	0.00
Si	0.03	0.05	0.03	0.08	0.02	0.02	0.02	0.06	0.02	0.01	0.01	0.01
ΣT	1.98	1.99	2.01	2.04	2.01	2.01	2.03	1.95	2.03	2.04	2.04	2.02

Note: Al, Bi, Ca, Cd, Cl, Fe, Mg, Pb and Mn below the detection limit.

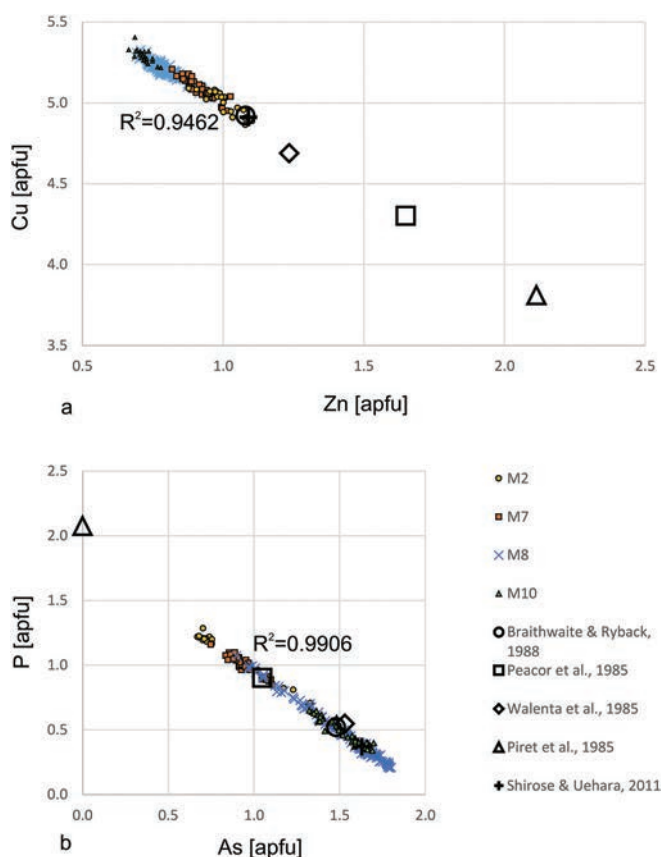


Fig. 6. Summary plot of Cu vs. Zn (a) and P vs. As (apfu) in the kipushite–philipsburgite solid solution. Symbols refer to four samples from Miedzianka (266 data points) supplemented by published data. (online version in colour)

However, the Zn deficiency observed in samples from Miedzianka suggests that some Cu is fourfold coordinated in kipushite–philipsburgite. For instance, the crystal-chemical formula for the sample with the smallest Zn content in Table 3 can be written as: $^{[4]}(\text{Zn}_{0.69}\text{Cu}_{0.31})^{[6]}\text{Cu}_{5.09}(\text{As}_{1.41}\text{P}_{0.49}\text{O}_4)_2(\text{OH})_6\cdot\text{H}_2\text{O}$. Whether Zn-free kipushite or philipsburgite can be stable structures is an open question. In our opinion, both minerals can crystallize only if Zn ion activity is sufficiently high in the solution. Therefore, there must be a limit on the content of tetrahedral Cu. This means that there may not be a complete solid solution between kipushite and philipsburgite with respect to Cu ↔ Zn substitutions. There are no such constraints on the AsO₄ and PO₄ substitutions and, accordingly, a complete anionic miscibility between both minerals is foreseen. However, as mentioned in the Introduction, a purely arsenate philipsburgite has not yet been observed.

Backscattered-electron images and X-ray element-distribution maps of philipsburgite aggregates show their chemical heterogeneity (Fig. 7), not only as zoning (shown also in Fig. 4) but also as lateral changes in chemical compositions.

Due to small amount of material for X-ray powder micro-diffraction analyses, the unit-cell parameters were determined only for two P-rich samples (Table 4). While in general the obtained unit-cell dimensions are similar to philipsburgite from the type locality, the higher beta angles in samples from Miedzianka are noticeable. Presumably, unlike in the cornwallite–pseudomalachite solid solution, there may not be a simple linear correlation between unit-cell dimensions and chemical composition in the kipushite–philipsburgite solid solution. The reason for that might be an opposite effect of cationic and anionic substitutions on the unit-cell dimensions. There is no clear correlation between

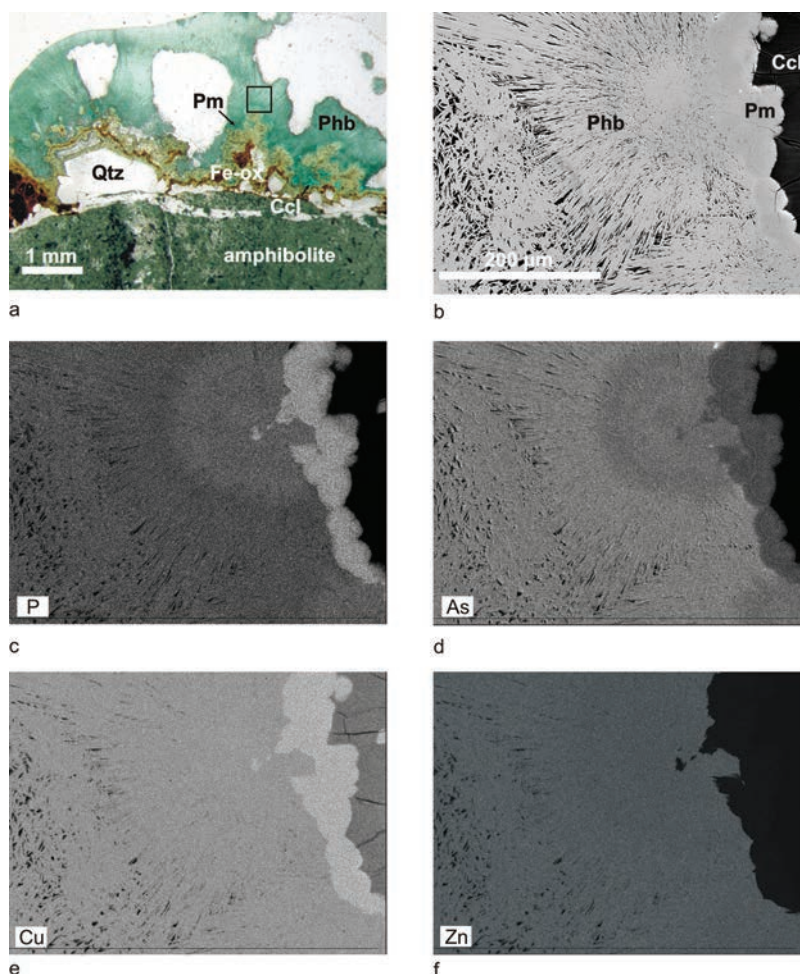


Fig. 7. (a) Thin section of a secondary mineral assemblage (Fe-hydroxides, chrysocolla, pseudomalachite, kipushite–philipsburgite) developed in a quartz-lined cavity within quartz vein in amphibolite. Symbols as in Fig. 1. BSE image of the boxed area is shown in b. X-ray element distribution maps: (c) P; (d) As; (e) Cu; (f) Zn. (online version in colour)

Table 4. Unit-cell dimensions of kipushite (Piret *et al.*, 1985), philipsburgite (Peacor *et al.*, 1985), and members of kipushite–philipsburgite series from Miedzianka (M2, M7).

	M2 this study	M7 this study	Kipushi, Zaire (Piret <i>et al.</i> , 1985)	Montana, USA (Peacor <i>et al.</i> , 1985)
a [Å]	12.364(1)	12.324(2)	12.197	12.33
b [Å]	9.218(1)	9.207(1)	9.156	9.20
c [Å]	10.711(2)	10.709(1)	10.667	10.69
β [°]	97.55(1)	97.44(1)	96.77	96.92
V [Å ³]	1210	1205	1183	1204

Zn/Cu and P/As in our analyses. Therefore, unit-cell dimension may depend on the proportion of the substituting cations and anions.

4.2.2. Raman spectroscopy

Raman spectra of three samples with different contents of P and As ($P/(P + As) = 0.63, 0.52, 0.19$) are reproduced in Fig. 8. There are no published Raman spectra of kipushite and philipsburgite with band assignment. Therefore, Raman bands were attributed to the specific vibration modes by analogy to chemically akin arsenates and phosphates.

Deconvoluted Raman spectra of As-kipushite (sample M2 in Fig. 8), of a sample with intermediate composition between kipushite and philipsburgite (sample M7 in Fig. 8) and of P-philipsburgite (sample M8 in Fig. 8) differ in number of bands, their positions and intensity. The most intense bands in the spectra of samples M2, M7 and M8 are at 869 (overlapped by 875), 867, and 865 (overlapped by 878) cm^{-1} , respectively (Fig. 8). These bands are assigned to the $\nu_1(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$ symmetric stretching vibrations (Frost *et al.*, 2014a, 2015). Bands at 843, 814, 796 cm^{-1} (M2), 837, 813, 794 cm^{-1} (M7) and at 847, 809, 791 cm^{-1}

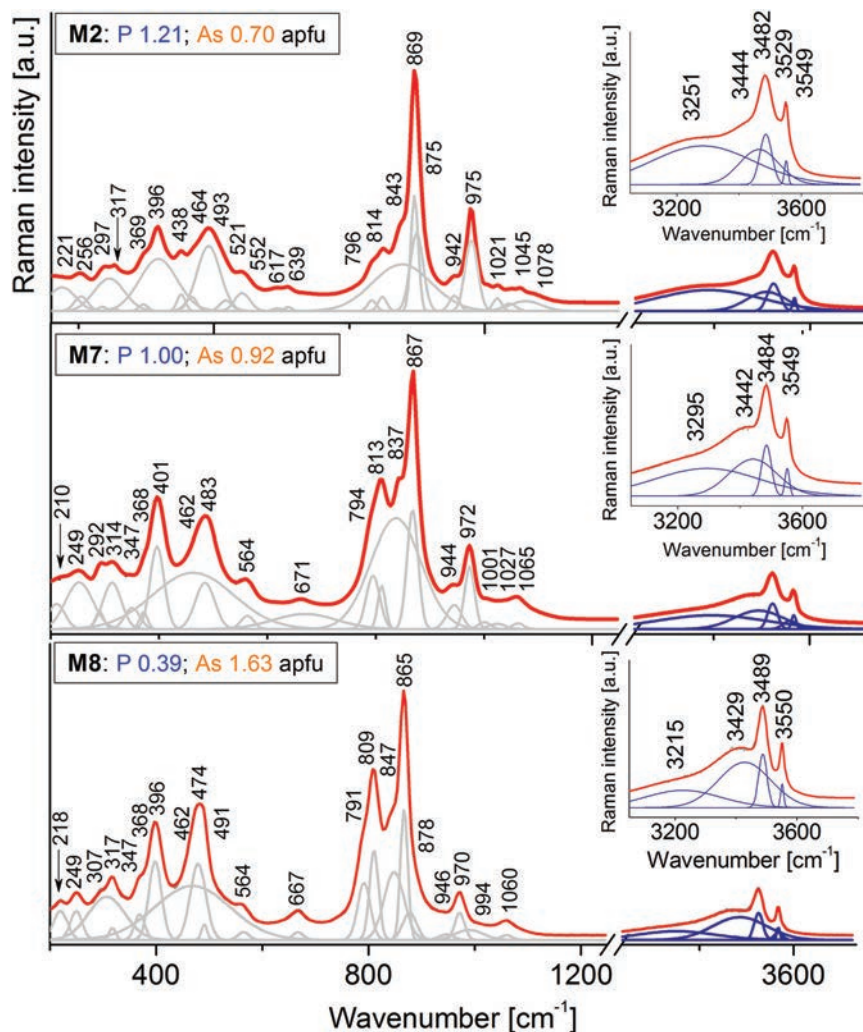


Fig. 8. Raman spectra of the kipushite–philipsburgite solid solution (samples M2, M7, M8). The hydroxyl region in all spectra was enlarged to better visualize components of the bands. (online version in colour)

(M8) arise from the $\nu_3(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$ anti-symmetric stretching vibrations (Frost *et al.*, 2014a, 2015) and their occurrence agrees well with the very strong splitting of the arsenate absorption band in the IR spectra of philipsburgite due to lowering of the symmetry of distorted tetrahedra (Braithwaite & Ryback, 1988).

The prominent band at 975 cm^{-1} in the spectrum of As-kipushite (Fig. 8) is assigned to the symmetric stretching vibration of PO_4 group by analogy to As-pseudomalachite (Fig. 5) and other hydroxy phosphates (*e.g.* Frost *et al.*, 2014b). The intensity of that band gradually diminishes and its position shifts to lower wavenumbers at 972 and 970 cm^{-1} with increasing amount of As in samples M7 and M8, respectively.

Similarly to the pseudomalachite–cornwallite solid solution, there is a simple correlation between the intensity ratio of $\nu_1(\text{AsO}_4)^{3-}/\nu_1(\text{PO}_4)^{3-}$ and the $\text{P}/(\text{P} + \text{As})$ ratio in the investigated samples of the kipushite–philipsburgite solid solution. The $\nu_1(\text{AsO}_4)^{3-}/\nu_1(\text{PO}_4)^{3-}$ ratio changes from 0.41 in As-kipushite ($\text{P}/(\text{P} + \text{As}) = 0.63$), through 1.08 in a mineral with intermediate composition

($\text{P}/(\text{P} + \text{As}) = 0.52$) to 4.17 in P-philipsburgite ($\text{P}/(\text{P} + \text{As}) = 0.19$).

The bands at 617 and 639 cm^{-1} in the M2 spectrum, 671 cm^{-1} in the M7 spectrum, and 667 cm^{-1} in the M8 spectrum are assigned to the deformation mode within AsOH group due to the delocalization of the hydroxyl proton (Martens *et al.*, 2003). Raman spectra of the kipushite–philipsburgite series can be divided into three regions in the range $600\text{--}200\text{ cm}^{-1}$: (a) 600 to 400 cm^{-1} corresponding to $\nu_4(\text{O-As-O})$ mode, (b) 400 to 300 cm^{-1} corresponding to $\nu_2(\text{O-P-O})$ mode, and (c) 300 to 200 cm^{-1} corresponding to rotational vibration of the whole molecular unit, lattice modes as well as Cu–O vibration (Frost *et al.*, 2002c). In the regions (a) and (b) of the Raman spectrum of As-kipushite (M2), bands are located at 552 , 521 , 493 , 464 , 438 , 396 , 369 cm^{-1} , whereas in the spectrum of P-philipsburgite (M8) bands are observed at 564 , 491 , 474 , 462 , 396 , 368 , and 347 cm^{-1} .

Bands observed at 317 and 297 cm^{-1} in the spectrum of As-kipushite and bands at 317 and 307 cm^{-1} in the

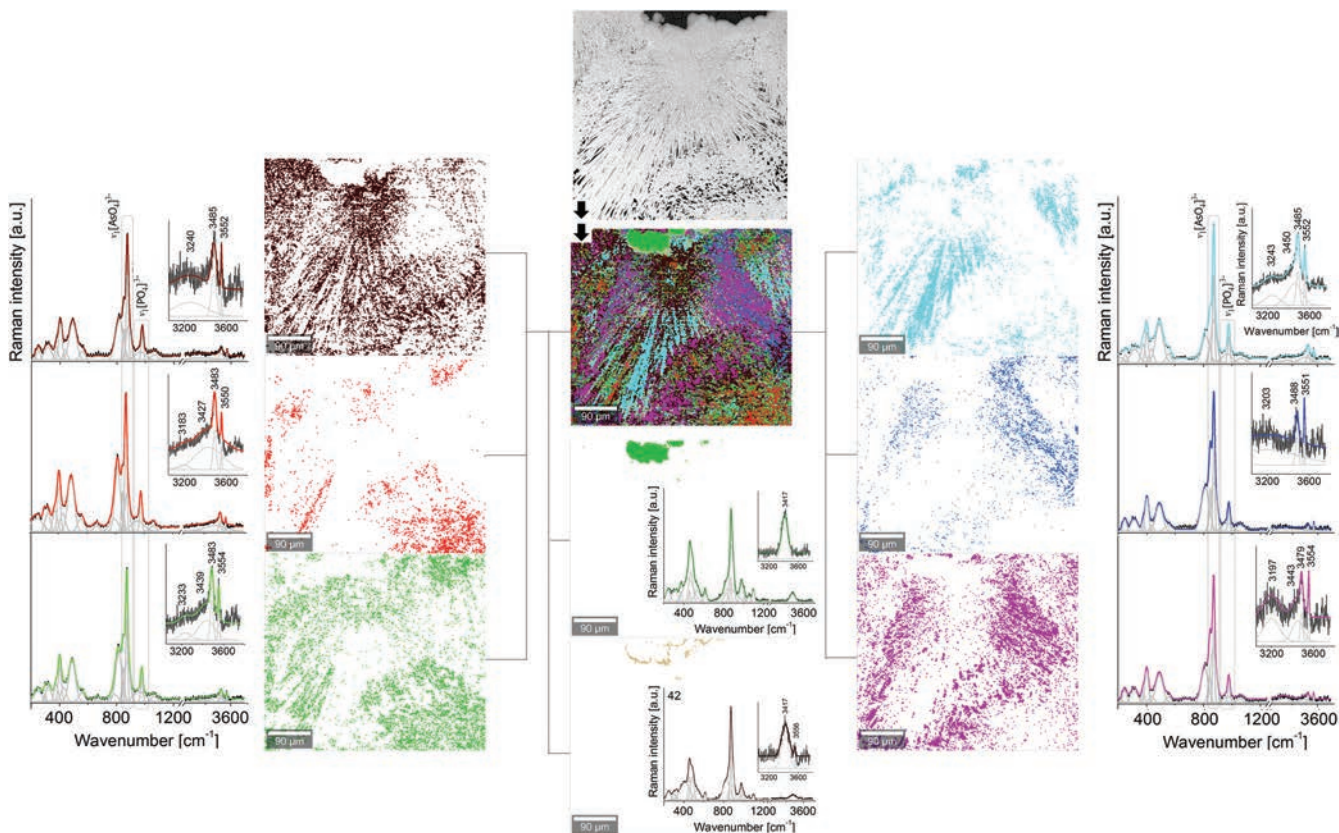


Fig. 9. Results of *K-means* Cluster Analysis of a radial aggregate of kipushite–philipsburgite from Miedzianka. Cluster tree with the root cluster and the first level of the cluster determine a solid-solution between philipsburgite and kipushite. The root cluster on the left and on the right relate to philipsburgite with various ratios between arsenate and phosphorous contents, while the root cluster in the centre depicts pseudomalachite. (online version in colour)

spectrum of As-philipsburgite may be attributed to the Cu–O stretching mode. The occurrence of two Cu–O vibrations may result from two types of groups, OH and AsO₄, coordinating the copper ion (Frost *et al.*, 2002c). Those two bands may also be attributed to the ZnO stretching vibration observed in hemimorphite (Frost *et al.*, 2007). Bands in the range 260–200 cm^{−1} may be assigned to combinational bands of bending vibration of O–Cu–O, O–As–O, O–P–O and lattice mode (Frost *et al.*, 2002c).

Two distinct bands in the hydroxyl stretching region observed in the Raman spectra of M2, M7 and M8 at 3482 and 3549 cm^{−1}, 3484 and 3549 cm^{−1}, and 3489 and 3550 cm^{−1}, respectively (Fig. 8) can be assigned to the OH-vibration modes related to (As,P)–OH group. Their position reflects relatively weak H-bonds (Libowitzky, 1999). Those two bands are characteristic features of kipushite–philipsburgite Raman spectra, distinguishing them from cornwallite–pseudomalachite spectra. Another two broad bands observed in the deconvoluted spectra of As-kipushite and P-philipsburgite at 3444 and 3251 cm^{−1} and at 3429 and 3215 cm^{−1}, respectively, are attributed to the stretching vibration of molecular water.

Raman imaging and *K-means* Cluster Analysis of radial aggregates of kipushite–philipsburgite (Fig. 9) confirm in

more detail the chemical heterogeneity seen in BSE images (Fig. 7). The *K-means* Cluster Analysis revealed six different clusters characteristic for the kipushite–philipsburgite series and two related to pseudomalachite. The deconvolution process of each spectrum was performed to analyze various band parameters, particularly for ν₁ stretching vibrations of [AsO₄]^{3−} and [PO₄]^{3−} groups (Table 5). There are linear negative correlations between band positions of ν₁(PO₄)^{3−} and ν₁(AsO₄)^{3−} modes as well as between FWHM of Raman bands and respective band positions (Fig. 10). The number of Raman bands and their positions and intensities depend on the type of substituting ions (Fig. 10a). Increases in FWHM are related to the distortion of XO₄ tetrahedra caused by As substituting P in kipushite and by P substituting As in philipsburgite. The structural adjustment caused by those substitutions generally increases the local disorder and this is reflected in increase in FWHM of Raman bands and in upshifts of those bands towards higher frequencies (Fig. 10b, c).

5. Conclusions

This study revealed a wide range of compositions covering 77.5 mol% of the expected solid solution

Table 5. Raman band parameters for the symmetric stretching vibrations of $(\text{AsO}_4)^{3-}$ (a) and $(\text{PO}_4)^{3-}$ (b) recorded in spectra shown in Fig. 9.

Band assignment	Spectrum 1			Spectrum 2			Spectrum 3		
	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM
ν_3 vibration of $(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$	814	0.28	51.6	816	0.46	33.5	814	0.40	60.5
	847	0.28	21.9	848	0.33	23.2	848	0.24	19.5
ν_1 vibration of $(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$	871	0.67	17.3	871	0.68	17.3	871	0.69	16.7
	879	0.25	38.8	877	0.31	39.4	876	0.31	41.2
Band assignment	Spectrum 4			Spectrum 5			Spectrum 6		
	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM
ν_3 vibration of $(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$	816	0.19	62.6	801	0.24	43.6	807	0.23	46.6
	845	0.13	18.4	845	0.16	14.4	844	0.17	16.4
ν_1 vibration of $(\text{AsO}_4)^{3-}$ and $(\text{HOAsO}_4)^{2-}$	871	0.30	48.6	858	0.52	57.4	863	0.43	49.4
	872	0.64	16.4	872	0.57	14.9	872	0.56	15.2

Band assignment	Spectrum 1			Spectrum 2			Spectrum 3		
	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM
ν_1 vibration of $(\text{PO}_4)^{3-}$	965	0.04	69.8	952	0.05	80.9	957	0.07	90.2
	976	0.18	19.1	976	0.020	19.4	976	0.18	19.1
Band assignment	Spectrum 4			Spectrum 5			Spectrum 6		
	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM	Band position [cm^{-1}]	Height	FWHM
ν_1 vibration of $(\text{PO}_4)^{3-}$	964	0.06	78.6	962	0.06	78.6	970	0.04	40.8
	977	0.18	18.9	976	0.14	18.8	977	0.14	17.7

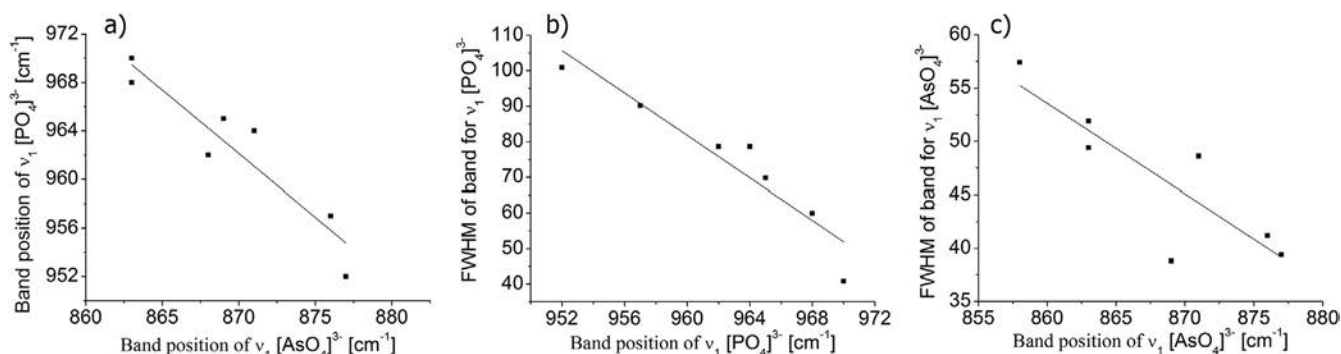
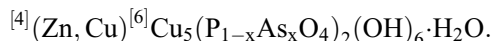


Fig. 10. Plots of correlation between: (a) Raman band positions of arsenate and phosphate ions in spectra of the kipushite–philipsburgite solid solution; (b) FWHM of $\nu_1(\text{PO}_4)^{3-}$ bands and position of those bands; (c) FWHM of $\nu_1(\text{AsO}_4)^{3-}$ bands and position of those bands.

between cornwallite and pseudomalachite; it demonstrates unambiguously that there are no crystal-chemical constraints to limit the $\text{P} \leftrightarrow \text{As}$ substitution in these minerals. The lack of chemical compositions close to the end-members of the cornwallite–pseudomalachite solid solutions is indicative of high activities of As and P ions during crystallization of these minerals. The same conclusion can be drawn concerning the kipushite–philipsburgite solid solution with respect to anionic miscibility. However, it is unclear whether unlimited $\text{Cu} \leftrightarrow \text{Zn}$ substitution does exist between kipushite and philipsburgite. Data obtained during this study extended this substitution to values lower than 1 Zn *apfu*. The Zn deficiency in tetrahedral sites in the kipushite–philipsburgite structure can be compensated by tetrahedral Cu. Therefore, the crystal-chemical formula of this series can be expressed as:



The number of bands, their positions and intensity in Raman spectra of pseudomalachite–cornwallite solid solutions depend on the P/As ratio. Particularly sensitive to the As content is the symmetric stretching mode of AsO_4 tetrahedra. Substitution of P by As in pseudomalachite causes significant up-shift of the Raman band assigned to that mode. We propose that this up-shift associated with broadening and enhanced intensity of the Raman band results from distortion of AsO_4 tetrahedra by shortening As–O bonds and adjustment of bond angles to accommodate the large As ions in the pseudomalachite structure. This feature is less evident in the arsenate kipushite, perhaps due its larger cell volume that can more easily accommodate larger ions in the anionic sublattice.

References

Artl, T. & Armbruster, T. (1999): Single-crystal X-ray structure refinement of cornwallite, $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$: A comparison

- with its polymorph cornubite and the PO_4 -analogue pseudomalachite. *N. Jb. Mineral. Mh.*, **1999**(10), 468–480.
- Berry, L.G. (1951): Observations on conicalcrite, cornwallite, euchroite, lironite and olivenite. *Am. Mineral.*, **36**, 484–503.
- Braithwaite, R.S.W. & Ryback, G. (1988): Philipsburgite from the Caldbeck Fells and kipushite from Montana, and their infrared spectra. *Mineral. Mag.*, **52**, 529–533.
- Ciesielczuk, J. & Bzowski, Z. (2003): Secondary (Cu,Zn)-oxyminerals from the Miedzianka copper deposit in Rudawy Janowickie, Sudetes Mts. Preliminary report. *Min. Soc. Poland – Special Papers*, **23**, 54–56.
- Claringbull, G.F., Hey, M.H., Davis, R.J. (1959): Cornubite, a new mineral dimorphous with cornwallite. *Mineral. Mag.*, **32**, 1–6.
- Dulski, M., Bilewska, K., Wojtyniak, M., Szade, J., Kusz, J., Nowak, A., Wrzalik, R., Kubacki, J., Galuskin, E.V. (2015): Rondorfite-type structure - XPS and UV–vis study. *Mater. Res. Bull.*, **70**, 920–927.
- Farmer, C.V. (1974): The Infrared Spectra of Minerals. Mineralogical Society of Minerals Monograph 4. The Mineralogical Society. London. 539 p.
- Frost, R.L., Klopogge, J.T., Williams, P.A., Martens, W., Johnson, T.E., Leverett, P. (2002a): Vibrational spectroscopy of the basic copper phosphate minerals: pseudomalachite, ludjibaite and reichenbachite. *Spectrochim. Acta A*, **58**, 2861–2868.
- Frost, R.L., Williams, P.A., Martens, W., Klopogge, J.T., Leverett, P. (2002b): Raman spectroscopy of the basic copper phosphate minerals cornetite, libethenite, pseudomalachite, reichenbachite and ludjibaite. *J. Raman Spectrosc.*, **33**, 260–263.
- Frost, R.L., Martens, W.N., Williams, P.A. (2002c): Raman spectroscopy of the phase-related basic copper arsenate minerals olivenite, cornwallite, cornubite and clinoclase. *J. Raman Spectrosc.*, **33**, 475–484.
- Frost, R.L., Martens, W.N., Williams, P.A. (2003): The basic copper phosphate minerals pseudomalachite, ludjibaite and reichenbachite: an infrared emission and Raman spectroscopic study. *N. Jb. Mineral. Mh.*, **2003**, 337–362.
- Frost, R.L., Bouzaid, J.M., Reddy, B.J. (2007): Vibrational spectroscopy of the sorosilicate mineral hemimorphite $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$. *Polyhedron*, **26**, 2405–2412.
- Frost, R.L., López, A., de Oliveira Gonçalves, G., Scholz, R., Xi, Y. (2014a): A vibrational spectroscopic study of the arsenate mineral bayldonite $(\text{Cu}, \text{Zn})_3\text{Pb}(\text{AsO}_3\text{OH})_2(\text{OH})_2$ – A comparison with other basic arsenates. *J. Mol. Struct.*, **1056–1057**, 267–272.

- Frost, R.L., López, A., Scholz, R., Xi, Yunfei, Lana, C. (2014b): The molecular structure of the phosphate mineral beraunite $\text{Fe}^{2+}\text{Fe}_5^{3+}(\text{PO}_4)_4(\text{OH})_5 \cdot 4\text{H}_2\text{O}$ – A vibrational spectroscopic study. *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **128**, 408–412.
- Frost, R.L., Scholz, R., Jirásek, J., Belotti, F.M. (2015): An SEM-EDX and Raman spectroscopic study of the fibrous arsenate mineral liskeardite and in comparison with other arsenates kaňkite, scorodite and yvonite. *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2015 Dec 5; **151**, 566–575. doi: 10.1016/j.saa.2015.07.005
- Gołębiewska, B. (1999): Strashimirite and cornwallite (copper arsenates) from Rędziny (Lower Silesia, Poland). *Mineralogia Polonica*, **30**(2), 3–11.
- Kharbish, S., Andráš, P., Luptáková, J., Milovská, S. (2014): Raman spectra of oriented and non-oriented Cu hydroxy-phosphate minerals: Liebethenite, cornetite, pseudomalachite, reichenbachite and ludjibaite. *Spectrochim. Acta A*, **130**, 152–163.
- Libowitzky, E. (1999): Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatsh. Chem.*, **130**, 1047–1059.
- Magalhães, M. C. F. Pedrosa de Jesus, J.D., Williams, P.A. (1986): Stability constants and formation of Cu(II) and Zn(II) phosphate minerals in the oxidized zone of base metal orebodies. *Mineral. Mag.*, **50**, 33–39.
- Magalhães, M. C. F. Pedrosa de Jesus, J.D., Williams, P.A. (1988): The chemistry of formation of some secondary arsenate minerals of Cu(II), Zn(II) and Pb(II). *Mineral. Mag.*, **52**, 679–690.
- Markl, G., Marks, M.A.W., Hölzapfel, J., Wenzel, T. (2014): Major, minor, and trace element composition of pyromorphite-group minerals as recorder of supergene weathering processes from the Schwarzwald mining district, SW Germany. *Am. Mineral.*, **99**, 1133–1146.
- Martens, W.N., Frost, R.L., Klopogge, J.T., Williams, P.A. (2003): The basic copper arsenate minerals olivenite, cornubite, cornwallite, and clinoclase: An infrared emission and Raman spectroscopic study. *Am. Mineral.*, **88**, 501–508.
- Mochmacka, K., Oberc-Dziedzic, T., Mayer, W., Pieczka, A. (2015): Ore mineralization related to geological evolution of the Karkonosze-Izera Massif (the Sudetes, Poland) – Towards a model. *Ore Geol. Rev.*, **64**, 215–238.
- Peacor, D.R., Dunn, P.J., Ramik, R.A., Sturman, B.D., Zeihen, L.G. (1985): Philipsburgite, a new copper zinc arsenate hydrate related to kipushite, from Montana. *Can. Mineral.*, **23**, 255–258.
- Piret, P., Deliens, M., Piret-Meunier, J. (1985): Occurrence and crystal structure of kipushite, a new copper-zinc phosphate from Kipushi, Zaire. *Can. Mineral.*, **23**, 35–42.
- Plášil, J., Sejkora, J., Čejka, J., Škoda, R., Goliáš, V. (2009): Supergene mineralization of the Medvědní uranium deposit, Krkonoše Mountains, Czech Republic. *J. Geosci.*, **54**, 15–56.
- Shirose, Y. & Uehara, S. (2011): Philipsburgite from the Yamato mine, Yamaguchi prefecture, Japan. *J. Miner. Petrol. Sci.*, **106**, 153–157.
- Shoemaker, G.L., Anderson, J.B., Kostiner, E. (1977): Refinement of the crystal structure of pseudomalachite. *Am. Mineral.*, **62**, 1042–1048.
- Siuda, R. & Borzęcki, R. (2014): Mining and metallurgy relics in the Miedzianka-Ciechanowice area as geotourists objects (in Polish). *Prz. Geol.*, **62**, 397–402. (in Polish with English abstract).
- Siuda, R. & Gołębiewska, B. (2011): New data on supergene minerals from Miedzianka-Ciechanowice deposit in the Rudawy Janowickie Mountains (Lower Silesia, Poland). *Prz. Geol.*, **59**, 226–234. (in Polish with English abstract).
- Števkó, M., Sejkora, J., Bačík, P. (2011): Mineralogy and origin of supergene mineralization at the Farbište ore occurrence near Poniky, central Slovakia. *J. Geosci.*, **56**, 273–298.
- Walenta, K., Belendorff, K., Dunn, P.J. (1985): Philipsburgit von Neubulach im württembergischen Schwarzwald. *Aufschluss*, **36**, 319–323. (with English abstract).
- Williams, P.A. (1990): Oxide zone geochemistry. Ellis Horwood Ltd, Chichester, 286 p. <http://ruff.info/cornwallite/display=default/R110146>.

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