

**CALCIOPETERSITE FROM DOMAŠOV NAD BYSTRICÍ, NORTHERN MORAVIA,
CZECH REPUBLIC, A NEW MINERAL SPECIES OF THE MIXITE GROUP**

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ABSTRACT

Calciopetersite, ideally $\text{CaCu}_6(\text{PO}_4)_2(\text{PO}_3\text{OH})(\text{OH})_6 \cdot 3\text{H}_2\text{O}$, occurs in cavities in quartz veins at an abandoned quarry near Domašov nad Bystřicí, 20 km northeast of Olomouc, northern Moravia, Czech Republic. It forms translucent to transparent minute acicular crystals, up to 0.4 mm in length and 5–20 μm in width, with a hexagonal outline, clustered in fine radiating sprays (up to 0.1×0.5 mm). It is soft and brittle with an uneven fracture, but the hardness and density could not be measured; no cleavage was observed. It has an olive green color, light olive green streak and vitreous luster. No fluorescence was observed in ultraviolet light. It originated by weathering of chalcopyrite and other copper sulfides and is associated with chrysocolla, the Ce-dominant analogue of petersite-(Y), malachite, allophane, goethite, lepidocrocite, chalcopyrite, pyrite, covellite, chalcocite and quartz. The name *calciopetersite* denotes that it is the Ca-dominant analogue of petersite-(Y). Calciopetersite is hexagonal, space group $P6_3/m$ inferred from the isotypic agardite-(Y) and mixite, a 13.284(4), c 5.902(4) Å, V 902.0(6) Å³, $Z = 2$, and D_{calc} 3.332 g/cm³. The strongest eight lines in the powder-diffraction pattern [d in Å(hkl)] are: 11.51(100)(100), 4.346(88)(210), 4.140(46)(201), 3.837(38)(300), 3.321(44)(220), 2.888(53)(221), 2.877(37)(400), and 2.510(37)(140). Calciopetersite is uniaxial positive, with indices of refraction ω 1.674(5) and $\epsilon > 1.739$ (~1.75) in Na light (590 nm), and dichroic: light green with yellowish tint (O) and green (E) with $\epsilon > \omega$. Chemical analyses yielded the average composition K_2O 0.09, CaO 4.39, CuO 51.25, Y_2O_3 1.61, La_2O_3 0.64, Ce_2O_3 1.98, Pr_2O_3 0.25, Nd_2O_3 1.40, Dy_2O_3 0.33, Yb_2O_3 0.21, Bi_2O_3 0.09, SiO_2 0.52, P_2O_5 20.98, As_2O_5 2.70, H_2O (12.45), total (98.89) wt.%, corresponding to $(\text{Ca}_{0.58}\text{Y}_{0.13}\text{Ce}_{0.11}\text{Nd}_{0.08}\text{La}_{0.04}\text{K}_{0.02}\text{Dy}_{0.02}\text{Pr}_{0.01}\text{Yb}_{0.01})_{\Sigma 1.00} (\text{Cu}_{5.90}\text{Ca}_{0.14})_{\Sigma 6.04} [(\text{PO}_4)_{2.06}(\text{PO}_3\text{OH})_{0.65}(\text{AsO}_4)_{0.22}(\text{SiO}_4)_{0.22}(\text{OH})_6] \cdot 3.00 \text{H}_2\text{O}$ on the basis of 21 atoms per formula unit. The ideal formula $\text{CaCu}_6[(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6] \cdot 3\text{H}_2\text{O}$ requires CaO 6.50, CuO 55.28, P_2O_5 24.66, H_2O 13.57, total 100.00 wt.%. The Gladstone–Dale compatibility index, calculated from incomplete optical data, is poor (–0.080). We provide a tentative interpretation of the infrared-absorption spectrum of calciopetersite.

Keywords: calciopetersite, new mineral species, X-ray powder diffraction, electron-microprobe data, infrared spectroscopy, mixite group, Domašov nad Bystřicí, Czech Republic.

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SOMMAIRE

On trouve la calciopetersite, dont la formule idéale serait $\text{CaCu}_6[(\text{PO}_4)_2(\text{PO}_3\text{OH})(\text{OH})_6]\cdot 3\text{H}_2\text{O}$, dans les cavités de veines de quartz dans une carrière abandonnée près de Domašov nad Bystřicí, à 20 km au nord-est de Olomouc, partie nord de la Moravie, en République Tchèque. Elle se présente en infimes cristaux aciculaires translucides à transparents atteignant une longueur de 0.4 mm et entre 5 et 20 μm de diamètre, avec une section hexagonale, regroupés en amas radiaires atteignant 0.1×0.5 mm. C'est un minéral mou et cassant, avec une fracture inégale, mais nous n'avons pas pu en établir la dureté ou la densité. Aucun clivage n'est évident. Sa couleur est vert olive, et sa rayure, vert olive pâle; l'éclat est vitreux. Aucune fluorescence n'a été observée en lumière ultraviolette. On attribue la calciopetersite à la météorisation de la chalcoppyrite et autres sulfures de cuivre; elle est associée au chrysocolle, l'analogue à dominance de Ce de la petersite-(Y), et à malachite, allophane, goéthite, lépidocrocite, chalcoppyrite, pyrite, covellite, chalcocite et quartz. Le nom *calciopetersite* rappelle la dominance de Ca dans un analogue de la petersite-(Y). La calciopetersite est hexagonale, groupe spatial $P6_3/m$, déduit à partir de l'agardite-(Y) et la mixite, phases isotypiques, a 13.284(4), c 5.902(4) Å, V 902.0(6) Å³, $Z = 2$, et D_{calc} 3.332 g/cm³. Les huit raies les plus intenses du spectre de diffraction X, méthode des poudres [d en Å(hkl)] sont: 11.51(100)(100), 4.346(88)(210), 4.140(46)(201), 3.837(38)(300), 3.321(44)(220), 2.888(53)(221), 2.877(37)(400), et 2.510(37)(140). La calciopetersite est uniaxe positive, avec les indices de refraction ω 1.674(5) et $\varepsilon > 1.739$ (~1.75) en lumière Na (590 nm), et dichroïque, de vert pâle avec une teinte jaunâtre (O) à vert (E), avec $\varepsilon > \omega$. Les analyses chimiques ont donné, en moyenne, K₂O 0.09, CaO 4.39, CuO 51.25, Y₂O₃ 1.61, La₂O₃ 0.64, Ce₂O₃ 1.98, Pr₂O₃ 0.25, Nd₂O₃ 1.40, Dy₂O₃ 0.33, Yb₂O₃ 0.21, Bi₂O₃ 0.09, SiO₂ 0.52, P₂O₅ 20.98, As₂O₅ 2.70, H₂O (12.45), pour un total de (98.89)% (poids), ce qui correspond à $(\text{Ca}_{0.58}\text{Y}_{0.13}\text{Ce}_{0.11}\text{Nd}_{0.08}\text{La}_{0.04}\text{K}_{0.02}\text{Dy}_{0.02}\text{Pr}_{0.01}\text{Yb}_{0.01})_{\Sigma 1.00}(\text{Cu}_{5.90}\text{Ca}_{0.14})_{\Sigma 6.04}[(\text{PO}_4)_{2.06}(\text{PO}_3\text{OH})_{0.65}(\text{AsO}_4)_{0.22}(\text{SiO}_4)_{0.22}(\text{OH})_6]\cdot 3.00 \text{ H}_2\text{O}$ sur une base de 21 atomes par formule unitaire. La formule idéale $\text{CaCu}_6[(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6]\cdot 3\text{H}_2\text{O}$ requiert CaO 6.50, CuO 55.28, P₂O₅ 24.66, H₂O 13.57, total 100.00%. L'indice de compatibilité de Gladstone et Dale, calculé en utilisant des données optiques incomplètes, est pauvre (-0.080). Nous interprétons de façon préliminaire le spectre d'absorption infrarouge de la calciopetersite.

(Traduit par la Rédaction)

Mots-clés: calciopetersite, nouvelle espèce minérale, diffraction X sur poudre, données de microsonde électronique, spectroscopie infrarouge, groupe de la mixite, Domašov nad Bystřicí, République Tchèque.

INTRODUCTION

Minerals of the mixite group have the general formula $MCu_6(XO_4)_3(\text{OH})_6\cdot 3\text{H}_2\text{O}$. Cations such as Al, Bi³⁺, Ca, Y³⁺ and the rare-earth elements (REE³⁺) are found to occupy the octahedrally coordinated M site; up to now, only As and P have been found in significant amounts at X , the tetrahedral site. We describe in this paper the physical properties and chemical composition of calciopetersite, a newly discovered member of the mixite group, from Domašov nad Bystřicí, northern Moravia, Czech Republic.

BACKGROUND INFORMATION

Minerals of the mixite group have been classified on the basis of the occupancy of the M and X sites: mixite [Bi; As], agardite-(Y) [Y; As], goudeyite [Al; As], petersite-(Y) [Y; P], zálesíte [Ca; As], agardite-(La) [La, As], approved mineral 2003–030 [Ce, As], approved mineral 2003–031a [Pb, As], and the new mineral species *calciopetersite*, described here [Ca; P]. The names “agardite-(Nd)”, “agardite-(Dy)”, “petersite-(Nd)”, “petersite-(Ca)” (Walenta 2003, Walenta & Theye 2004) and “agardite-(Ca)” were occasionally used, but these minerals and their names have not been approved by the Commission of New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA).

Compositional variation in the proportion of the major cations, especially the substitution $P \rightarrow As$ in mixite (Schrauf 1880, Sejkora & Šrein 1996), $As \rightarrow P$ in petersite-(Y) (Peacor & Dunn 1982), and the REEs in agardite-(Y), agardite-(Ce) and agardite-(La), was documented on the intermediate members of this group at some occurrences in Sardinia, Italy (Olmi *et al.* 1991). Subordinate contents of Ca were found in many members of the mixite group by Olmi *et al.* (1991). Furthermore, Dietrich *et al.* (1969) described 14 mol.% Ca at the M site in mixite and 25 mol.% in agardite-(Y), and Peacor & Dunn (1982) found 40 mol.% Ca at the M site in petersite-(Y), respectively. On the other hand, Ca in goudeyite is considered to occupy the Cu site (Wise 1978). Aruga & Nakai (1985) described the crystal structure of Ca-rich agardite-(Y) (44 mol.% of Ca at the M site) and assumed that substitution of a trivalent cation (Bi³⁺ or REE³⁺) at the M site by divalent Ca²⁺ cation is charge-balanced by a concomitant substitution of OH⁻ for O²⁻ at the O(3) site in the crystal structure (attributed to a HAsO₄ or AsO₃OH group). Zálesíte, $\text{CaCu}_6[(\text{AsO}_4)(\text{AsO}_3\text{OH})(\text{OH})_6]\cdot 3\text{H}_2\text{O}$, was described by Sejkora *et al.* (1999) as the first Ca-dominant member of the mixite group; however, the phase corresponding to zálesíte was described as agardite-(Ca) from Monte Cervandone (Italy), Vosges (France) and Black Forest (Germany) (Albertini 1994, Kolitsch 1997a, Walenta 1992). The new mineral species *calciopetersite* was incompletely described as the unnamed “Ca-dominant analogue of petersite-(Y)” from the mine Altväter samt

Eschig near Sayda, Saxony by Kolitsch (1997b) or as “petersite-(Ca)” from Herrensegen mine near Schapbach, Black Forest by Walenta (1992, 2003).

Calciopetersite, the newly recognized hydrated hydroxophosphate of calcium and copper, has been approved by CNMMN of IMA (#2001-004). The name is derived from its composition and relationship to petersite-(Y). The holotype specimen is deposited in the mineralogical collection of the Natural History Museum, National Museum, Prague, Czech Republic, under the number P1p-20/2000.

OCCURRENCE AND DESCRIPTION

Calciopetersite was found at a large abandoned quarry located about 1.5 km south of Domašov nad Bystřicí, 20 km northeast of Olomouc, northern Moravia, Czech Republic. The quarry was opened in the Lower Carboniferous (Upper Visean) graywackes, with layers of conglomerates and small intercalations of shales. Several generations of hydrothermal quartz, quartz-carbonate and calcite veins with a small amount of common sulfides (pyrite, chalcopyrite, sphalerite, galena; Zimák *et al.* in press) were found in the quarry. The steeply dipping hydrothermal vein in which the secondary calciopetersite was found is up to 10 cm thick and cuts greywacke and conglomerate. Quartz is a dominant gangue mineral besides subordinate carbonate (calcite + dolomite-ankerite), pyrite and chalcopyrite. Some minerals locally underwent a strong supergene alteration: chalcopyrite was largely replaced

by chalcocite and covellite, and carbonate, by a porous mixture of goethite and lepidocrocite. Other secondary minerals associated with calciopetersite include chrysocolla, malachite, allophane and the unnamed Ce-analogue of petersite-(Y), with an ideal formula $(\text{Ce,REE,Ca})\text{Cu}_6[(\text{PO}_4)_3(\text{OH})_6]\cdot 3\text{H}_2\text{O}$, which is indistinguishable in hand specimen from calciopetersite. It occurs in cavities of the quartz vein closely associated with pale pink carbonate (calcite + dolomite-ankerite) veins with rare pyrite. Only a few samples of the very rare calciopetersite were found.

Calciopetersite forms translucent to transparent minute acicular crystals, attaining 0.4 mm in length and 5–20 μm in width, with a hexagonal outline, clustered in fine radiating sprays up to 0.1 \times 0.5 mm (Fig. 1). Crystals and their aggregates grow on quartz or host graywacke, and locally are coated by chrysocolla. Calciopetersite is soft and brittle with an uneven fracture, but the Mohs hardness was not determined owing to the size and character of aggregates; no cleavage was observed. The mineral is olive green, with a light olive green streak, a vitreous luster and pleochroism, from light green with yellowish tint (O) to dark green (E). It is uniaxial positive, with ω 1.674(5) and $\varepsilon > 1.739$ (~1.75) in Na light (590 nm, immersion liquids). No fluorescence at 254 and 366 nm of ultraviolet light was observed. The Gladstone-Dale compatibility index of calciopetersite, calculated from incomplete optical data, is poor (–0.080), as are calculated compatibilities of other members of the mixite group (–0.06 to –0.10; Sejkora *et al.* 1999).

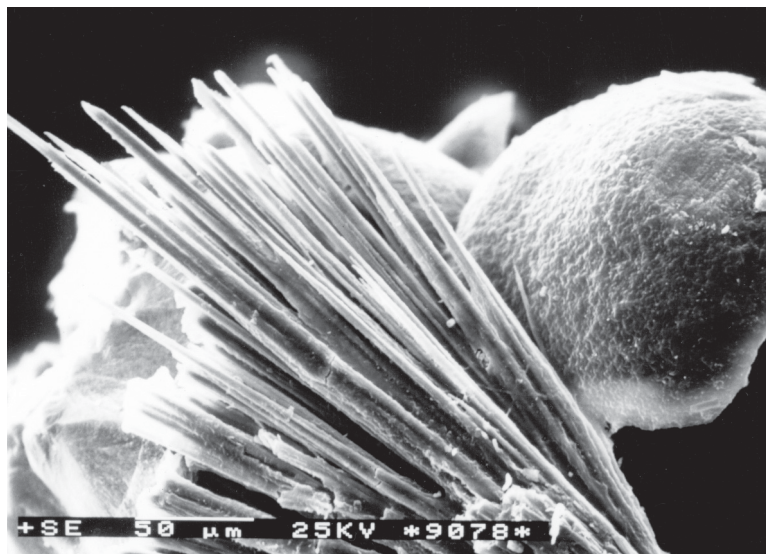


FIG. 1. Scanning electron photomicrograph of calciopetersite from Domašov nad Bystřicí, Czech Republic, in fine radiating sprays; note the hexagonal outline of crystals. Tesla BS 340, photo by J. Sejkora.

X-RAY SINGLE-CRYSTAL
AND POWDER-DIFFRACTION DATA

A pale greenish fragment of calciopetersite, about $0.01 \times 0.01 \times 0.05 \text{ mm}^3$ in size, was measured on a Bruker AXS three-circle diffractometer (equipped with a CCD 1000K area detector and a flat graphite monochromator) using $\text{MoK}\alpha$ X-radiation emitted from a fine-focus sealed tube. The X-ray-diffraction data (734 reflections) were found to be of very poor quality, with a mean $I/\sigma_I = 2.82$. For the structure refinement, the space group was set to $P6_3/m$ in accordance with mixite and agardite-(Y) (Mereiter & Preisinger 1986, Aruga & Nakai 1985). The structure was refined with fixed isotropic thermal parameters for all atoms ($U_{\text{iso}} = 0.01$), and full occupancy was assumed for all atomic sites. Despite the poor data available, we can consider that the refined structure-model is isotypic with the one of Ca-rich agardite, reported by Aruga & Nakai (1985). However, the structures can only be compared on a topological level; the poor quality of the underlying data does not allow a discussion of bond lengths and angles. The following unit-cell parameters were obtained: a 13.3045(18), c 5.8711(8) Å, V 900.0(4) Å³; attempts to solve the crystal structure from these data were not successful.

A hand-picked sample of calciopetersite was used to collect the X-ray powder-diffraction pattern using a Philips APD diffractometer operated in the step-scan mode. The diffraction lines are similar to the pattern of other phases of the mixite group. The unit-cell parameters were obtained from the powder X-ray-diffraction pattern (Table 1). It was collected in the range $3\text{--}66^\circ 2\theta$ in the step-scan mode (0.02°/15 s) with $\text{CuK}\alpha$ X-radiation. Positions and intensities of reflections were calculated using the Pearson VII profile-shape function with the ZDS program package (Ondruš 1995). The measured pattern was indexed by analogy of isotypic

TABLE 1. POWDER X-RAY-DIFFRACTION PATTERN OF
CALCIOPETERSITE FROM DOMAŠOV NAD BYSTRICÍ

I_{rel}	d_{obs}	d_{calc}	h	k	l	I_{rel}	d_{obs}	d_{calc}	h	k	l
100	11.51	11.50	1	0	0	37	2.510	2.510	1	4	0
88	4.346	4.348	2	1	0	13	2.4076	2.4094	3	2	1
46	4.140	4.119	2	0	1	20	2.2031	2.2060	2	2	2
38	3.837	3.835	3	0	0	15	2.0654	2.0663	1	5	0
30	3.494	3.501	2	1	1	13	2.0601	2.0597	4	0	2
44	3.321	3.321	2	2	0	31	1.9650	1.9673	3	2	2
35	3.184	3.191	1	3	0	28	1.8909	1.8913	3	4	0
		3.191	3	1	0	17	1.6927	1.6927	2	2	3
53	2.888	2.894	2	2	1			1.6926	5	1	2
37	2.877	2.876	4	0	0	22	1.6592	1.6605	4	4	0
33	2.641	2.639	3	2	0	19	1.5939	1.5924	4	3	2
		2.639	2	3	0	18	1.4483	1.4472	4	4	2
14	2.589	2.586	4	0	1	20	1.4390	1.4381	8	0	0

Philips APD powder X-ray diffractometer, step-scan 0.02°/15 s, $\text{CuK}\alpha$ radiation. Positions and intensities of reflections were calculated using the Pearson VII profile shape function of the ZDS program package (Ondruš 1995).

hexagonal ($P6_3/m$) Ca-rich agardite (Aruga & Nakai 1985), mixite (Mereiter & Preisinger 1986) and zálešítite (Sejkora *et al.* 1999). The unit-cell parameters of calciopetersite [a 13.284(4) Å, c 5.902(4) Å, V 902.0(6) Å³, $Z = 2$] were calculated by the least-squares refinement program of Burnham (1962). The density, 3.332 g/cm³, is calculated for $Z = 2$ and the chemical composition of calciopetersite.

CHEMICAL COMPOSITION

Quantitative chemical analyses (Table 2) were carried out by means of a JEOL JXA-50A electron microprobe in wavelength mode (Geological Institute, Academy of Science of the Czech Republic, Prague, performed by A. Langrová and V. Šrein), operated at an acceleration potential 20 kV, a sample current 25 nA, and an electron beam size of 2 µm. We used the following standards: diopside (Ca), libethenite (Cu, P), clinoclase (As), pucherite (Bi), K-feldspar (K) and synthetic glasses (REE) (Drake & Weill 1972). The X-ray intensity of each element was measured three times with an exposure time of ten seconds. The data were corrected with the program based on the conventional ZAF methods of Duncumb & Reed (1968) and Philibert (1963).

A direct determination of H₂O was not possible because of small amount of available material. The H₂O content was calculated from the empirical formula (on the basis $H = 12.65 \text{ apfu}$ derived from valence balance), and it is very close to the H₂O content derived from the ideal formula. The analytical results calculated on the basis of 21 (O,OH) gave the following empirical formulae (average from eight spot-analyses): $(\text{Ca}_{0.58}$

TABLE 2. CHEMICAL COMPOSITION OF CALCIOPETERSITE
FROM DOMAŠOV NAD BYSTRICÍ

constituent	mean	range	ideal comp.**
K ₂ O	0.09	0.06–0.12	
CaO	4.39	3.72–4.80	6.50
CuO	51.25	50.66–51.70	55.28
Y ₂ O ₃	1.61	1.31–1.77	
La ₂ O ₃	0.64	0.36–0.85	
Ce ₂ O ₃	1.98	1.71–2.28	
Pr ₂ O ₃	0.25	0.13–0.42	
Nd ₂ O ₃	1.40	1.11–1.71	
Dy ₂ O ₃	0.33	0.22–0.51	
Yb ₂ O ₃	0.21	0.13–0.38	
Bi ₂ O ₃	0.09	0.03–0.23	
SiO ₂	0.52	0.37–0.59	
P ₂ O ₅	20.98	19.70–22.38	24.66
As ₂ O ₃	2.70	2.08–3.89	
H ₂ O*	(12.45)		13.57
Total	(98.89)		100.00

JEOL JXA-50A electron microprobe, mean result and range of eight spot analyses.

* calculated content of H₂O on the base $H = 12.65 \text{ apfu}$ derived from valence balance with the empirical formula.

** ideal chemical composition calculated on the basis of the formula $\text{CaCu}_4(\text{PO}_4)_2(\text{PO}_3\text{OH})(\text{OH})_2 \cdot 3\text{H}_2\text{O}$.

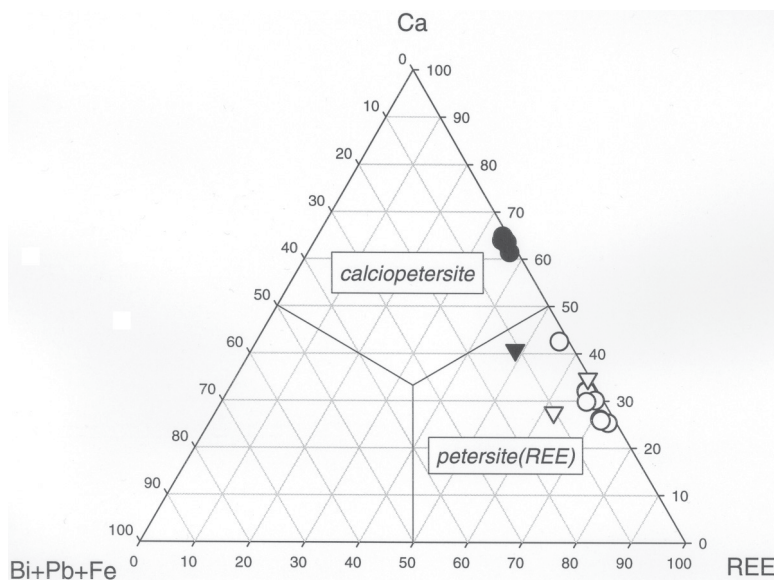
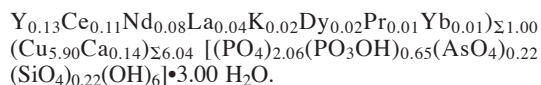


FIG. 2. Plot of Ca – REE – other elements (at the *M* site) in P-dominant members of the mixite group. ●: calciopetersite, Domašov (this paper), ○: unnamed Ce-analogue of petersite-(Y), Domašov (this paper), ▼ petersite-(Y) (Peacor & Dunn 1982), ▽ (PO₄)- and REE-dominant members of the mixite group (Olmí *et al.* 1991).



Results of the individual spot-analyses of calciopetersite from Domašov nad Bystřicí as well as published analyses of P-dominant members of the mixite group are plotted in Figure 2. The substitution Ca for REE at the *M* site is apparent and similar to that observed in As-dominant members of the mixite group (Olmí *et al.* 1991, Sejkora *et al.* 1999). The results lead to the ideal simplified formula $\text{CaCu}_6[(\text{PO}_4)_2(\text{PO}_3\text{OH})(\text{OH})_6] \cdot 3 \text{H}_2\text{O}$. In view of the existence of only one *X* site (*e.g.*, one As in the *X* site described by Aruga & Nakai 1985) and the disordered character of the substitution of OH⁻ for O²⁻ at the O(3) site in the crystal structure of calciopetersite-type minerals, it seems better to assign a general formula $\text{CaCu}_6[\text{PO}_3(\text{O}_{2/3}(\text{OH})_{1/3})_3(\text{OH})_6] \cdot 3 \text{H}_2\text{O}$ to calciopetersite.

INFRARED SPECTROSCOPY

The infrared-absorption spectrum of calciopetersite (Fig. 3) was recorded with the Nicolet Magna IR microscope in the range 4000–600 cm⁻¹ owing to a very small amount of sample available. The sample (less than 0.05 mg) was dispersed in a mixture with KBr. A tentative assignment of individual bands in the spectrum (Table 3) is based on the findings of Keller (1971),

TABLE 3. INFRARED-ABSORPTION SPECTRUM OF CALCIOPETERSITE FROM DOMAŠOV NAD BYSTRICÍ

Wavenumbers [cm ⁻¹]		Tentative assignment	
3501	m		
3390	m	br	ν OH-stretching vibrations
3326	mw	sh	
1650	m		
1635	m	sh	δ H ₂ O-bending vibrations
1623	mw	sh	
1498	vw		δ P–OH in-plane bending vibration or overtones or combination bands
1379	vw		
1108	m	sh	
1059	vs		ν ₃ (PO ₄) ³⁻ antisymmetric stretching vibrations
1032	vs		
1018	s	sh	
1001	vs		
982	s		
933	m		ν ₁ (PO ₄) ³⁻ antisymmetric stretching vibrations
924	m	sh	
829	mw	sh	
811	m		δ P–OH out-of-plane bending vibrations or H ₂ O libration modes (or both)
770	mw		
750	w	sh	
722	vw	sh	

Nicolet Magna IR microscope. Character of absorption maxima: sh: shoulder, b: broad. Intensity scale: vs: very strong, s: strong, m: medium, mw: medium weak, w: weak, vw: very weak.

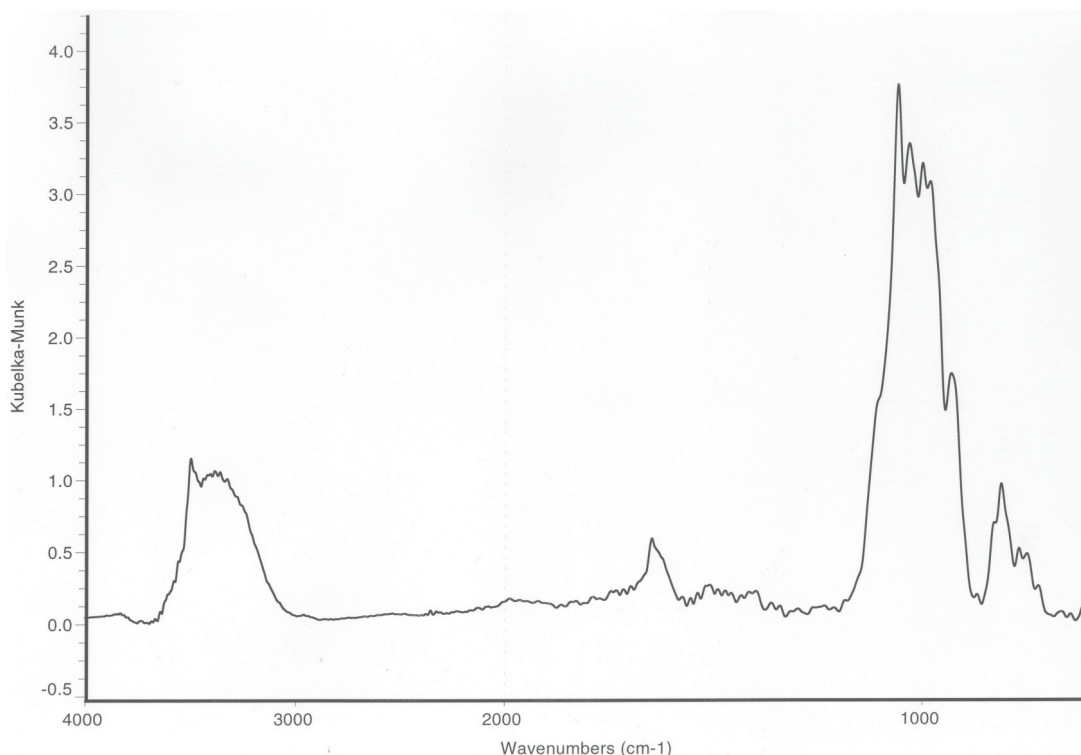


FIG. 3. The infrared-absorption spectrum of calciopetersite from Domašov nad Bystřicí. A digital version of this spectrum is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

Farmer (1974), Sejkora *et al.* (1999) and Martens & Frost (2003).

Bands in the range 3800–2900 cm^{-1} were assigned to the ν OH stretching vibrations in H_2O molecules (broad bands at 3390 and 3326 cm^{-1}) and hydroxyl groups (sharp band at 3501 cm^{-1}) in the structure of calciopetersite, and those in the range 1700–1550 cm^{-1} to the δ H–O–H bending vibrations of H_2O molecules.

The existence of more bands and shoulders in both regions of the infrared spectrum indicates that several structurally nonequivalent hydroxyl groups and H_2O groups, bonded with different hydrogen bonds, are present in the structure. Approximate O–H...O hydrogen bond lengths are ~ 2.7 , ~ 2.79 – 2.8 and ~ 2.9 Å (Libowitzky 1999). Some H_2O groups may well have a zeolitic character, as proposed by Zemann (1991) and Miletich & Zemann (1993) for other members of this group. The presence of zeolitic H_2O in agardite was also reported by Dietrich *et al.* (1969) on the basis of a thermal analysis. The crystal structure of Ca-rich agardite (Aruga & Nakai 1985) consists of infinite chains of CuO_4 groups running along the c axis, which are alternately connected to MO_9 polyhedra and XO_4 tetrahedra. The

charge compensation required by the substitution of a divalent cation (Ca^{2+}) for a trivalent cation (*e.g.*, Bi^{3+} , REE^{3+}) is assured by the concomitant substitution of $(\text{OH})^-$ for O^{2-} . The square-planar CuO_4 groups share a pair of the opposite edges to form chains along a axis. The MO_9 polyhedra and the XO_4 tetrahedra alternately stack parallel to the c axis and join the CuO_4 chains. The large temperature-factor of one of the oxygen atoms (Aruga & Nakai 1985) confirms the zeolitic nature of the H_2O molecules.

The $(\text{XO}_4)^{3-}$ tetrahedron in the structure of mixite-group minerals is distorted, and its point symmetry is lower than T_d (Sejkora *et al.* 1999). Therefore, all vibrations (ν_1 , ν_3 in our data range) become active in the infrared spectrum, and the triply degenerate ν_3 vibration is split. At least six bands in the region 1200–950 cm^{-1} were assigned to the triply degenerate antisymmetric stretching vibration ν_3 $(\text{PO}_4)^{3-}$, and a band at 933 cm^{-1} with shoulder at 924 cm^{-1} , to the symmetric stretching vibration ν_1 $(\text{PO}_4)^{3-}$. The six bands assigned to the ν_3 and two bands to the ν_1 vibrations of $(\text{PO}_4)^{3-}$ indicate the presence of at least two structurally nonequivalent phosphate groups in calciopetersite.

The presence of a (PO₃OH) group in the structure can be inferred from the study of its infrared spectra (Keller 1971). The in-plane δ (P–OH) vibrations were observed in the range 1550–1200 cm⁻¹, with weak maxima at 1498 and 1379 cm⁻¹; some coincidences with overtones and combination bands are possible. The bands in the range 850–700 cm⁻¹ (with maxima at 829, 811, 770, 750 and 722 cm⁻¹) can be related to the out-of-plane bending vibration δ (P–OH). In this range, some coincidences with libration modes of molecular H₂O and some M–OH vibrations cannot be excluded.

CONCLUDING REMARKS

Calciopetersite is the Ca- and P-dominant member of the mixite group. Calcium is dominantly incorpo-

rated at the *M* site (0.58 *apfu*) of the general formula $MCu_6(XO_4)_3(OH)_6 \cdot 3H_2O$; however, part of the Ca (0.14 *apfu*) is very likely present at the Cu site as well.

An identification of individual members of the mixite group merely on the basis of their X-ray powder-diffraction patterns and calculated unit-cell parameters is ambiguous owing to extensive substitutions at the *M* and *X* site, respectively, resulting in competing influences on their unit-cell parameters (Table 4). A quantitative chemical analysis is necessary for a correct determination of the mineral phases.

Calciopetersite represents a rare product of the leaching of chalcopyrite and other copper sulfides in an oxidizing and hydrous environment at a low temperature during weathering processes. The individual elements forming calciopetersite were derived from chalcopyrite,

TABLE 4. COMPARISON OF MINERAL PHASES IN THE MIXITE GROUP

P-dominant members						
mineral	calciopetersite	Ca analogue of petersite	petersite-(Y)			
reference	this paper	Kolitsch (1997)	Peacor & Dunn (1982)			
formula	CaCu ₆ (PO ₄) ₂ (PO ₃ OH)(OH) ₆ •3H ₂ O	CaCu ₆ (PO ₄) ₃ (OH,H ₂ O) ₆ •3H ₂ O	YCu ₆ (PO ₄) ₃ (OH) ₆ •3H ₂ O			
crystal system	Hexagonal	Hexagonal	Hexagonal			
space group	<i>P</i> 6 ₃ / <i>m</i>	-	<i>P</i> 6 ₃ / <i>m</i>			
unit-cell	<i>a</i> [Å] 13.284(4) <i>c</i> [Å] 5.902(4)	-	13.288(5) 5.877(5)			
parameters	<i>V</i> [Å ³] 902.0(6)	-	898.6(8)			
selected	11.51(100)	-	11.6(100)			
strongest	4.346(88)	-	4.36(50)			
X-ray	2.888(53)	-	2.877(40)			
powder	2.641(33)	-	2.634(15)			
lines	2.510(37)	-	2.509(30)			
ω	1.674(5)	1.681(4)	1.664(4)			
ε	>1.739	1.743(5)	1.747(4)			
As-dominant members						
mineral	zálesítite	Ca-rich agardite	agardite-(Y)	agardite-(Ce)	mixite	goudeyite
reference	Sejkora <i>et al.</i> (1999)	Aruga & Nakai (1985)	Dietrich <i>et al.</i> (1969)	Walenta & Theye (2004)	Mereiter & Preisinger (1986)*	Wise (1978)
formula	CaCu ₆ (AsO ₄) ₂ (AsO ₃ OH)(OH) ₆ •3H ₂ O	(Ca _{0.5} Y _{0.3} ...)-dominant member	(Y,CaH)Cu ₆ (AsO ₄) ₂ (OH) ₆ •3H ₂ O	CeCu ₆ (AsO ₄) ₃ (OH) ₆ •3H ₂ O	(Bi,CaH)Cu ₆ (AsO ₄) ₃ (OH) ₆ •3H ₂ O	AlCu ₆ (AsO ₄) ₃ (OH) ₆ •3H ₂ O
crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
space group	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 6 ₃ / <i>m</i>
unit-cell	<i>a</i> [Å] 13.571(1) <i>c</i> [Å] 5.880(1)	13.583(2) 5.895(1)	13.55(5) 5.87(2)	13.59(2) 5.89(1)	13.646(2) 5.920(1)	13.472(1) 5.902(4)
parameters	<i>V</i> [Å ³] 937.8(2)	941.9(2)	933(10)	942.1	954.7	927.7
selected	11.64(100)	11.76(100)	11.73(100)	11.88(100)	12.03(100)*	11.63(100)
strongest	4.431(41)	4.45(24)	4.43(70)	4.47(80)	4.47(50)*	4.41(43)
X-ray	2.935(42)	2.942(36)	2.938(80)	2.95(80)	2.95(70)*	2.920(50)
powder	2.693(29)	2.699(17)	2.692(60)	2.70(50)	2.70(60)*	2.677(42)
lines	2.562(30)	2.567(14)	2.558(60)	2.57(50)	2.57(60)*	2.546(40)
ω	1.688(2)	-	1.701(5)	1.725(3)	1.750(3)*	1.704
ε	1.765(2)	-	1.782(5)	1.810(3)	>1.80*	1.765

* See also Walenta (1960).

chalcocite and covellite (Cu), the host graywackes (Ca, P), and associated carbonate veins (Ca, Y, REE) containing the REE mineral calkingsite-(Ce) (Zimák & Novotný 2002).

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