ONDRUŠITE, CaCu₄(AsO₄)₂(AsO₃OH)₂•10H₂O, A NEW MINERAL SPECIES FROM THE JÁCHYMOV ORE DISTRICT, CZECH REPUBLIC: DESCRIPTION AND CRYSTAL-STRUCTURE DETERMINATION

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Abstract

Ondrušite, CaCu₄(AsO₄)₂(AsO₃OH)₂•10H₂O, is a new supergene mineral species from the Geister vein (Rovnost mine) and the Geschieber vein (Svornost mine), at the Jáchymov (St. Joachimsthal) ore district, Czech Republic. It is commonly associated with lindackerite, geminite, lavendulan, slavkovite, strashimirite, olivenite, picropharmacolite and köttigite. It forms white, whitish green, grey-green or apple-green crystalline crusts or aggregates composed of fine platy or lath-shaped translucent crystals up to 2 mm in size, on fissures of partly weathered mineralized quartz veins. It has a white to greyish white streak with a greenish tint, and a vitreous luster; it does not fluoresce under both short- and long-wave ultraviolet light. Cleavage on {001} is perfect, the Mohs hardness is ~2–3, and the mineral is very brittle with an irregular fracture. The measured density, 3.26 g/cm³ (affected by a lavendulan admixture), is slightly higher than a calculated one of 3.12 g/cm³. Ondrušite is biaxial positive; the indices of refraction are α' 1.640(2) and γ' 1.708(2), and it is strongly pleochroic, from colorless to light yellowish green. Ondrušite is triclinic, space group $P\overline{1}$, *a* 6.432(1), *b* 7.986(1), *c* 10.827(1) Å, α 85.75(1), β 81.25(1), γ 85.04(1)°, *V* 546.6(1) Å³, Z = 1, *a:b:c* = 0.8054:1:1.3557. The strongest eight lines in the X-ray powder-diffraction pattern [*d* in Å(I)(*hkl*)] are: 10.671(100)(001), 3.970(10)(020), 3.648(11)(02$\overline{1}$), 3.560(18)(003), 3.286(10)(022), 3.173(13)(01$\overline{3}$, 200, 201), 2.922(10)(20$\overline{1}$, 202) and 2.736(10) (023). The chemical analyses by electron microprobe and the thermal analysis for H₂O yielded MgO 0.42, CaO 5.27, NiO 0.03, CoO 0.08. CuO 29.90, PbO 0.16, P₂O₅ 0.33, As₂O₅ 44.92, H₂O 19.40, for a total of 100.51 wt.%. The resulting empirical formula, calculated on the basis of 26 (O, OH, H₂O) anions, is (Ca₀.₉₆Co₀.₀₁Pb₀.₀₁)∑₀.₉₈ (Cu₃.₈₄Mg₀.₁₁)∑₃.₉₅ [(AsO₄)₁.₇₃(PO₄)₀.₀₅]∑₁.₇₈ (AsO₃OH)₂.₂₆•9.86H₂O. The ideal end-member formula, CaCu₄(AsO₄)₂(AsO₃OH)₂•10H₂O, requires CaO 5.43, CuO 30.83, As₂O₅ 44.53, H₂O 19.20, total 100.00 wt.%. The crystal structure of ondrušite was solved by direct method and refined to a R_1 index of 9.80% based on all 2888 reflections collected on a single-crystal diffractometer with Mo*K*α X-radiation. The crystal structure consists of CuO₆–AsO₄–AsO₃OH chains two polyhedra thick that form sheets connected through the bridging CaO₆ octahedra. In the sheet-to-sheet bonding, CaO₆ octahedra and AsO₄ groups are involved, whereas the AsO₃OH groups bond the CuO₆ polyhedra only. One other H₂O group is located between the sheets. Ondrušite represents the Ca–Cu-dominant member of the ondrušite – geigerite – chudobaite subgroup of the lindackerite group.

Keywords: ondrušite, new mineral species, lindackerite group, X-ray powder data, crystal structure, electron-microprobe data, thermal analysis, infrared spectroscopy, Jáchymov ore district, Czech Republic.

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Sommaire

Nous décrivons la ondrušite, $CaCu_4(AsO_4)_2(AsO_3OH)_2•10H_2O$, nouvelle espèce minérale supergène découverte dans la veine Geister (mine Rovnost) et la veine Geschieber (mine Svornost) du camp minier de Jáchymov (St. Joachimsthal), en République Tchèque. Elle est généralement associée à lindackerite, géminite, lavendulane, slavkovite, strashimirite, olivenite, picropharmacolite et köttigite. Elle se présente en encroûtements cristallins blanc, vert très pâle, gris-vert ou vert pomme, ou en agrégats de cristaux en plaquettes atteignant 2 mm le long de fissures traversant les veines lessivées de quartz minéralisées. Elle possède une rayure blanche à blanc grisâtre avec une teinte de vert, et un éclat vitreux. Elle ne montre aucune fluorescence en lumière ultraviolette (longueur d'onde courte ou longue). Le clivage {001} est parfait, et la dureté de Mohs est environ 2–3. La densité mesurée d'un échantillon contaminé avec la lavendulane est 3.26 g/cm^3, légèrement supérieure à la densité calculée, 3.12 g/cm^3. La ondrušite est biaxe positive; les indices de réfraction sont α' 1.640(2) et γ' 1.708(2);le minéral est fortement pléochroïque, passant de l'incolore à vert jaunâtre pâle. Il est triclinique, groupe spatial $P\bar{1}$, a 6.432(1), b 7.986(1), c 10.827(1) Å, α 85.75(1), β 81.25(1), γ 85.04(1)°, V 546.6(1) Å^3, Z = 1, a:b:c = 0.8054:1:1.3557. Les huit raies les plus intenses du spectre de diffraction X, méthode des poudres [d en Å(I)(hkl)], sont: 10.671(100)(001), 3.970(10)(020), 3.648(11)(02$\bar{1}$), 3.560(18)(003), 3.286(10)(022), 3.173(13)(01$\bar{3}$, 200, 201), 2.922(10)(20$\bar{1}$, 202) et 2.736(10)(023). Les analyses chimiques effectuées avec une microsonde électronique et une analyse thermique pour H$_2$O ont donné MgO 0.42, CaO 5.27, NiO 0.03, CoO 0.08. CuO 29.90, PbO 0.16, P$_2$O$_5$ 0.33, As$_2$O$_5$ 44.92, H$_2$O 19.40, pour un total de 100.51% (poids). La formule empirique, calculée sur une base de 26 anions (O, OH, H$_2$O), est $(Ca_{0.96}Co_{0.01}Pb_{0.01})_{\Sigma 0.98}$ $(Cu_{3.84}Mg_{0.11})_{\Sigma 3.95}$ $[(AsO_4)_{1.73}(PO_4)_{0.05}]_{\Sigma 1.78}(AsO_3OH)_{2.26}•9.86H_2O$. La formule idéale du pôle, $CaCu_4(AsO_4)_2(AsO_3OH)_2•10H_2O$, requiert CaO 5.43, CuO 30.83, As$_2$O$_5$ 44.53, H$_2$O 19.20, total 100.00%. Nous avons résolu la structure cristalline de la ondrušite par méthodes directes, et nous l'avons affiné jusqu'à un résidu R_1 de 9.80% en utilisant toutes les 2888 réflexions prélevées sur monocristal avec un diffractomètre utilisé avec rayonnement MoKα. La structure contient des chaînes CuO$_6$–AsO$_4$–AsO$_3$OH d'une épaisseur de deux polyèdres, connectées entre elles par les octaèdres de CaO$_6$. Dans les agencements de feuillets, les octaèdres CaO$_6$ et les groupes AsO$_4$ sont impliqués, tandis que les groupes AsO$_3$OH ne sont liés qu'aux polyèdres CuO$_6$. Un group additionnel de H$_2$O est situé entre les feuillets. La ondrušite représente le pôle à dominance de Ca–Cu de la série ondrušite – geigerite – chudobaïte du groupe de la lindackerite.

(Traduit par la Rédaction)

Mots-clés: ondrušite, nouvelle espèce minérale, groupe de la lindackerite, diffraction X, méthode des poudres, structure cristalline, données de microsonde électronique, analyse thermique, spectroscopie infrarouge, camp minier de Jáchymov, République Tchèque.

Introduction

In the context of extensive mineralogical research focused chiefly on supergene minerals of the Jáchymov ore district in the Czech Republic, minerals of the lindackerite group have been studied, and their crystal structure was solved by Hybler *et al.* (2003). In the crystal structure of Cu-rich lindackerite-group minerals, the five metal atoms occupy three cationic sites. Two of these (M1 and M2) are fully occupied by four Cu atoms, and the remaining position (the special M3 site) is preferentially occupied by Ca, Co, Ni and Zn atoms. This substitution of Ca, Co, Ni and Zn for Cu at the M3 position is an important feature in their nomenclature. The discovery of a Ca–Cu-dominant mineral of the lindackerite group and its complete description resulted in the approval of the new mineral species by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2008–010). The new species, ondrušite, is identical to the so-called "pseudo-lindackerite" (code UM 1997–06–AsO:CaCuH) of Ondruš *et al.* (1997b) and unnamed mineral 51–1476 of the PDF database.

Ondrušite is named in honor of the Ing. Petr Ondruš (born 1960), mineralogist associated with the Czech Geological Survey, Prague, Czech Republic. The name recognizes the exceptional contribution of Ing. Ondruš, the author of more than 30 published papers, including the description of seven new minerals (čejkaite, pseudojohannite, švenekite, vajdakite, veselovskýite, metarauchite and slavkovite) from the Jáchymov ore district. The holotype specimen of ondrušite has been deposited in the mineral collection of the National Museum, Prague (Czech Republic), catalogue number P1P 1/2008.

Occurrence

Ondrušite was found in material from old workings at the Geister vein, Rovnost mine, and the Geschieber vein at the Daniel level, at the Svornost mine, Jáchymov ore district (St. Joachimsthal), Krušné hory Mountains, approximately 20 km north of Karlovy Vary, northwestern Bohemia, Czech Republic. The Jáchymov ore district is a classic example of Ag + As + Co + Ni + Bi and of U vein-type hydrothermal mineralization. The ore veins cut a complex of medium-grade metasedimentary rocks of Cambrian to Ordovician age, in the envelope of a Variscan granite pluton. The majority of the ore minerals were deposited during Variscan mineralization from mesothermal fluids (Ondruš *et al.* 2003b, 2003c, 2003e). Primary and supergene miner-

alization in this district resulted in extraordinarily rich associations; more than 400 mineral species there have been described up to now (Ondruš *et al.* 1997a, 1997b, 2003d, 2003e). The following seven new mineral species were described from this ore district: vajdakite (Ondruš *et al.* 2002), čejkaite (Ondruš *et al.* 2003a), švenekite (Ondruš *et al.* 2003d), pseudojohannite (Brugger *et al.* 2006), veselovskýite (Sejkora *et al.* 2010a), metarauchite (Plášil *et al.* 2010), and slavkovite (Sejkora *et al.* 2010b). The new mineral ondrušite was found in the association of lindackerite, geminite, lavendulan, slavkovite, strashimirite, olivenite, picropharmacolite and köttigite; it was formed by the weathering in strongly acidic conditions of primary sulfides (tennantite and chalcopyrite) disseminated in a quartz gangue.

PHYSICAL AND OPTICAL PROPERTIES

Ondrušite occurs as crystalline crusts or aggregates composed of fine platy or lath-shaped crystals (Fig. 1) up to 2 mm in size, on fissures of partly weathered and mineralized quartz veins. Ondrušite has a white, whitish green, grey-green or apple-green color; it is translucent and has a white to greyish white streak with a greenish tint and a vitreous luster. It does not fluoresce under both short- and long-wave ultraviolet light. The cleavage on {001} is perfect, the Mohs hardness is ~2–3, and the mineral is very brittle with an irregular fracture. The measured density (flotation), D_{obs}, is 3.26 g/cm^3, slightly higher than the density, D_{calc} = 3.12 g/

cm^3, calculated on the basis of an empirical formula and unit-cell volume refined from powder data. This difference is probably caused by the presence of some admixed lavendulan (D = 3.58 g/cm^3).

Ondrušite from Jáchymov has strong pleochroism, from colorless to light yellowish green. It is biaxial positive, forms tabular crystals with a perfect cleavage on {001}, and has an extinction angle 9(1)°. Its indices of refraction were measured in polarized Na light (589 nm) by the Becke line method; the indices of refraction of immersion liquids were measured by the minimum deviation method. The measured indices are: α' = 1.640(2) and γ' = 1.708(2). It was not possible to find the exact position of the individual optical orientations relative to the indices α, β, γ in this triclinic mineral with one cleavage plane. The Gladstone–Dale compatibility index, $1 - (K_P / K_C)$, calculated from incomplete optical data $[(2\alpha' + \gamma')/3)]$, is equal to –0.056 (good).

CHEMICAL COMPOSITION AND THERMOGRAVIMETRIC DATA

Samples of ondrušite were analyzed with a Cameca SX–100 electron microprobe (joint laboratory of electron microscopy and microanalysis of the Masaryk University and Czech Geological Survey, Brno), operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 4 nA, and a beam diameter of 20 μm. The following lines and standards were used: $K\alpha$: andradite (Ca, Fe), sanidine (Al, Si, K), metallic Co (Co), fluorapatite (P), metallic
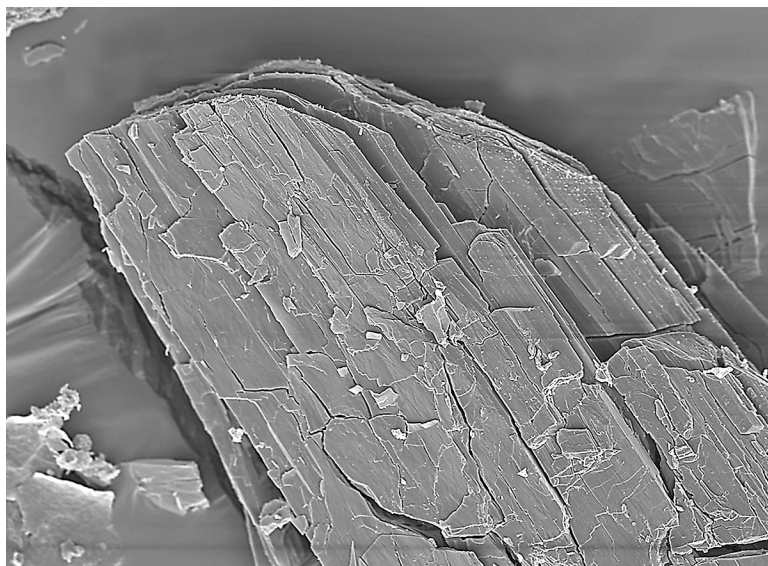

FIG. 1. Photo of ondrušite from Jáchymov showing the individual lath-shaped crystals; the width of view is 200 μm (scanning electron micrograph).

Ni (Ni), ZnO (Zn), olivine (Mg), rhodonite (Mn), vanadinite (Cl, V), topaz (F); $L\alpha$: InAs (As), dioptase (Cu); $L\beta$: metallic Sb (Sb), and $M\alpha$: Pb (vanadinite). Peak counting times (CT) were 20 s for main elements and 60 s for minor elements; CT for each background was one half of peak time. The raw intensities were converted to concentrations automatically using the PAP (Pouchou & Pichoir 1985) matrix-correction software. The elements Al, Fe, Na, K, Mn, Sb, Si, V, S, Zn, Cl and F were sought but found to be below the detection limit (about 0.01–0.03 wt.%). The presence and quantity of (OH) and (H$_2$O) groups were established by thermal analyses and calculated from charge balance.

Table 1 gives the chemical composition of ondrušite from Jáchymov (mean of seven determinations). Results of the chemical analyses correspond very well with the ideal formula $MCu_4[(AsO_4)_2(AsO_3OH)_2] \cdot 10H_2O$, in which the M position (structurally, $M3$) is dominantly occupied by Ca atoms (0.87–1.04 $apfu$). In the anionic position, phosphorus substitutes for As in the range of 0–0.15 $apfu$. It is possible to express the empirical formula of ondrušite based on 26 (O, OH, H$_2$O) anions as $(Ca_{0.96}Co_{0.01}Pb_{0.01})_{\Sigma0.98} (Cu_{3.84}Mg_{0.11})_{\Sigma3.95} [(AsO_4)_{1.73}(PO_4)_{0.05}]_{\Sigma1.78}(AsO_3OH)_{2.26} \cdot 9.86H_2O$. For the end-member formula of ondrušite, $CaCu_4(AsO_4)_2 (AsO_3OH)_2 \cdot 10H_2O$, the oxide contents should be CaO

5.43, CuO 30.83, As$_2$O$_5$ 44.53, H$_2$O 19.20, total 100.00 wt.%.

The thermogravimetric curve of ondrušite from Jáchymov (Fig. 2) was recorded with a TG 750 Stanton Redcroft Thermobalance. The operating conditions were: weight: 1.475 mg, heating rate: 10°C/min, dynamic air atmosphere: 10 mL/min, and temperature range: 20–880°C. Ondrušite dehydrates in three steps (Table 2). About 3.5 H$_2$O molecules were first liberated at 20–100°C, 1.5 H$_2$O molecules were released in the range of 100–230°C, and six additional H$_2$O molecules (in part corresponding to AsO$_3$OH groups) were driven off in the range of 230–330°C. The general decrease in mass over the range 20–330°C is 19.40 wt.%, which is related to about eleven molecules of H$_2$O. The weight loss in the range of 330–600°C, 5.90 wt.%, is probably caused by the release of parts of As$_2$O$_3$ and O$_2$. The thermal decomposition processes at temperatures higher than 600°C are unclear; there is an observed increase in weight of 0.90 wt.% (600–650°C) followed by a gradual decrease 0.70 wt.% in the range of 650–880°C. The greyish black residue after thermal analysis is amorphous, according to powder XRD.
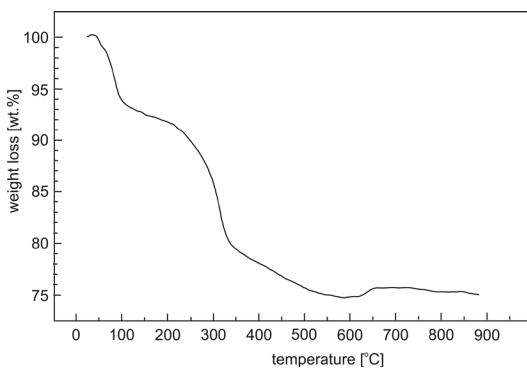
FIG. 2.   Thermogravimetic curve of ondrušite from Jáchymov.

TABLE 1. CHEMICAL COMPOSITION OF ONDRUŠITE

	Jáchymov		ideal[1]
	mean	range (7 points)	
MgO wt.%	0.42	0.19 - 0.54	
CaO	5.27	4.83 - 5.74	5.43
NiO	0.03	0.00 - 0.07	
CoO	0.08	0.00 - 0.15	
CuO	29.90	29.48 - 30.31	30.83
PbO	0.16	0.00 - 0.24	
As$_2$O$_5$	44.92	43.62 - 46.92	44.53
P$_2$O$_5$	0.33	0.00 - 1.02	
H$_2$O*	19.40		19.20
Total	100.51		100.00
Mg^{2+} $apfu$	0.106		
Ca^{2+}	0.959		1.000
Ni^{2+}	0.004		
Co^{2+}	0.011		
Cu^{2+}	3.836		4.000
Pb^{2+}	0.007		
Σ	4.923		5.000
As^{5+}	3.989		4.000
P^{5+}	0.047		
Σ	4.036		4.000
OH	2.262		2.000
H$_2$O	9.855		10.000

Atom proportions are calculated on the basis (O,OH,H$_2$O) = 26; H$_2$O*: contents of H$_2$O were derived from thermal analysis; ideal[1]: theoretical composition calculated from the ideal formula CaCu$_4$(AsO$_4$)$_2$(AsO$_3$OH)$_2$ •10H$_2$O.

TABLE 2. THERMAL ANALYSIS OF ONDRUŠITE

Temperature range (°C)	Weight loss (wt.%)	Tentative assignment	Theoretical weight-loss*
20 – 100	6.1	3.5 H$_2$O	6.11
100 – 230	2.7	1.5 H$_2$O	2.62
230 – 330	10.6	6 H$_2$O	10.47
20 – 330	Σ19.4	Σ11 H$_2$O	19.20
330 – 600	5.9	As$_2$O$_3$ + O$_2$	
600 – 650	–0.9		
650 – 880	0.7		

theoretical weight-loss*: theoretically expected values (wt.%) for H$_2$O molecules.

The number of H_2O groups in minerals structurally related to lindackerite (ondrušite, veselovskýite, lindackerite, pradetite, chudobaite and geigerite) is in the range 9–10. The H_2O content of geigerite (Graeser *et al.* 1989) and chudobaite (Dorner & Weber 1976) was described on the basis of crystal-structure refinements as 10 H_2O molecules, but distinctly lower on the basis of measured H_2O contents (Strunz 1960, Graeser *et al.* 1989). Sarp & Dominik (1995) proposed for lindackerite from Jáchymov 9.62 H_2O, and for pradetite from Cap Garonne, 9.56 H_2O, but these H_2O contents were derived only by difference from 100%. Guillemin (1956) found 8.77 H_2O in lindackerite from Jáchymov. Hybler *et al.* (2003) documented 9 H_2O for lindackerite from Jáchymov on the basis of crystal-structure refinements (some OW sites in crystal structures are not fully occupied). The ideal content of H_2O in veselovskýite (Sejkora *et al.* 2010a) is assumed to be 9 H_2O by analogy with lindackerite. The H_2O content in ondrušite was determined by TG analysis to be 9.86 H_2O; on the basis of its crystal-structure refinement, however, the content of H_2O is 10 molecules (five fully occupied OW sites). We thus infer that the ideal content of molecular H_2O in ondrušite is 10 H_2O.

INFRARED ABSORPTION SPECTROSCOPY

The powder infrared absorption spectrum of ondrušite (dispersed in a KBr disk) was recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000–400 cm^{-1} (Figs. 3a, b). The following tentative assignment is based on the data published by Keller (1971), Vansant *et al.* (1973), Farmer (1974), Myneni *et al.* (1998) and Đorđević & Karanović (2008). In the crystal structure of ondrušite, $(AsO_4)^{3-}$, $(AsO_3OH)^{2-}$ groups and H_2O molecules are present.

The intense band at 3429 cm^{-1} with a shoulder at 3210 cm^{-1} was assigned to the ν OH stretching vibrations of hydrogen-bonded H_2O molecules ($R_{O-H\cdots O}$ 2.83 and 2.71 Å, respectively: Libowitzky 1999), and those bands in the range of 1520–1750 with a maximum at 1633 cm^{-1}, to the δ H–O–H bending vibrations of H_2O molecules. The presence of shoulders in these regions of the spectrum indicates the existence of more structurally non-equivalent H_2O molecules in ondrušite, which is in agreement with the results of the crystal-structure study. The $(AsO_4)^{3-}$ and $(AsO_3OH)^{2-}$ tetrahedra in the crystal structure of ondrušite are distorted, and their point symmetries are lowered. Therefore, all vibrations may become active in the infrared spectrum, and degenerate vibrations may split. The stretching vibrations ν (O–H) in strongly hydrogen bonded (AsO_3OH) groups can be related to indistinct shoulders in the range of 3000–2500 cm^{-1}. The δ (As–OH) in-plane bending vibrations were observed in the range of 1520–1000 cm^{-1} with maxima at 1458, 1318, 1204, 1122, 1094 and 1024 cm^{-1}. Some coincidences with overtones and combination bands in this region are possible. The shoulder at 877 and

bands at 849 and 801 cm^{-1} were assigned to the split triply degenerate antisymmetric stretching vibration ν_3 $(AsO_4)^{3-}$, with possible coincidence with the ν_1 $(AsO_4)^{3-}$ symmetric stretching and the ν_3 $(AsO_3OH)^{2-}$ antisymmetric stretching vibration. The shoulder at 741 cm^{-1} is assigned to the ν As–OH stretching vibrations, and the band at 551 cm^{-1}, to the δ As–OH bending vibrations. The band at 467 and shoulder at 426 cm^{-1} are connected with the ν_4 $(AsO_4)^{3-}$ and ν_4 $(AsO_3OH)^{2-}$ bending vibrations.

X-RAY POWDER DIFFRACTION

A hand-picked sample of ondrušite from Jáchymov was used to collect the X-ray powder-diffraction pattern using a Philips X'Pert MPD diffractometer at 40 kV, 40 mA, with graphite-monochromated Cu$K\alpha$ X-radiation (λ = 1.54178 Å). To minimize the background, the ground sample was placed on a flat low-background silicon wafer. The powder pattern was collected in the range from 3 to 65°2θ with a step size of 0.01°2θ and a counting time of 9 seconds per step. The powder-diffraction pattern obtained (Table 3) is close to data calculated by the LAZY PULVERIX program (Yvon *et al.* 1977) from the crystal-structure information of ondrušite. Positions and intensities of individual reflections were calculated using the Pearson VII profile-shape function with the ZDS package of programs (Ondruš 1995). The unit-cell parameters were refined by the least-squares refinement program of Burnham (1962): *a* 6.432(1), *b* 7.986(1), *c* 10.827(1) Å, α 85.75(1), β 81.25(1), γ 85.04(1)°, *V* = 546.6(1) Å^3 and *a*:*b*:*c* ratio 0.8054:1:1.3557. The refined parameters agree very well with results from our single-crystal study (Table 4).

CRYSTAL-STRUCTURE SOLUTION AND REFINEMENT

A light grey to green prismatic crystal of ondrušite from Jáchymov, with dimensions of 0.08 × 0.03 × 0.02 mm, was selected and mounted on a glass fiber, and diffraction data were collected on the Nonius Kappa CCD area detector single-crystal diffractometer using monochromatized Mo$K\alpha$ radiation at room temperature. The φ and ω scans were measured to fill the Ewald sphere. The unit-cell dimensions (Table 4) were refined from 9993 diffraction maxima using the least-squares method (COLLECT program: Hooft 1998). The data were reduced and corrected for Lorentz and polarization effects (DENZO program: Otwinowski & Minor 1997). The absorption correction based on the multiscan method was applied (SORTAV program: Blessing 1997), leading to R_{int} of 9.8%. A total of 9993 diffraction maxima were measured; 2888 of them are independent, and 1823 reflections are classified as observed [$I > 2\sigma(I)$].

The crystal structure of ondrušite was solved by the structure-invariant direct methods (SIR92: Altomare *et al.* 1994). The structure was solved in space
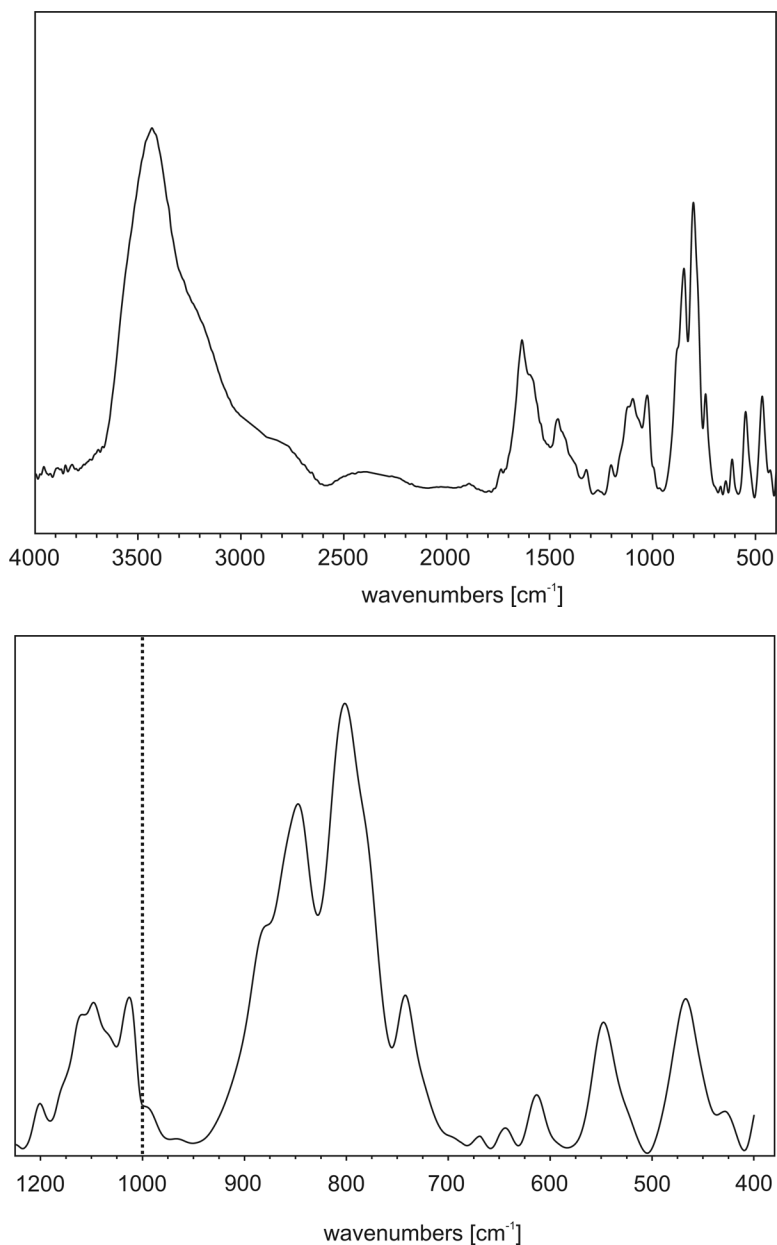
Fɪɢ. 3.   a. Infrared absorption spectrum of ondrušite from Jáchymov. b. Detail of this
       spectrum in the range of 1250–400 cm^{-1} (split at 1000 cm^{-1}).

group $P\bar{1}$, and subsequently verified by refinement in SHELXL97 (Sheldrick 1997, 2008). The crystal structure was refined on the basis of F^2 involving all reflections (SHELX command ACTA). The final refinement included positional parameters of atoms, and allowed for anisotropic atomic displacement parameters for all non-hydrogen atoms. The position of the hydrogen atoms forming part of the AsO_3OH group was deduced from the difference-Fourier map, and parameters of the H atom were constrained during subsequent refinement. The refinement converged to R_1 = 9.7%, with the goodness of fit 1.07. In the last cycle

TABLE 3. X-RAY POWDER-DIFFRACTION PATTERN OF ONDRUŠITE

I	$d_{meas.}$	$d_{calc.}$	h	k	l	I	$d_{meas.}$	$d_{calc.}$	h	k	l	I	$d_{meas.}$	$d_{calc.}$	h	k	l
100.0	10.671	10.681	0	0	1	1.6	2.8502	2.8511	2	$\bar{1}$	1	3.8	1.9750	1.9739	0	4	1
6.8	7.934	7.941	0	1	0	1.0	2.8370	2.8379	2	1	2	2.3	1.9456	1.9468	2	3	3
2.0	6.564	6.570	0	1	1	0.7	2.8104	2.8104	1	$\bar{2}$	2			1.9465	1	3	4
3.9	6.191	6.192	0	1	$\bar{1}$	3.6	2.7596	2.7599	1	$\bar{1}$	$\bar{3}$	1.3	1.9323	1.9317	0	2	5
1.4	5.839	5.840	1	0	1	10.0	2.7357	2.7362	0	2	3	1.8	1.9005	1.8997	0	4	2
8.9	5.339	5.340	0	0	2	4.1	2.6692	2.6702	0	0	4	3.6	1.8721	1.8723	2	3	$\bar{2}$
4.4	5.145	5.149	1	1	0	3.2	2.6476	2.6527	2	$\bar{1}$	2	1.6	1.8420	1.8419	3	1	$\bar{2}$
1.5	4.957	4.957	1	1	1			2.6471	0	3	0	1.4	1.8129	1.8135	2	$\bar{3}$	$\bar{2}$
1.1	4.781	4.780	1	$\bar{1}$	0	6.0	2.5988	2.5989	2	2	1			1.8129	3	$\bar{2}$	1
1.2	4.568	4.564	0	1	2	3.2	2.5740	2.5728	0	2	$\bar{3}$	2.6	1.8062	1.8065	1	$\bar{2}$	5
2.0	4.482	4.487	1	$\bar{1}$	1	4.6	2.5646	2.5654	2	0	$\bar{2}$	4.2	1.7752	1.7768	1	$\bar{3}$	$\bar{4}$
0.7	4.417	4.416	1	0	2	1.9	2.5600	2.5612	2	0	3			1.7718	1	1	6
2.0	4.375	4.374	1	1	$\bar{1}$	6.2	2.5338	2.5330	0	3	$\bar{1}$	0.6	1.7597	1.7604	0	1	6
3.6	4.307	4.310	0	1	$\bar{2}$	3.3	2.4787	2.4787	2	2	2			1.7587	2	4	1
0.6	4.038	4.042	1	1	2	1.2	2.4338	2.4324	0	3	2	1.1	1.7440	1.7440	1	$\bar{4}$	2
10.2	3.970	3.971	0	2	0	1.8	2.3887	2.3898	2	$\bar{2}$	0	2.2	1.7093	1.7097	1	$\bar{1}$	6
3.2	3.798	3.799	0	2	1	1.4	2.3832	2.3837	1	3	$\bar{1}$	1.1	1.7081	1.7074	3	$\bar{1}$	4
4.0	3.701	3.699	1	$\bar{1}$	2	0.8	2.3782	2.3790	1	$\bar{3}$	0	0.5	1.6832	1.6847	2	4	$\bar{1}$
10.9	3.648	3.649	0	2	$\bar{1}$	3.5	2.3388	2.3382	1	2	$\bar{3}$	0.8	1.6631	1.6610	3	$\bar{1}$	$\bar{3}$
18.2	3.560	3.560	0	0	3	2.2	2.3223	2.3224	1	$\bar{3}$	$\bar{1}$	2.2	1.6578	1.6595	2	0	6
0.8	3.485	3.487	1	2	0			2.3218	1	$\bar{3}$	1	1.1	1.6516	1.6519	1	0	$\bar{6}$
3.0	3.438	3.438	1	$\bar{1}$	$\bar{2}$	2.6	2.3158	2.3154	0	3	$\bar{2}$	3.1	1.6315	1.6310	1	4	$\bar{3}$
9.5	3.286	3.285	0	2	2	3.3	2.2821	2.2821	1	$\bar{2}$	4			1.6296	1	$\bar{1}$	$\bar{6}$
13.0	3.173	3.176	0	1	$\bar{3}$	1.4	2.2648	2.2645	2	2	3	2.3	1.6020	1.6020	4	0	1
		3.169	2	0	0	2.1	2.2312	2.2297	1	1	$\bar{4}$	3.4	1.5886	1.5899	1	$\bar{3}$	$\bar{5}$
		3.168	2	0	1	0.8	2.1876	2.1869	2	2	$\bar{2}$			1.5893	3	2	$\bar{3}$
3.9	3.137	3.135	1	$\bar{2}$	1	1.3	2.1563	2.1549	0	2	$\bar{4}$	3.8	1.5845	1.5849	4	0	0
7.7	3.098	3.096	0	2	$\bar{2}$	4.6	2.1357	2.1387	2	1	$\bar{3}$			1.5839	4	0	2
2.5	3.025	3.024	2	1	0			2.1362	0	0	5	1.8	1.5601	1.5593	2	4	4
4.4	2.964	2.961	1	$\bar{1}$	3	3.3	2.0936	2.0947	1	1	5						
9.9	2.922	2.924	2	0	$\bar{1}$	0.9	2.0630	2.0640	0	3	$\bar{3}$						
		2.920	2	0	2	1.4	2.017	2.0166	2	3	$\bar{1}$						

of refinement, the mean parameter shift/su was less than 0.001, and the maximum peak value in the final difference-Fourier map was 3.39 and –2.22 e Å^{-3}. The final coordinates and anisotropic-displacement parameters of atoms are listed in Tables 5 and 6, respectively. Selected interatomic distances are reported in Table 7, and bond-valence sums for atoms in the crystal structure of ondrušite are given in Table 5. The VESTA software (Momma & Izumi 2008) was used to prepare plots of the structure. Bond-valence sums were calculated by the routine DIST implemented in JANA2006 (Petříček *et al*. 2006). A table of structure factors and a cif file are available from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document ondrušite CM49_885].

CRYSTAL STRUCTURE

Cation coordination and structural connectivity

There are two symmetrically independent Cu^{2+} atoms in the asymmetric part of the unit cell of ondrušite. The Cu^{2+} atoms (Table 7) are octahedrally coordinated by anions ($\Phi = O^{2-}$, H_2O). The copper-based octahedra are distorted, with four short (1.95–2.01 Å) and two long (2.37–2.54 Å) $Cu^{2+}\Phi$ bonds. This type of distortion is characteristic of Cu^{2+} polyhedra owing to the Jahn–Teller effect (Jahn & Teller 1937, Burns & Hawthorne 1995, Hawthorne & Schindler 2000, Hybler *et al*. 2003, Krivovichev *et al*. 2006, Sejkora *et al*. 2010b). We note that the polyhedron based on the Cu1 atom is more distorted than the second Cu, and it is not dependent on the type of Φ ligands. A bond-length distortion index Δ for Cu1 polyhedron (after Brown & Shannon 1973) is equal to 0.10, with angular variance $\sigma^2 = 78.94°^2$ (after Robinson *et al*. 1971), whereas for the Cu2 polyhedron, Δ is 0.09 and σ^2 is 45.83°^{2}.

There is one unique Ca atom in the crystal structure of ondrušite. The calcium atom is octahedrally coordinated by four H_2O groups and two oxygen atoms forming part of the AsO_4 groups. According to the bond lengths found in $Ca(H_2O)_4O_2$ polyhedron, it is a quite regular octahedron ($\Delta = 0.004$, $\sigma^2 = 26.58°^2$). The crystal structure of ondrušite contains two symmetrically unique As atom sites: As1 atoms belong to the AsO_3OH groups, whereas As2 atom belongs to the AsO_4 tetrahedra (Table 5).

The crystal structure of ondrušite consists of the copper–arsenato–hydrogenarsenate chains two polyhedra thick connected through the bridging $Ca(H_2O)_4O_2$ octahedra (Fig. 4). The sheets consist of the transversely oriented staircase chains formed by the edge-sharing

Crystal data

Unit-cell parameters	
a, b, c	6.439(1), 7.999(1), 10.849(2) Å
α, β, γ	85.78(1), 81.22(1), 85.05(1)°
V	549.1(2) Å^3
Space group	$P\bar{1}$
Z	1
D_{calc}	3.06 g cm^{-3}
F_{000}	498
μ	10.15 mm^{-1}
Crystal size	0.08 × 0.03 × 0.02 mm^3

Data collection

Diffractometer	Nonius Kappa CCD-area detector
Scan mode	φ and ω scans to fill Ewald sphere
Absorption correction	multiscan (SORTAV: Blessing 1997)
T_{min}, T_{max}	0.584, 0.822
θ range for data collection	3.10–30.85°
Completeness	83.5%
Limiting Miller indices	-8 < h < 9, -11 < k < 11, -14 < l < 15
Reflections measured	9993
Independent reflections	2888
Observed (I > 2σ(I))	1823
R_{int}	0.098

Refinement: full-least squares on F^2

R (F^2)	0.097
wR (F^2)	0.282
S	1.07
Parameters refined	162
$(\Delta/\sigma)_{max}$	<0.001
$\Delta\rho$ max/min (e Å^{-3})	3.39, −2.22
$w = 1/[\sigma^2(F_o^2) + (0.1605P)^2 + 2.4645P]$, $P = (F_o^2 + 2F_c^2)/3$	

$^{[4+2]}CuO_6$ polyhedra (Fig. 5). The sheet-to-sheet bonding *via* $Ca(H_2O)_4O_2$ octahedra take place through the arsenate group, whereas the hydrogenarsenate groups bond the copper polyhedra only. Also, one oxygen atom belonging to the H_2O groups (Table 5) is located between the sheets (Fig. 4).

Bond-valence analysis and hydrogen bonding; the structural formula of ondrušite

A bond-valence analysis of the ondrušite structure was performed on the basis of the parameters taken from Brown & Altermatt (1985) and Brown (2002) using the routine DIST included in the JANA2006 software (Petříček *et al.* 2006), with additional calculations performed in the VESTA software (Momma & Izumi 2008). The bond-valence sums deduced from the analysis are displayed in Table 5. The assignment of a particular valence-state is consistent with the results of the bond-valence analysis in general. Few sums deserve further comment. The bond-valence sum in the case of the Ca5 atom is slightly higher than might be expected. The bond-length corresponding to the bond-valence parameters input (R = 1.967, B = 0.37; taken from Brown & Altermatt 1985) should be 2.37 Å, whereas the average bond-length in the Ca5 octahedron is 2.30 Å. This small deviation is expressed by the quadratic elongation 1.0077. Even if we were not able to locate additional hydrogen atoms in addition to that of the AsO$_3$OH group, few bond-valence sums justify the involvement of additional atoms of oxygen in the

TABLE 5. POSITIONS AND BOND-VALENCE SUMS OF ATOMS IN ONDRUŠITE

site		x	y	z	U_{eq}	ΣBV
As1	2i	−0.0872(2)	0.38181(17)	0.37135(14)	0.0231(4)	5.03(7)
As2	2i	0.4154(2)	−0.01774(17)	0.34141(14)	0.0223(4)	4.97(7)
Cu1	2i	0.3891(3)	0.3667(2)	0.44060(17)	0.0252(5)	2.00(3)
Cu2	2i	0.8936(3)	−0.0745(2)	0.40596(17)	0.0246(4)	2.13(3)
Ca	1d	0.5000	0.0000	0.0000	0.0331(10)	2.42(4)
O1	2i	−0.0049(18)	0.5165(13)	0.2547(11)	0.035(3)	1.35(3)
O2	2i	−0.3284(15)	0.4351(12)	0.4541(10)	0.026(2)	2.05(4)
O3	2i	0.0900(15)	0.3278(12)	0.4668(9)	0.022(2)	1.95(5)
O4	2i	−0.1284(16)	0.2035(13)	0.3026(10)	0.028(2)	2.08(5)
O5	2i	0.3935(16)	−0.0917(12)	0.2040(9)	0.027(2)	1.69(4)
O6	2i	0.1837(15)	−0.0374(12)	0.4371(9)	0.023(2)	2.11(4)
O7	2i	0.6061(17)	−0.1321(12)	0.4065(10)	0.030(2)	1.89(4)
O8	2i	0.4668(18)	0.1876(12)	0.3180(9)	0.027(2)	1.67(3)
OW1	2i	0.9805(18)	−0.1526(13)	0.2369(10)	0.032(2)	0.46(1)
OW2	2i	0.414(2)	0.5458(15)	0.2366(10)	0.042(3)	0.10(2)
OW3	2i	0.798(2)	0.102(2)	0.0484(13)	0.055(4)	0.42(2)
OW4	2i	0.320(3)	0.2481(17)	0.0667(14)	0.056(4)	0.39(2)
OW5	2i	0.233(2)	0.5439(17)	0.9337(13)	0.052(4)	0
H1	2i	−0.2687	0.2224	0.2785	0.050*	0.83(4)

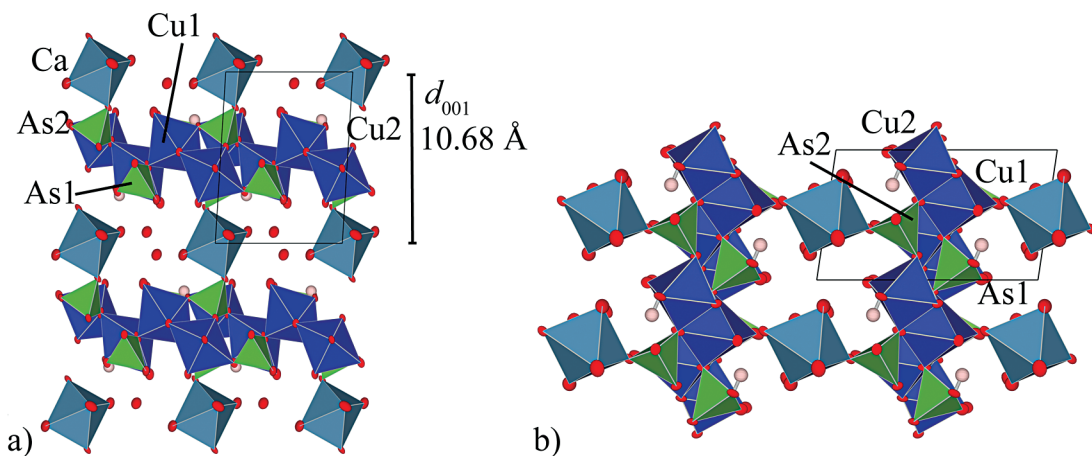ΣBV: the sum of bond valences. * The U_{eq} value was refined isotropically.

FIG. 4. The crystal structure of ondrušite viewed along **a** (a) and **b** (b). The green polyhedra are AsO_4 and AsO_3OH groups, the navy blue color represents CuO_6 octahedra, and a lighter blue color is chosen for the CaO_6 octahedra. Oxygen atoms are depicted as red thermal ellipsoids, the white spheres correspond to the hydrogen atom of the AsO_3OH group. The value of the basal spacing d_{001} is sketched in the left image.
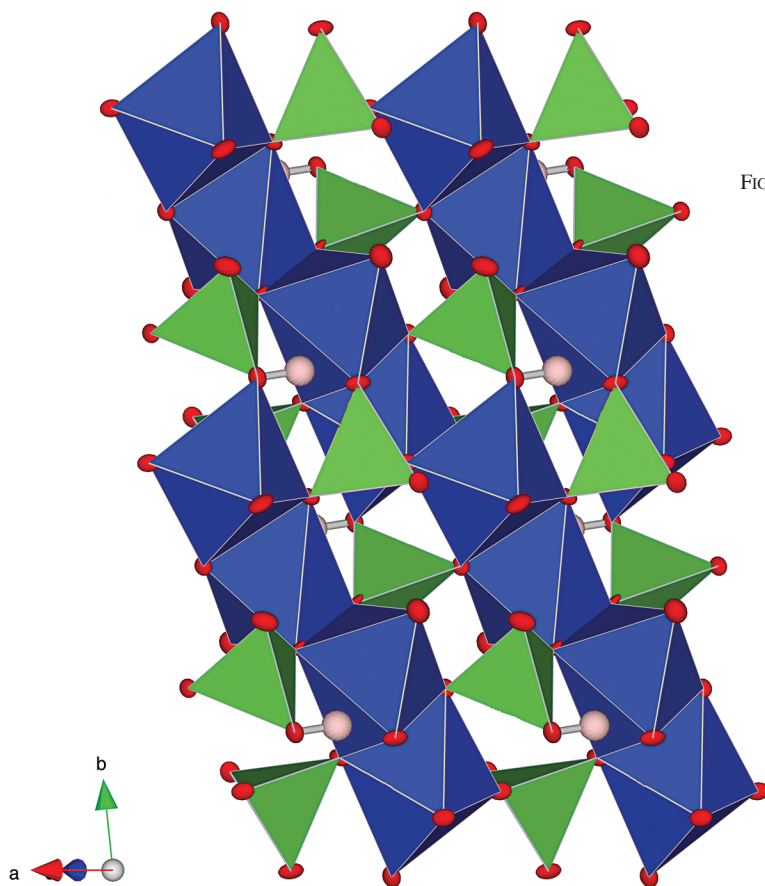

FIG. 5. A staircase sheet of edge-sharing CuO_6 polyhedra (blue) in the crystal structure of ondrušite. Shown in green are the AsO_4 and AsO_3OH groups, the oxygen atoms are shown in red, and the white spheres represent the hydrogen atoms. The structure is viewed along a general direction.

TABLE 6. ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN ONDRUŠITE

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As1	0.0158(7)	0.0168(7)	0.0373(9)	0.0003(5)	−0.0054(6)	−0.0046(5)
As2	0.0170(7)	0.0154(6)	0.0354(8)	−0.0004(5)	−0.0062(6)	−0.0042(5)
Cu1	0.0159(9)	0.0182(8)	0.0429(11)	−0.0005(6)	−0.0062(7)	−0.0087(7)
Cu2	0.0174(8)	0.0204(8)	0.0369(10)	0.0008(6)	−0.0059(7)	−0.0069(7)
Ca	0.029(2)	0.031(2)	0.039(3)	0.0013(18)	−0.0066(19)	−0.0034(18)
O1	0.036(7)	0.022(5)	0.043(6)	0.005(5)	−0.004(5)	−0.001(4)
O2	0.015(5)	0.021(5)	0.046(6)	−0.008(4)	−0.004(4)	−0.018(4)
O3	0.014(5)	0.020(5)	0.033(5)	0.000(4)	−0.006(4)	−0.001(4)
O4	0.020(5)	0.025(5)	0.041(6)	0.006(4)	−0.012(4)	−0.009(4)
O5	0.028(6)	0.024(5)	0.030(5)	0.009(4)	−0.011(4)	−0.015(4)
O6	0.020(5)	0.017(4)	0.030(5)	0.000(4)	0.002(4)	−0.006(4)
O7	0.024(5)	0.016(5)	0.050(7)	0.000(4)	−0.014(5)	0.005(4)
O8	0.037(6)	0.014(4)	0.028(5)	−0.001(4)	−0.004(4)	−0.007(4)
OW1	0.035(6)	0.021(5)	0.044(6)	−0.012(5)	−0.006(5)	−0.005(4)
OW2	0.037(7)	0.033(6)	0.058(8)	0.004(5)	−0.020(6)	−0.005(5)
OW3	0.053(9)	0.067(10)	0.050(8)	−0.011(7)	−0.009(7)	−0.021(7)
OW4	0.076(11)	0.035(7)	0.057(8)	0.008(7)	−0.016(8)	0.003(6)
OW5	0.062(9)	0.043(7)	0.057(8)	0.000(7)	−0.030(7)	0.002(6)

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) FOR ONDRUŠITE

As1-O1	1.654(12)	Cu2-O3		2.370(11)
As1-O2	1.708(13)	Cu2-O4		2.419(12)
As1-O3	1.665(12)	Cu2-O6		1.959(11)
As1-O4	1.716(12)	Cu2-O6		1.999(11)
<As1-O>	1.69	Cu2-O7		1.945(12)
		Cu2-O1W		1.965(12)
As2-O5	1.673(11)	<Cu2-Φ>		2.11
As2-O6	1.695(11)			
As2-O7	1.679(11)	Ca-O3W	×2	2.29(2)
As2-O8	1.697(11)	Ca-O4W	×2	2.32(2)
<As2-O>	1.69	Ca-O5	×2	2.300(11)
		<Ca-Φ>		2.30
Cu1-O2	1.999(11)			
Cu1-O2	1.973(11)	O4-H		0.975(11)
Cu1-O3	1.952(11)	O8-H		1.73(1)
Cu1-O7	2.413(11)			
Cu1-O8	2.006(11)			
Cu1-O2W	2.538(14)			
<Cu1-Φ>	2.15			

hydrogen bonding network. The bond-valence sum for the oxygen atom O11 is lower, but not so low as to assign this atom to be an oxygen atom of an OH⁻ group.

Considering the results of the crystal-structure refinement and bond-valence analysis, the structural formula of ondrušite is $^{[6]}Ca(H_2O)_8{}^{[4+2]}Cu_4[(AsO_4)_2(AsO_3OH)_2](H_2O)_2$.

FURTHER DISCUSSION

Ondrušite is a new mineral species of the lindackerite group. A comparison of its chemical and physical properties with other members of this group is given in Table 8. Besides the chemical composition, the strongest diffraction maximum in the powder pattern of ondrušite, corresponding to the d_{001} value of 10.67 Å, is distinctly different from the values of 10.18–10.20 Å observed in the other Cu-rich members of this group.

Other differences were discovered during crystallographic investigations of ondrušite. In the crystal structure of ondrušite, both copper atoms are coordinated so as to define a tetragonal bipyramid, whereas in the crystal structure of lindackerite-group phases (Hybler *et al.* 2003), one of the copper atoms exhibits a square pyramidal coordination. But the most important difference lies in the type of the *Me* atom in interlayer and its coordination. In the crystal structure of ondrušite, the calcium atom is coordinated octahedrally *via* two symmetrically independent H_2O groups (Table 7) and one oxygen atom belonging to the As2 tetrahedron. The coordination of the *Me* cation in the crystal structure of lindackerite takes place *via* eight H_2O molecules, in four independent positions with reduced occupancies, forming two interpenetrating $MeO_2(H_2O)_4$ octahedra, with the corners consisting of oxygen atoms forming part of the As tetrahedra. The significant difference between bond lengths in Ca–O (2.3 Å) and Cu–O (1.98 Å) (axial or bridging bonds) is 0.32 Å, hence comparable (0.47 Å) with the above-mentioned differences between the strongest diffraction maxima in the powder-diffraction patterns of the phases discussed here. The coordination arrangement found in the structure of ondrušite is the same as described by Graeser *et al.* (1989) for geigerite, ideally $Mn_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2(H_2O)_2$, an analogue of the isostructural chudobaite $(Mg,Zn)_5(H_2O)_8(AsO_3OH)_2(AsO_4)_2(H_2O)_2$ (Dorner & Weber 1976, Graeser *et al.* 1989). On the basis of the coordination arrangement, there is a possibility to distinguish two series within the lindackerite group. The first is ondrušite – geigerite – chudobaite, and the second one is lindackerite –

TABLE 8. COMPARISON OF ONDRUŠITE WITH
LINDACKERITE-GROUP MINERAL SPECIES

ondrušite – geigerite – chudobaite series

	ondrušite Jáchymov this paper	geigerite Fallota Graeser et al. (1989)	chudobaite Tsumeb Strunz (1960), Dorner & Weber (1976)
M^*	Cu	Mn	Mg
Me^* (ideal)	Ca	Mn	Zn?
Me^* (meas.)	$Ca_{0.92}Co_{0.01}Pb_{0.01}$	Mn	Zn?
n^*	10	10	10
system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a	6.432(1)	6.770(1)	6.616
b	7.986(1)	7.944(1)	7.797
c	10.827(1)	10.691(1)	10.485
α	85.75(1)	81.85(1)	82.12
β	81.25(1)	80.97(1)	80.53
γ	85.04(1)	84.20(1)	84.23
V	546.6(1)	560.3(1)	526.8
Z	1	1	1
selected	10.671/100	10.45/100	10.163/100
lines in	7.934/7	7.85/13	7.694/30
X-ray	3.970/10	3.92/9	4.058/40
powder	3.648/11	3.837/9	3.746/50
pattern	3.438/3	3.507/21	3.440/80
	3.286/10	3.340/20	3.273/80

lindackerite – pradetite – veselovskýite series

	lindackerite Jáchymov Sarp & Dominik (1995)	lindackerite Jáchymov Hybler et al. (2003)	pradetite Cap Garonne Sarp & Dominik (1995), Burke et al. (2007)	veselovskýite Jáchymov Sejkora et al. (2010a)
M^*	Cu	Cu	Cu	Cu
Me^* (ideal)	Cu	Cu	Co	Zn
Me^* (meas.)	$Cu_{0.78}Co_{0.18}Ni_{0.07}$	$Cu_{0.79}$-$Cu_{0.95}$	$Co_{0.46}Cu_{0.18}$	$Zn_{0.43}Cu_{0.24}Co_{0.13}$
n^*	10	9	10	9
crystal	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ or $P1$	$P\bar{1}$	$P\bar{1}$ or $P1$	$P\bar{1}$
a	6.453(2)	6.415-6.440	6.434(5)	6.4022(4)
b	8.035(2)	8.048-8.065	8.059(5)	8.0118(4)
c	10.368(4)	10.332-10.411	10.399(8)	10.3665(4)
α	86.17(3)	85.41-85.44	85.70(6)	85.491(3)
β	79.60(3)	79.38-79.50	79.41(7)	79.377(4)
γ	84.83(3)	84.65-84.71	84.87(7)	84.704(5)
V	525.9(2)	521.2-528.1	526.9(7)	519.34(4)
Z	1	1	1	1
selected	10.2/100	-	10.2/100	10.185/100
lines in	8.02/70	-	8.01/60	7.974/15
X-ray	4.001/40	-	4.001/50	3.987/16
powder	3.668/60	-	3.667/60	3.637/15
pattern	3.399/25	-	3.404/35	3.395/24
	3.264/30	-	3.258/30	3.238/16

M^*, Me^*, n^*: symbols in the formula: $MeM_4(AsO_4)_2(AsO_3OH)_2 \cdot nH_2O$ (M^* = $M1$ and $M2$ position; Me^* = $M3$ position in the crystal structure).

pradetite – veselovskýite (Table 8). Ondrušite with a structural formula of $Ca(H_2O)_8Cu_4[(AsO_4)_2(AsO_3OH)_2](H_2O)_2$ thus represents the Ca–Cu-dominant member of the ondrušite – geigerite – chudobaite subgroup of the lindackerite group.

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