

НОВЫЕ МИНЕРАЛЫ

LEDNEVITE, $\text{Cu}[\text{PO}_3(\text{OH})]\cdot\text{H}_2\text{O}$, A NEW MINERAL FROM MURZINSKOE Au DEPOSIT, ALTAI KRAI, RUSSIA

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Lednevite, ideally $\text{Cu}[\text{PO}_3(\text{OH})]\cdot\text{H}_2\text{O}$, is a new mineral discovered at the 255 m level of the Murzinskoe Au deposit, Krasnoshchyokovskiy District, Altai Krai, Western Siberia, Russia. It forms spherulites up to 0.1 mm in diameter, composed of very thin fibers and grouped in aggregates up to 1.5 mm across. Lednevite overgrows philipsburgite crystals on a matrix of epidote-andradite skarn and quartz and associates with malachite, chrysocolla, kaolinite, goethite and P-bearing cornubite. The new mineral is transparent, has sky blue color, very pale blue streak and vitreous lustre. Cleavage is not observed. The Mohs' hardness is ~ 3 . $D_{\text{meas}} = 3.18(2) \text{ g cm}^{-3}$, $D_{\text{calc}} = 3.196 \text{ g cm}^{-3}$. The chemical composition of lednevite is (electron microprobe, wt.%; H_2O by stoichiometry): CuO 40.20, ZnO 3.92, P_2O_5 36.29, As_2O_5 4.80, H_2O 14.98, total 100.15. The empirical formula calculated on the basis of 3 H and 5 O *apfu* is $(\text{Cu}_{0.91}\text{Zn}_{0.09})_{\Sigma 1.00}[(\text{P}_{0.92}\text{As}_{0.08})_{\Sigma 1.00}\text{O}_3(\text{OH})]\cdot\text{H}_2\text{O}$. The crystal structure was refined by the Rietveld method to $R_p = 0.0042$, $R_{wp} = 0.0061$, $R_{obs} = 0.0354$. Lednevite is monoclinic, space group $P2_1/a$, with $a = 8.6459(6)$, $b = 6.3951(4)$, $c = 6.8210(5) \text{ Å}$, $\beta = 93.866(2)^\circ$, $V = 376.28(4) \text{ Å}^3$ and $Z = 4$. The strongest lines of the powder X-ray diffraction pattern [d , Å (I , %) (hkl)] are: 5.135 (100) (110), 4.648 (33) (011), 3.241 (28) (21-1), 3.095 (49) (211), 2.891 (27) (11-2), 2.775 (53) (112), 2.568 (29) (220). The new mineral is isotypic to the synthetic $\text{CuHPO}_4\cdot\text{H}_2\text{O}$. Some optical and spectroscopic data, which could not be obtained on natural sample, were obtained from the synthesized material. The crystal structure of the synthetic analogue of lednevite was solved from single-crystal X-ray diffraction data and refined to $R_1 = 0.0173$ for 1159 independent reflections with $I > 2\sigma(I)$. All positions of H atoms were determined. Lednevite is named for Vladimir Sergeevich Lednev, amateur mineralogist from Barnaul (Altai Krai) who collected the sample with the new mineral.

Keywords: lednevite, new mineral, synthetic analogue, chemistry, crystal structure, Murzinskoe Au deposit, Altai Krai

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INTRODUCTION

Over the last eight years, our team has systematically investigated the mineralogy of the actively exploited Murzinskoe gold deposit located in the Krasnoshchyokovskiy District of the Altai Krai in Western Siberia (51°35'44" N, 82°36'34" E). During this period, more than 180 mineral species were identified by instrumental methods including >80 minerals of secondary origin (various sulfides, oxides, carbonates, nitrates, sulfates, chromates, arsenates, phosphates, vanadates and silicates). This article describes a new secondary mineral ledneveite (pronounced: led nə vait; Cyrillic: ледневит), a copper hydrophosphate monohydrate with the ideal formula $\text{Cu}[\text{PO}_3(\text{OH})]\cdot\text{H}_2\text{O}$.

Ledneveite is named for Vladimir Sergeevich Lednev (born April 5th, 1968), an amateur mineralogist from Barnaul (the capital of Altai Krai, Russia), teacher of mineralogy and geology in the center of local history and tourism "Altai" and co-founder of the local mineralogical museum "Mir Kamnya" ("World of Stones"). All the minerals from Murzinskoe deposit studied by our team, including the new mineral, described here were collected by him during numerous field trips to the locality in 2016–2023.

The new mineral, its name and symbol (Led) were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA No. 2023-094). The holotype specimen is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the catalogue number 98432.

OCCURRENCE AND GENERAL APPEARANCE

Murzinskoe Au deposit in Altai Krai has a long history. It has been discovered in 1740 and was periodically mined for copper, gold and silver in 1740–1850, 1910–1914 and 1935–1950 (Gusev, 2014). In the middle of XXth century, the workings ceased due to unprofitability and the deposit was mothballed. In 1987, the geological exploration resumed. Since 1993, the deposit is mined for gold by the prospector company "Poisk" as an open pit.

Geologically, Murzinskoe deposit is confined to the Main Fault of the Akimovskaya zone, along which Lower Devonian sandstones, siltstones and limestones come into contact (Fig. 1). A rubbly-ocherous argillaceous weathering crust, which dates back to the Cretaceous-Paleogene time, runs along the fault. The formation of the deposit took place in three main stages: 1) formation of skarns; 2) formation of hydrothermal quartz veins; 3) formation of the oxidation zone. Average gold grade is 3.6–3.8 g/t in skarns, 3.9–4.9 g/t in quartz veins and 2–3 g/t in the oxidation zone. The main rocks of the deposit are garnet-diopside and garnet-epidote skarns, as well as epidosites forming lenticular bodies. Skarns and epidosites are intersected by quartz veins with ore mineralization represented mainly by chalcopyrite, chalcocite, covellite, less often sphalerite, pyrite, galena and gold. The oxidation zone is well developed; its depth reaches 130 m. The main minerals here are chrysocolla, malachite, azurite and goethite (Babich et al., 2006; Murzin et al., 2015; Gusev and Tabakaeva, 2017; Gusev and Gusev, 2018).

The sample containing ledneveite was collected by Vladimir S. Lednev in March 2023 at the 255 m level of the deposit (Fig. 2). The new mineral is extremely rare. Despite big collecting efforts made in order to find additional samples with ledneveite, the original specimen remains the only one known to date.

Ledneveite forms spherulites up to 0.1 mm in diameter, composed of very thin fibers and grouped in aggregates up to 1.5 mm across. They overgrow philipsburgite crystals on a matrix of epidote-andradite skarn and quartz (Figs. 3 and 4). Some grains of ledneveite are intimately intergrown with minor amounts of spertiniite and kaolinite. Other associated minerals in the holotype sample are malachite, chrysocolla, goethite and P-bearing cornubite.

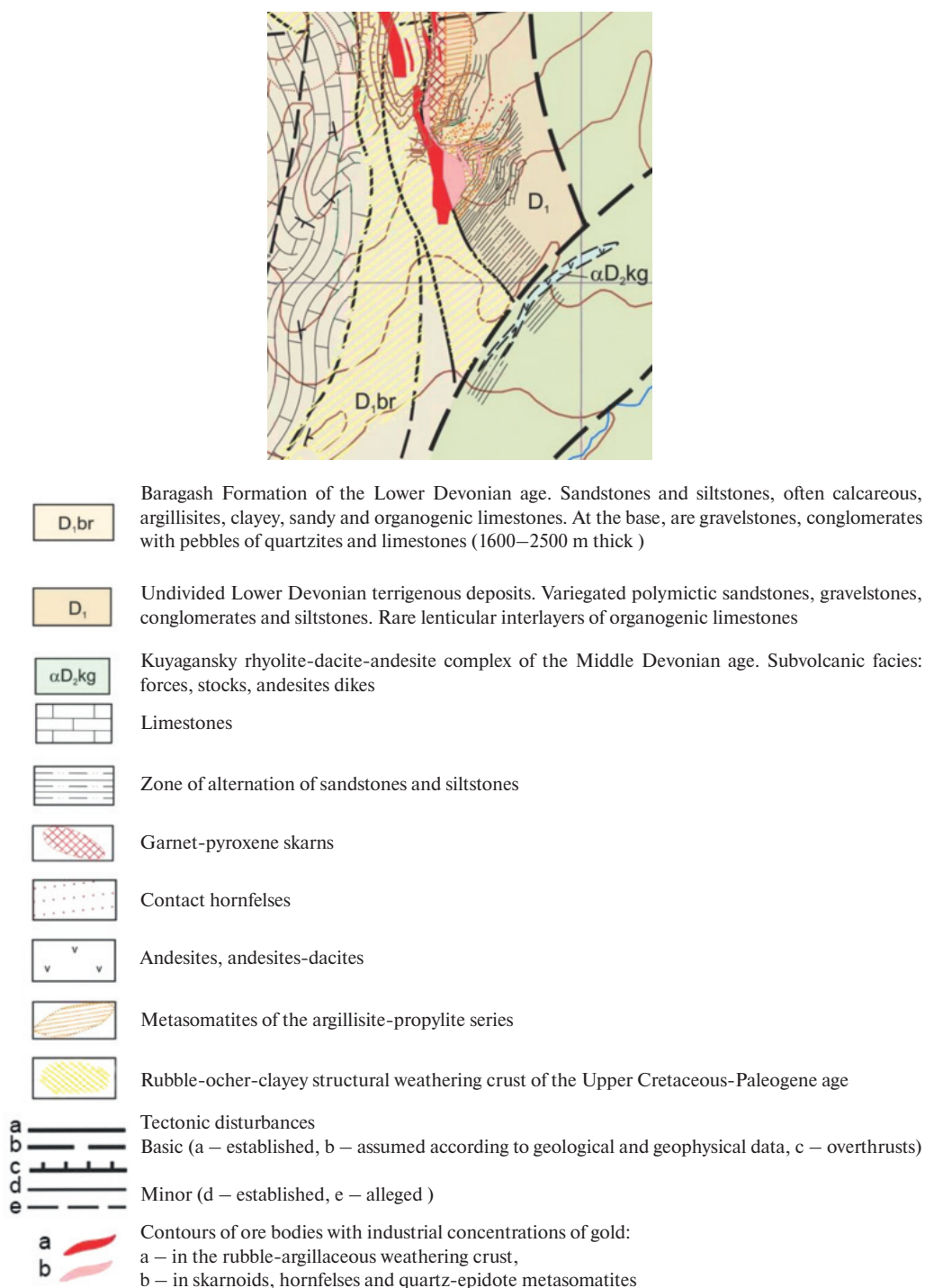


Fig. 1. Geological map of the Murzinskoe deposit (after Murzin et al. (2015) with changes). FOV: 1.4×1.7 km.

Рис. 1. Геологическая схема Мурзинского месторождения (по данным статьи: Мурзин и др. (2015), с изменениями). Поле зрения: 1.4×1.7 км.



Fig. 2. Open pit of the Murzinskoe Au deposit, 255 m level. May 2023. Photo by Vladimir S. Lednev.

Рис. 2. Карьер Мурзинского золоторудного месторождения, горизонт 255 м. Май 2023 г. Фото: В.С. Леднев.

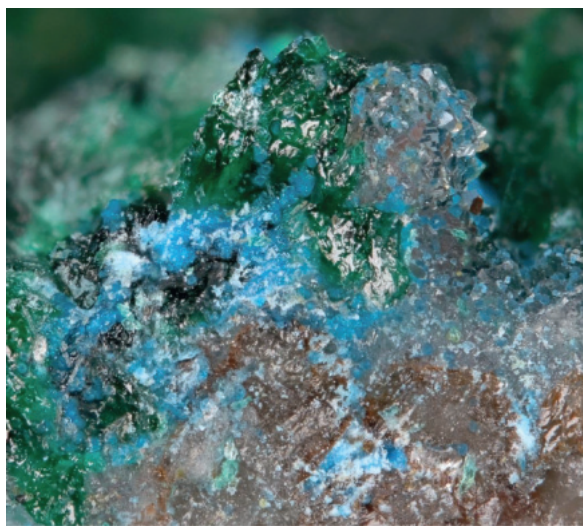


Fig. 3. Lednevit (sky-blue) on philipsburgite (green) with quartz. FOV: 3.3×3.7 mm. Photo by Maria D. Milshina.

Рис. 3. Ледневит (небесно-голубой) на филипсбергите (зеленый) с кварцем. Поле зрения: 3.3×3.7 мм. Фото: М.Д. Мильшина.

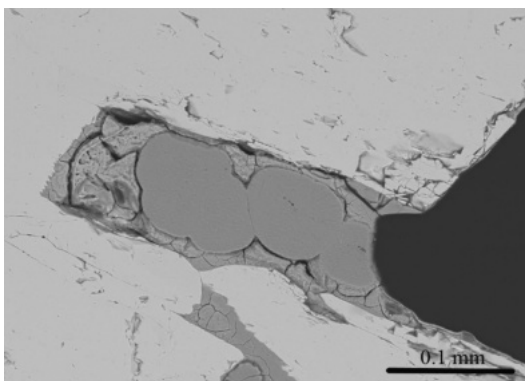


Fig. 4. Lednevite spherical aggregates (grey) on philipsburgite (light grey). Polished section. SEM (BSE) image.

Рис. 4. Сферолиты ледневита (серые) в филипсбургите (светло-серый). Аншлиф. Фото в отраженных электронах.

Lednevite belongs to so-called “philipsburgite association”. The association got its name due to the find of first-class specimens of philipsburgite as spherules and rosettes up to 1.5 cm in diameter composed of bright-green elongate crystals. Other minerals of the above association (but not in direct contact with lednevite) include both primary (baryte, bornite, chalcopryrite, cuprite, fluorapatite, hematite, kutnohorite, titanite) and supergene minerals (members of mixite group [agardite-(Ce), agardite-(Y), zálesřite], conichalcite, cornwallite, Cu-rich coronadite, covellite, djurleite, duftite, goldhillite, langite, mottramite, nontronite, posnjakite, pseudomalachite). All of them were collected at the 255 m level of the deposit. Lednevite is probably one of the latest minerals of the association.

SYNTHETIC ANALOGUE OF LEDNEVITE

Since lednevite occurs in spherical aggregates composed of tiny fibres, which complicated exact determination of some properties, its synthetic analogue was laboratory grown in order to complete the missing data. The synthesis was inspired by the paper of Boudjada (1980). A fragment (2 g) of pure natural malachite was placed into the beaker and poured by 30 ml of 10 M orthophosphoric acid. Malachite slowly dissolved by releasing of CO_2 and the colour of the solution changed to sky blue. The beaker with the solution was kept at 40 °C for several days to increase the concentration of the solution by evaporating of water. Crystallization of synthetic analogue of lednevite began when volume of the initial solution was reduced to *circa* 1/10. Synthetic material, in a form of bright sky-blue spherical aggregates composed of acicular crystals, was removed from the solution and washed in deionised water. The compliance of synthesized material with lednevite was confirmed by chemical analysis (Table 1) and powder X-ray diffraction (PXRD, see Table 2). As a result, some optical properties and spectroscopic data missing for the natural lednevite were obtained on this material. Also, despite the fact that the structural model of synthetic $\text{CuHPO}_4\cdot\text{H}_2\text{O}$ was already given by Boudjada (1980), we were able to collect a much better quality single-crystal X-ray diffraction data on our synthesized material and, in particular, to determine all positions of H sites.

PHYSICAL PROPERTIES AND OPTICAL DATA

Lednevite is transparent, has a sky-blue color, very pale blue streak and vitreous lustre. It is brittle with splintery fracture. Cleavage and parting are not observed. Lednevite does not fluoresce under ultraviolet light. Mohs' hardness based on scratch tests is ~3. The density

Table 1. Chemical composition of lednevite and its synthetic analogue

Таблица 1. Химический состав ледневита и его синтетического аналога

Constituent	Lednevite			Synthetic analogue			Reference Material
	Wt %	Range	Stand. Dev.	Wt %	Range	Stand. Dev.	
CuO	40.20	39.88–40.49	0.25	45.22	44.68–45.71	0.10	lammerite
ZnO	3.92	3.59–4.37	0.28	-			gahnite
P ₂ O ₅	36.29	35.96–36.65	0.26	40.35	39.64–40.82	0.12	fluorapatite
As ₂ O ₅	4.80	4.55–5.15	0.19	-			lammerite
H ₂ O*	14.94			15.36			
Total	100.15			100.93			

*By stoichiometry (H = 3 *apfu*)

measured by flotation in Clerici solution is 3.18(2) g cm⁻³ while the density value calculated using the empirical formula and the unit-cell parameters refined from PXRD data is equal to 3.196 g cm⁻³.

Due to the spherical character of the mineral, optical properties of lednevite were only partly determined. The mineral is biaxial, with $\alpha' = 1.638(4)$ and $\gamma' = 1.652(4)$ (589 nm). The pleochroism is barely noticeable, from colorless (*Z'*) to very pale bluish (*X'*). The observation in transmitted plane polarized light shows that lednevite spherules are composed of very thin fibrous individuals up to 25 × 1 μm. The character of extinction in spherules shows that the individual fibers in it are twisted (relative to elongation). No individual grains suitable for conoscopic observations and the determination of β were found. Thus, no conclusions could be made regarding the optical sign and 2*V* angle on natural material.

The missing optical properties of lednevite were obtained on its synthetic analogue. They are as follows: biaxial (+), $\alpha = 1.6422(5)$, $\beta = 1.6451(4)$, $\gamma = 1.6766(4)$ (589 nm). 2*V* measured is equal to 36(2)°. 2*V* calculated from refractive indices by equation of Wright (1951) is 34°. Dispersion is strong, *r* > *v*. Orientation: *X*∧*c* ~ -5°, *Y*∧*a* ~ +10°, *Z* = *b*. The synthetic analogue of lednevite is pale blue in transmitted plane polarized light, non-pleochroic. Tiny acicular crystals show an inclined extinction (~ 10°).

SPECTROSCOPIC STUDIES

Infrared spectroscopy

Due to scarcity of available natural material, the infrared spectrum (IR) was obtained from synthetic analogue of lednevite. The sample of the latter was powdered, mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm⁻¹. A total of 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectrum of synthetic analogue of lednevite (Fig. 5) is typical for hydrous acid phosphates (Chukanov, 2014; Chukanov and Chervonnyi, 2016; Chukanov and Vigasina, 2020). It contains bands of O–H stretching vibrations of H₂O molecules and POH groups (in the ranges 3200–3400 and 2200–2900 cm⁻¹, respectively), H–O–H and P–O–H bending modes (at 1637 and 907+927 cm⁻¹, respectively), P–O stretching vibrations (in the range 990–1300 cm⁻¹) and O–P–O bending vibrations (in the range 520–630 cm⁻¹). In particular, the bands in the range 2200–2440 cm⁻¹ may be due to translational vibrations of proton H⁺ belonging to the virtual predissociation state of the acid phosphate group, O₃P–O⋯H (Chukanov, 2014).

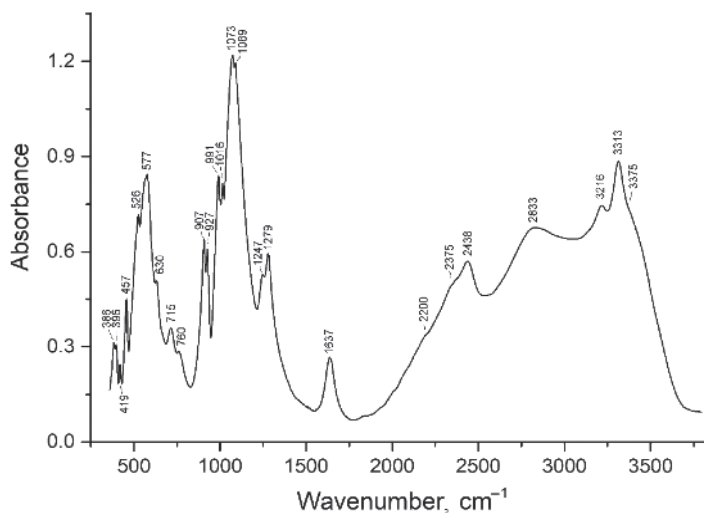


Fig. 5. The infrared spectrum of the synthetic analogue of lednevite.

Рис. 5. Инфракрасный спектр синтетического аналога ледневита.

According to the correlation $\nu_{\text{O-H}} (\text{cm}^{-1}) = 3592 - 304 \cdot 10^9 \cdot \exp[-d(D\cdots A)/0.1321]$ (Libowitzky, 1999), the bands at 3375, 3313, 3216, 2833 and 2438 cm^{-1} correspond to the $D\cdots A$ distances in hydrogen bonds of 2.78, 2.75, 2.71, 2.62 and 2.56 Å, respectively. These values are close to the $D\cdots A$ distances of 2.8018, 2.7019 and 2.5897 Å determined as a result of the crystal structure refinement (see below). The presence of three bands in the range 3200–3400 cm^{-1} (instead two bands expected from the structural data) is due to the Fermi resonance splitting (resonance with the first overtone of the H–O–H bending mode). The shoulders at 2375 and 2200 cm^{-1} may correspond to additional predissociation states of the acid phosphate group occurring in minor concentrations. Relatively broad bands at 715 and 760 cm^{-1} may be due to H_2O librations. Bands in the range 450–630 cm^{-1} correspond to bending (partly mixed with Cu–O stretching, involving short Cu–O bonds below 1.97 Å) modes of the PO_4 tetrahedron. Peaks below 420 cm^{-1} are related to soft lattice modes involving translations and librations of the HPO_4^{2-} anionic group as a whole.

Raman spectroscopy

The Raman spectra of lednevite (Fig. 6a) and its synthetic analogue (Figs. 6b,c) were obtained by means of a Horiba Labram HR Evolution spectrometer. This dispersive, edge-filter-based system is equipped with an Olympus BX 41 optical microscope, a diffraction grating with 600 grooves per millimetre, and a Peltier-cooled, Si-based charge-coupled device (CCD) detector. The Raman signal was excited by 532 nm laser. The nominal laser beam energy of 50 mW was attenuated to 10% using a neutral density filter to avoid the thermal damage of the analysed area. Raman signal was collected in the range of 50–4000 cm^{-1} with a 100× objective and the system being operated in the confocal mode, beam diameter was $\sim 2.6 \mu\text{m}$ and the axial resolution $\sim 5 \mu\text{m}$. Time acquisition was 60 s per spectral window, 5 accumulations and 7 spectral windows were applied to cover the 50–4000 cm^{-1} range. Wavenumber calibration was done using the Rayleigh line and low-pressure Ne-lamp emissions. The wavenumber accuracy was $\sim 0.5 \text{ cm}^{-1}$, and the spectral resolution was $\sim 2 \text{ cm}^{-1}$. Band fitting was done after appropriate background correction, assuming combined Lorentzian-Gaussian band shapes using Voigt function (*PeakFit*; Jandel Scientific Software).

Table 2. PXRD data (d in Å) and unit cell parameters of lednevite and its synthetic analogue $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$
Таблица 2. Порошковые рентгенограммы (d в Å) и параметры элементарных ячеек ледневита и его синтетического аналога $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$

Lednevite				Synthetic CuHPO ₄ ·H ₂ O							hkl
				Our data				Boudjada, 1980 ICDD 01-083-1857			
<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{calc} [*]	<i>I</i> _{calc} ^{**}	<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{calc} [*]	<i>I</i> _{calc} ^{**}	<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{calc} ^{***}	
5.135	100	5.137	100	5.104	100	5.106	100	5.09	100	5.10	1 1 0
4.648	33	4.660	25	4.642	9	4.640	21	4.62	3.7	4.64	0 1 1
4.321	2	4.313	5	4.306	8	4.301	4	4.29	1.8	4.29	2 0 0
4.179	6	4.182	6	4.170	2	4.171	6	4.16	1.2	4.17	1 1 -1
		4.023	1	3.998	1	4.001	2				1 1 1
3.555	11	3.576	1	3.559	1	3.560	<1	3.51	0.7	3.52	2 1 0
3.241	28	3.241	9	3.235	2	3.235	8	3.23	3.0	3.23	2 1 -1
3.095	49	3.095	17	3.079	8	3.079	16	3.08	0.7	3.08	2 1 1
3.002	20	3.004	4			2.997	4	2.995	0.6	2.995	0 1 2
		2.998	4	2.977	5	2.977	3	2.975	3.0	2.976	1 2 0
2.891	27	2.891	22	2.890	8	2.889	22	2.885	3.0	2.885	1 1 -2
						2.875	<1	2.875	1.2	2.875	0 2 1
2.775	53	2.786	23	2.775	13	2.775	26	2.773	4.6	2.773	1 1 2
		2.764	24			2.768	28	2.763	5.3	2.763	2 0 -2
		2.720	1			2.753	<1	2.752	1.4	2.752	1 2 -1
2.622	7	2.623	11	2.612	15	2.613	13	2.608	10.8	2.608	3 1 0
		2.588	4	2.576	1	2.577	4				2 0 2
2.568	29	2.569	27	2.554	31	2.553	32	2.552	71.0	2.551	2 2 0
2.537	6	2.537	6			2.537	6	2.533	1.6	2.533	2 1 -2
2.435	4	2.436	5	2.425	3	2.425	5	2.424	2.8	2.423	2 2 -1
2.399	5	2.399	4	2.388	2	2.388	5	2.384	1.4	2.385	2 1 2
		2.398	<1			2.387	<1			2.383	3 1 1
2.373	2	2.371	1	2.357	2	2.357	2	2.355	1.4	2.355	2 2 1
2.330	9	2.330	12	2.320	3	2.320	12	2.319	2.3	2.319	0 2 2
		2.157	2	2.149	2	2.150	2	2.146	0.9	2.146	4 0 0
2.141	9	2.142	5	2.140	2	2.142	6	2.138	1.2	2.138	3 1 -2
		2.138	2	2.127	1	2.127	2	2.125	2.1	1.125	3 2 0
2.091	3	2.091	6	2.086	1	2.086	6	2.084	1.4	2.084	2 2 -2
2.076	5	2.070	<1			2.062	<1	2.058	1.2	2.060	3 2 -1
		2.069	3	2.054	3	2.054	3			2.054	1 3 0
		2.045	<1			2.039	<1	2.037	1.2	2.037	1 1 3
		2.044	1	2.035	1	2.037	1	2.033	1.1	2.033	4 1 0

Таблица 2. Окончание

Lednevice				Synthetic CuHPO ₄ ·H ₂ O							<i>hkl</i>
				Our data				Boudjada, 1980 ICDD 01-083-1857			
<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{calc} *	<i>I</i> _{calc} **	<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{calc} *	<i>I</i> _{calc} **	<i>d</i> _{obs}	<i>I</i> _{obs}	<i>d</i> _{calc***}	
2.017	12	2.018	7	2.000	3	2.008	7			2.005	3 1 2
		2.017	<1					2.005	1.6		4 0 1
		2.012	3			2.001	5			1.999	2 2 2
		2.011	1			2.000	<1	1.999	1.8	1.997	3 2 1
1.994	2	1.993	1			1.989	1			1.985	4 1 -1
1.955	3	1.954	3			1.948	3	1.985	0.7	1.945	2 0 3
		1.853	1	1.848	1	1.849	1	1.945	0.6	1.847	3 2 -2
		1.850	1			1.845	1			1.843	0 2 3
		1.826	2	1.814	1	1.813	1	1.846	0.7		2 3 1
1.782	8	1.788	1	1.780	4	1.780	2				4 2 0
		1.781	4			1.772	4				1 3 -2
1.756	4	1.756	5	1.745	1	1.745	5				1 3 2
1.710	13	1.712	7	1.702	8	1.702	9				3 3 0
1.668	3	1.666	4	1.660	3	1.660	4				5 1 0
1.638	4	1.635	5	1.635	3	1.635	5				1 1 -4
1.621	6	1.621	7	1.618	2	1.618	7				4 2 -2
1.598	2	1.594	<1	1.587	2	1.587	3				0 4 0
		1.572	2			1.560	2				1 4 0
1.547	10	1.548	7	1.540	3	1.539	7				4 2 2
1.505	6	1.506	4	1.496	1	1.496	5				3 3 2
1.446	4	1.445	4	1.445	1	1.444	4				2 2 -4
1.391	8	1.388	1	1.388	2	1.384	2				3 1 4
1.342	2	1.341	2	1.335	7	1.335	2				5 3 0
1.307	4	1.311	2	1.306	2	1.306	2				6 2 0
		1.304	2			1.299	2				1 3 4
Unit cell parameters, monoclinic lattice, Sp. Gr. <i>P</i> ₂ / <i>a</i>											
8.6459(6)				8.624(3)		8.6245(1)		8.63(6)		<i>a</i> , Å	
6.3951(4)				6.345(2)		6.3455(1)		6.35(3)		<i>b</i> , Å	
6.8210(5)				6.820(3)		6.8191(1)		6.82(5)		<i>c</i> , Å	
93.866(2)				94.22(3)		94.186(1)		94.14(6)		β, °	
376.28(4)				372.15(9)		372.19(1)		371.0		<i>V</i> , Å ³	

* For the calculated patterns, reflections with intensities < 2 are given only for comparison with the observed or reported in (Boudjada, 1980).

** For the unit-cell parameters calculated from structural data.

*** *I*_{calc} are not reported.

Strongest reflections are given in boldtype.

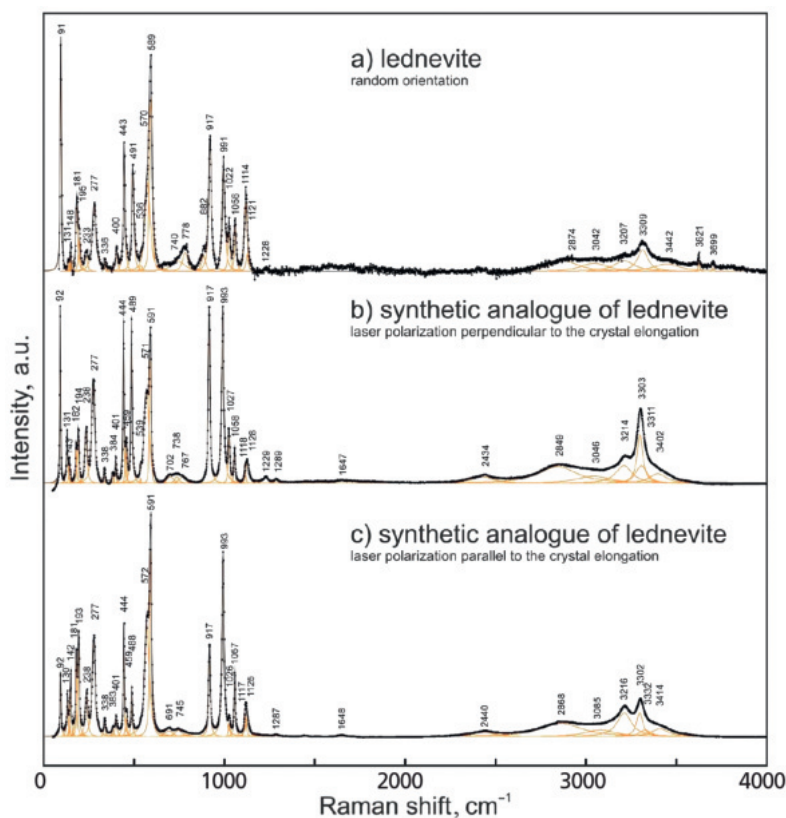


Fig. 6. The Raman spectra of **a)** lednevite, and **b), c)** its synthetic analogue excited by 532 nm laser in the 50–4000 cm^{-1} region. The measured spectrum is shown by dots. The curve matching to dots is a result of spectral fit as a sum of individual Voigt peaks shown below the curve. Spectra **b)** and **c)** were collected with the laser polarization perpendicular and parallel to the crystal elongation, respectively.

Рис. 6. КР-спектры **a)** ледневита и **b), c)** его синтетического аналога, полученные при возбуждающем лазерном излучении с длиной волны 532 нм в диапазоне 50–4000 см^{-1} . Измеренный спектр показан точками. Аппроксимирующая его кривая, полученная как суперпозиция индивидуальных фойгтовских пиков, показана под экспериментальной кривой. Спектры **(b)** и **(c)** получены при лазерном излучении, поляризованном перпендикулярно и параллельно удлинению кристалла соответственно.

Raman spectra of lednevite and its synthetic analogue are very similar, however, natural material shows significantly stronger luminescence. It is not seen in the Fig. 6, as it shows background-subtracted spectra, however it resulted in lower signal-to-noise ratio in the natural sample. Intensities of individual Raman bands can mutually differ among the 3 recorded spectra, such variation is caused by different crystal orientation with respect to the laser polarization (cf. Figs. 6b,c).

The assignment of Raman bands was performed on natural sample and is as follows. Raman scattering in the range 3000–3400 cm^{-1} and the band at 2874 cm^{-1} correspond to O–H stretching vibrations of H_2O molecules and acid POH groups, respectively. A weak band at 1647–1648 cm^{-1} in the Raman spectrum of the synthetic analogue of lednevite corresponds to bending vibrations of H_2O molecules. The weak peak at 2434–2440 cm^{-1} (more distinct in the Raman spectrum of the synthetic analogue of lednevite) may be due to translational

vibrations of proton H^+ belonging to the virtual predissociation state of the acid phosphate group $\text{O}_3\text{PO}\cdots\text{H}$, (Chukanov, 2014; Chukanov and Vidasina, 2020). Raman scattering in the ranges 880–1120 and 400–590 cm^{-1} corresponds to stretching (partly mixed with P–O–H bending) and bending (partly mixed with Cu–O stretching, involving short Cu–O bonds below 1.97 Å) modes of the PO_4 tetrahedron, respectively. The relatively broad band at 778 cm^{-1} may be due to librations of H_2O molecule forming strong hydrogen bonds. Peaks below 350 cm^{-1} are related to soft lattice modes involving translations and librations of the HPO_4^{2-} anionic group as a whole. The bands were assigned using reference data on Raman spectra of acid phosphates and minerals with distorted Cu-centered polyhedra (Chukanov and Vidasina, 2020). Very narrow and weak bands at 3699 and 3621 cm^{-1} in lednevite are due to admixed kaolinite (Wang et al., 2015).

CHEMICAL DATA

Chemical analyses (8 spots for lednevite and 5 spots for its synthetic analogue) were carried out with a Cameca SX-100 electron microprobe instrument (WDS mode, 15 kV, 10 nA, 4 μm beam diameter). The amount of H_2O was not determined directly due to the scarcity of pure material and was calculated by stoichiometry on the basis of H = 3 and O = 5 atoms per formula unit (*apfu*). The crystal structure, IR and Raman spectroscopy data confirm the presence of acid OH groups and H_2O molecules and the absence of B–O, C–O and N–O bonds in the mineral. Contents of other elements with atomic numbers higher than that of carbon are below detection limits. Analytical data are given in Table 1.

The empirical formulas calculated on the basis of 3 H and 5 O *apfu* are $(\text{Cu}_{0.91}\text{Zn}_{0.09})_{\Sigma 1.00}[(\text{P}_{0.92}\text{As}_{0.08})_{\Sigma 1.00}\text{O}_3(\text{OH})]\cdot\text{H}_2\text{O}$ (lednevite) and $\text{Cu}_{1.00}[\text{P}_{1.00}\text{O}_3(\text{OH})]\cdot\text{H}_2\text{O}$ (synthetic analogue). The ideal formula of the new mineral is $\text{Cu}[\text{PO}_3(\text{OH})]\cdot\text{H}_2\text{O}$, which requires (wt.%) CuO 44.80, P_2O_5 39.98, H_2O 15.22, total 100.

The Gladstone–Dale compatibility index $(1 - K_p/K_c)$ calculated for lednevite using its empirical formula, unit-cell parameters determined from PXRD data and assuming an average index of refraction (1.645) is 0.013 rated as superior (Mandarino, 1981). The Gladstone–Dale compatibility for the synthetic analogue of lednevite is –0.028 (excellent).

Both lednevite and its synthetic analogue do not react with water but slowly dissolve in dilute HCl, H_2SO_4 and HNO_3 at room temperature.

X-RAY DIFFRACTION DATA AND CRYSTAL STRUCTURE

Single-crystal X-ray diffraction (SCXRD) studies of lednevite could not be carried out due to the absence of suitable single crystals. However, PXRD data (Table 2) undoubtedly show that the mineral is a natural analogue of the synthetic compound $\text{CuHPO}_4\cdot\text{H}_2\text{O}$ (Boudjada, 1980). PXRD data for lednevite were obtained from a sample containing spertiniite impurity (13.9 wt %). The pattern was recorded in Debye–Scherrer geometry by means of a Rigaku RAXIS Rapid II diffractometer equipped with curved (cylindrical) imaging plate detector ($r = 127.4$ mm; angular resolution is $0.045\ 2\theta = \text{pixel size } 0.1$ mm), using $\text{CoK}\alpha$ radiation ($\lambda = 1.79021$ Å) generated by a rotating anode (40 kV, 15 mA) with microfocus optics (VariMAX); exposure time was set to 10 min. The image-to-profile data processing was performed using *Osc2xrd* software (Britvin et al., 2017).

PXRD data for the synthetic analogue of lednevite (Table 2) were obtained using a Panalytical X'Pert PRO MPD diffractometer operated with $\text{CoK}\alpha$ radiation ($\lambda = 1.79021$ Å), Fe filter and 1-D RTMS (X'Celerator) detector in the reflection geometry. Pulverised sample was placed on a zero-background Si wafer. Step size: $0.033^\circ\ 2\theta$, time per step: 160 s, angular range: $5\text{--}100^\circ\ 2\theta$, total scan duration: 3665 s.

Unit-cell parameters calculated from these PXRD data using *UnitCell* software (Holland and Redfern, 1997) are reported in Table 2.

SCXRD data for the synthetic analogue of lednevite were collected using a Supernova Rigaku-Oxford Diffraction diffractometer equipped with a micro-source MoK α radiation ($\lambda = 0.71073$ Å; 50 kV, 0.8 mA) and a Pilatus 200K Dectris detector. The data were collected by 3424 frames over 35 runs; the exposure time was 60 second per frame. The data were processed by *CrysAlisPro* 1.171.41.123a software (Rigaku Oxford Diffraction). Crystal data, data collection information and structure refinement details for the synthetic analogue of lednevite are given in Table 3.

Supplementary crystallographic data were deposited in the Inorganic Crystal Structure Database (ICSD) and can be obtained by quoting the CSD 2324814 and 2324815 (for lednevite and its synthetic analog, respectively) *via* www.ccdc.cam.ac.uk/structures.

The crystal structure of lednevite was refined on a powder sample using the Rietveld method (Fig. 7). The Rietveld structure analysis were carried out using JANA2006 program package (Petříček et al., 2006). The structure model of synthetic CuHPO₄·H₂O (Boudjada, 1980) was taken as the starting one. The profiles were modeled using a pseudo-Voigt function. The structure was refined in isotropic approximation of atomic displacements, the values of U_{iso} for O atoms except Ow (oxygen atom of the water molecule) were restricted to be equal. The cation-anion interatomic distances were softly restricted nearby the values of the starting structure model. Impurity of As was added to the P site to obtain the correspondence

Table 3. SCXRD data collection information and structure refinement parameters for the synthetic analogue of lednevite

Таблица 3. Данные монокристалльного рентгенодифракционного эксперимента и параметры уточнения кристаллической структуры синтетического аналога ледневита

Formula	Cu[PO ₃ (OH)]·H ₂ O
Formula weight	177.53
Temperature, K	293(2)
Radiation and wavelength, Å	MoK α ; 0.71073
Crystal system, space group, Z	Monoclinic, $P2_1/a$, 4
Unit cell dimensions, Å/°	$a = 8.62452(13)$ $b = 6.34546(9)$ $\beta = 94.1859(13)$ $c = 6.81905(9)$
V , Å ³	372.188(9)
Absorption coefficient μ , mm ⁻¹	6.184
F_{000}	348
Crystal size, mm	$0.05 \times 0.06 \times 0.12$
Diffractometer	Rigaku SuperNova with Pilatus 200K
θ range for data collection, ° / Collection mode	2.995 – 31.839 / full sphere
Index ranges	$-12 \leq h \leq 12$, $-9 \leq k \leq 9$, $-10 \leq l \leq 9$
Reflections collected	22264
Independent reflections	1236 ($R_{\text{int}} = 0.0235$)
Independent reflections with $I > 2\sigma(I)$	1159
Data reduction	CrysAlisPro 1.171.41.123a (Rigaku OD, 2022)
Absorption correction	Multi-scan
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	80
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0173$, $wR_2^* = 0.0518$
R indices (all data)	$R_1 = 0.0188$, $wR_2^* = 0.0526$
GoF	1.088
Largest diff. peak and hole, e/Å ³	0.50 and -0.77

* $w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.3565P]$; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

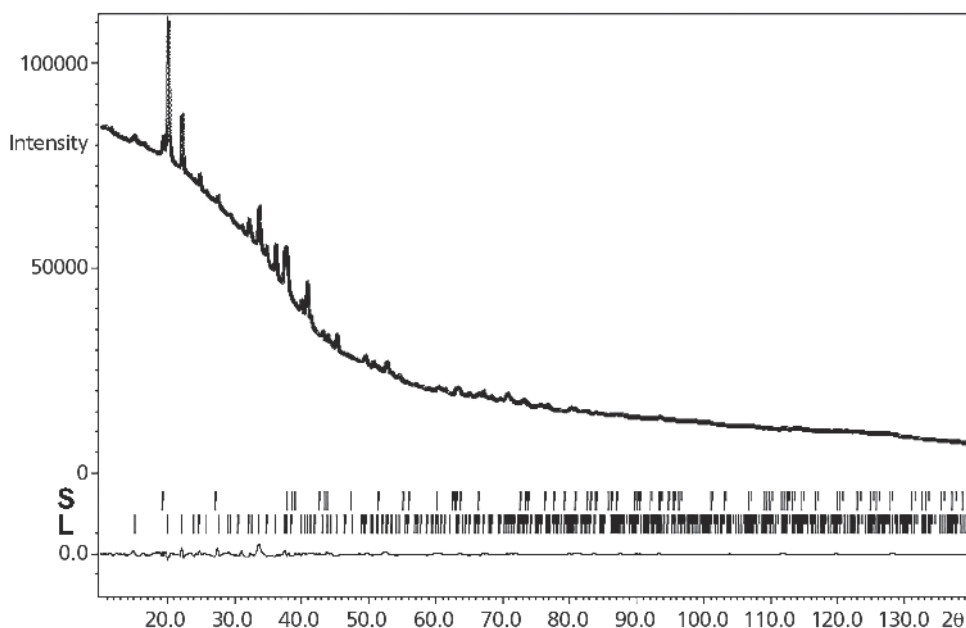


Fig. 7. Observed and calculated PXRD patterns of the sample containing lednevite (L) and spertiniite (S). The solid line corresponds to calculated data, the crosses correspond to the observed pattern, vertical bars mark all possible Bragg reflections. The upper row refers to spertiniite and the lower one to lednevite. The difference between the observed and calculated patterns is shown at the bottom.

Рис. 7. Экспериментальная (крестики) и расчетная (сплошная линия) рентгенограммы двухфазного образца, состоящего из ледневита (L) и спертиниита (S). Вертикальные штрихи показывают местоположение рефлексов расчетной порошковой диаграммы (верхняя часть для спертиниита, нижняя для ледневита), а кривая в нижней части рисунка — разностная кривая интенсивностей экспериментальной и расчетной рентгенограмм.

with chemical composition data. The structural analysis was complemented by addition of spertiniite, $\text{Cu}(\text{OH})_2$, as an impurity, to account for a few diffraction peaks in the powder pattern. The refined ratio of the two minerals in the powder mixture is 86.08(17) wt% for lednevite and 13.9(2) wt% for spertiniite. The final agreement factors are: $R_p = 0.0042$, $R_{wp} = 0.0061$, $R_{obs} = 0.0354$.

The crystal structure of the synthetic analogue of lednevite was solved from SCXRD data and refined with the use of SHELX software package (Sheldrick, 2015) to $R_1 = 0.0173$ for 1159 independent reflections with $I > 2\sigma(I)$. All positions of H atoms were determined through the difference Fourier synthesis and O-H distances were softly restrained to be 0.85(1) Å. Coordinates and displacement parameters of atoms for lednevite and its synthetic analogue are given in Table 4 and selected interatomic distances including the system of hydrogen bonds for the synthetic analogue of lednevite in Table 5. Lednevite is isotypic with synthetic $\text{CuHPO}_4\cdot\text{H}_2\text{O}$ (Boudjada, 1980; our data). Its crystal structure is based on the heteropolyhedral pseudoframework built by PO_4 tetrahedra and $\text{CuO}_4(\text{H}_2\text{O})_2$ octahedra distorted by the Jahn-Teller effect (Figs 8 a, b). Cu-centred octahedra share edges to form chains along *c* axis. Neighbouring chains are connected *via* (P,As) $\text{O}_3(\text{OH})$ tetrahedra forming the heteropolyhedral pseudoframework. Minor As impurity was added to the P site in natural sample according to chemical composition data. The system of H-bonds is shown at Fig. 9.

Table 4. Atom coordinates, displacement parameters (U_{iso} (lednevite)/ U_{eq} (synthetic analogue except H atoms), in $\text{\AA}^2$) of atoms and bond valence sums (BVS) calculated using the parameters from Gagné and Hawthorne (2015) for lednevite (the first line of each row) and its synthetic analogue (the second line of each row). Parameters for hydrogen bonding for the synthetic analogue of lednevite were taken from (Ferraris and Ivaldi, 1988).

Таблица 4. Координаты атомов, параметры их тепловых смещений (U_{iso} (ледневит)/ U_{eq} (синтетический аналог ледневита, кроме атомов H), $\text{\AA}^2$) и результаты расчета баланса валентных усилий (BVS) (параметры взяты из Gagné and Hawthorne (2015)) для ледневита (каждая первая строка позиции) и его синтетического аналога (каждая вторая строка позиции). Для расчета вклада водородных связей использованы параметры из Ferraris and Ivaldi, 1988.

Site	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$	BVS	H-bonding	BVS
Cu1	0	0	0	0.0197(10)	1.96		
	0	0	0	0.00914(9)	2.02		
Cu2	0	0	0.5	0.0167(11)	2.04		
	0	0	0.5	0.01016(9)	2.02		
P*	0.2340(4)	0.2982(3)	0.2222(4)	0.0047(8)	5.08		
	0.23489(4)	0.29935(5)	0.22482(5)	0.00762(9)	4.98		
O1	0.1346(3)	0.1002(7)	0.22348(13)	0.0051(10)	1.93		
	0.13389(11)	0.10228(16)	0.22265(14)	0.01035(19)	1.91		
O2	0.3481(5)	0.2890(6)	0.0597(8)	0.0051(10)	1.78		
	0.34092(12)	0.29706(16)	0.05496(15)	0.01126(19)	1.76	+0.29(O_{OH})	2.05
O3	0.3102(4)	0.3467(8)	0.4257(5)	0.0051(10)	1.81		
	0.32210(12)	0.32164(17)	0.42552(15)	0.0128(2)	1.78	+0.18(O_{w})	1.96
O_{OH}	0.1187(4)	0.4904(6)	0.1851(7)	0.0051(10)	1.13		
	0.12219(14)	0.49440(16)	0.19211(18)	0.0153(2)	1.12	−0.29(O_2) +0.23(O_{w})	1.06
H	–	–	–	–			
	0.144(3)	0.590(3)	0.113(3)	0.032(7)			
O_{w}	0.4279(6)	0.7409(4)	0.32514(16)	0.0062**	0.43		
	0.41232(13)	0.73305(18)	0.32302(17)	0.0152(2)	0.43	−0.23(O_{OH}) −0.18(O_3)	0.02
H_a	–	–	–	–			
	0.477(2)	0.831(3)	0.316(4)	0.031(6)			
H_b	–	–	–	–			
	0.3262(17)	0.785(4)	0.351(4)	0.040(8)			

* $\text{P} = \text{P}_{0.92}\text{As}_{0.08}$ for lednevite and $\text{P}_{1.00}$ for its synthetic analogue.

** Fixed during the refinement.

DISCUSSION

Lednevite does not have any structural analogues or relatives among minerals. It contains the same combination of species-defining elements (Cu, P, H, O) as five other mineral species: cornetite $\text{Cu}_3(\text{PO}_4)(\text{OH})_3$, libethenite $\text{Cu}_2(\text{PO}_4)(\text{OH})$ and three polymorphs – ludjibaite, pseudomalachite and reichenbachite with the same formula $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$, however, all of these minerals do not contain molecular water, have completely different stoichiometry and crystal structures. Another mineral, geminite, $\text{Cu}(\text{AsO}_3\text{OH}) \cdot \text{H}_2\text{O}$, despite the similarity of its chemical formula with lednevite, is not the As-analogue of the latter. Both minerals possess different symmetries and crystal structures.

Most likely, crystallization of lednevite in the supergene zone of the Murzinskoe deposit took place in several stages. The oxidation of pyrite and other primary sulfides yielded the formation of sulfuric acid that leached fluorapatite from the host rocks leading to the forma-

Table 5. Selected interatomic distances (Å) in the structure of lednevite and its synthetic analogue
Таблица 5. Выборочные межатомные расстояния (Å) в кристаллической структуре ледневита и его синтетического аналога

Lednevite		Synthetic analogue				
Cu1 – O2	1.945(4) · 2	1.9381(10) · 2				
Cu1 – O1	1.962(2) · 2	1.9504(9) · 2				
Cu1 – Ow	2.805(2) · 2	2.8024(12) · 2				
Cu2 – O3	1.949(4) · 2	1.9440(10) · 2				
Cu2 – Ow	2.021(3) · 2	2.0204(11) · 2				
Cu2 – O1	2.370(2) · 2	2.3770(10) · 2				
P – O3	1.528(4)	1.5193(10)				
P – O1	1.531(5)	1.5234(10)				
P – O2	1.534(6)	1.5273(10)				
P – O _{OH}	1.592(5)	1.5794(11)				
		H-bonding				
		<i>D</i> –H··· <i>A</i>	<i>d</i> <i>D</i> –H, Å	<i>d</i> H··· <i>A</i> , Å	<i>d</i> <i>D</i> ··· <i>A</i> , Å	∠ <i>D</i> –H··· <i>A</i> , °
		O _{OH} –H···O2	0.839(10)	1.757(11)	2.5897(15)	171(3)
		OwHa···O _{OH}	0.841(9)	1.912(13)	2.7019(16)	156(2)
		Ow–Hb···O3	0.847(10)	2.072(18)	2.8018(15)	144(3)

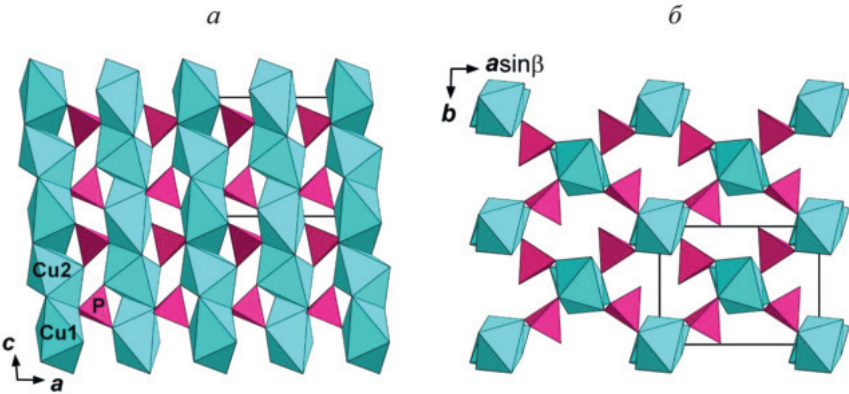


Fig. 8. The crystal structure of lednevite projected along *b* axis (a) and *c* axis (b). The unit cell is outlined.
Рис. 8. Кристаллическая структура ледневита в проекции вдоль оси *b* (a) и *c* (b). Показана элементарная ячейка.

tion of orthophosphoric acid. The latter, in its turn, reacted with malachite. Consequently, the formation of lednevite probably followed the same scheme as the synthesis of its analogue described above. It's interesting to note the coexistence of P and As in the chemical composition of secondary copper minerals of the “philipsburgite association”. Besides a minor admixture of As in lednevite, we recorded a solid solution series between pseudomalachite and its As-analogue cornwallite, P admixture in copper arsenates (conichalcite, cornubite, goldhillite, members of mixite group) and, finally, an abundance of the only ordered

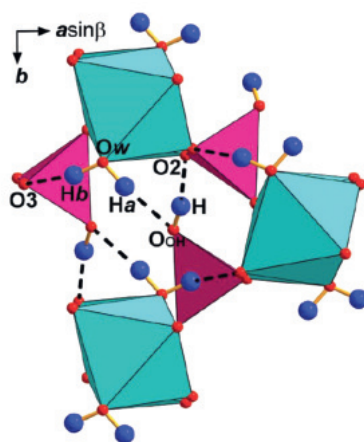


Fig. 9. H-bonding system in the crystal structure of the synthetic analogue of lednevitte.

Рис. 9. Система водородных связей в структуре синтетического аналога ледневита.

phosphate-arsenate found at the deposit that gave its name to the studied association – philipsburgite. While fluorapatite is the obvious source of phosphorous, there are no recorded arsenopyrite and arsenides at the deposit that could justify the presence of As. We believe that As can be sourced from pyrite and fahlores (tennantites and tetrahedrites of different chemical compositions) that are rather common here.

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REFERENCES

- Babich V.V., Zadorozhnyi M.V., Gaskov I.V., Akimtsev V.A., Naumov E.A. Murzinskoe deposit – an example of new type of gold mining in Northern Altai. In: *Actual problems of ore formation and metallogeny*. Novosibirsk: Geo, **2006**. P. 26–28 (in Russian).
- Boudjada A. Structure cristalline de l' orthophosphate monoacide de cuivre monohydrate $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$. *Mater. Res. Bull.* **1980**. Vol. 15. P. 1083–1090 (in French).
- Britvin S.N., Dolivo-Dobrovolsky D.V., Krzhizhanovskaya M.G. Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zapiski RMO (Proc. Russian Miner. Soc.)*. **2017**. Vol. 146(3). P. 104–107 (in Russian).
- Chukanov N.V. Infrared spectra of mineral species: Extended library. Springer-Verlag GmbH, Dordrecht–Heidelberg–New York–London, **2014**. 1716 pp. DOI: 10.1007/978-94-007-7128-4.
- Chukanov N.V., Chervonnyi A.D. Infrared Spectroscopy of Minerals and Related Compounds. Springer: Cham–Heidelberg–Dordrecht–New York–London, **2006**. 1109 p.
- Chukanov N.V., Vidasina M.F. Vibrational (Infrared and Raman) Spectra of Minerals and Related Compounds. Springer-Verlag GmbH, Dordrecht, **2020**. 1376 pp. DOI: 10.1007/978-3-030-26803-9.
- Ferraris G., Ivaldi G. Bond valence vs bond length in $\text{O} \cdots \text{O}$ hydrogen bonds. *Acta Crystallogr.* **1988**. Vol. B44. P. 341–344.
- Gagné O.C., Hawthorne F.C. Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Cryst.* **2015**. Vol. B71. P. 562–578.
- Gusev A.I. Geochemical peculiarities of gold ore mineralization of Murzinskoe ore field of Mountain Altai. *Advances in current natural sciences*. **2014**. Vol. 9. P. 96–100 (in Russian).

Gusev A.I., Gusev N.I. New data on substantial composition ores and minerals of Murzinskoe copper-gold deposit (Altai krai). *Bull. Altai Branch Russian Geogr. Soc.* **2018**. Vol. 4. P. 27–36 (in Russian).

Gusev A.I., Tabakaeva E.M. Magmatism and ore deposits of Murzinskoe gold ore field (Gorny Altai). *Bull. Tomsk Polytechnic University. Geo Assets Engineering.* **2017**. Vol. 328. P. 16–29 (in Russian).

Holland T.J.B., Redfern S.A.T. Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Miner. Mag.* **1997**. Vol. 61. P. 65–77.

Libowitzky E. (1999) Correlation of O–H stretching frequencies and O–H...O hydrogen bond lengths in minerals. *Monatsh. Chem.* **1999**. Vol. 130. P. 1047–1059.

Mandarino J.A. The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Canad. Miner.* **1981**. Vol. 41. P. 989–1002.

Murzin O.V., Alyamkin A.V., Ivanov V.N. Report on the results of prospecting and appraisal work within the Murzinskiy area, carried out in 2008–2013, with the calculation of gold reserves as of 1.01.2015. **2015**. 233 p. (in Russian).

Petríček V., Dušek M., Palatinus L. Jana2006. Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic, **2006**.

Rigaku Oxford Diffraction, *CrysAlisPro Software system, version 1.171.41.123a*. **2022**.

Sheldrick G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**. Vol. C71. P. 3–8.

Wang A., Freeman J.J., Jolliffe B.L. Understanding the Raman spectral features of phyllosilicates. *J. Raman Spectr.* **2015**. Vol. 46. P. 829–845.

Wright F.E. Computation of the optic axial angle from the three principal refractive indices. *Amer. Miner. J. Earth Planet. Mat.* **1951**. Vol. 36. P. 543–556.

Ледневит $\text{Cu}[\text{PO}_3(\text{OH})]\cdot\text{H}_2\text{O}$ – новый минерал из Мурзинского золоторудного месторождения, Алтайский край

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Ледневит, новый минерал с идеализированной формулой $\text{Cu}[\text{PO}_3(\text{OH})]\cdot\text{H}_2\text{O}$, найден на горизонте 255 м Мурзинского золоторудного месторождения (Краснощековский район, Алтайский край). Он образует тонковолокнистые сферолиты диаметром до 0.1 мм, сгруппированные в агрегаты до 1.5 мм. Ледневит обрастает кристаллы филипсбергита на эпидот-андрадитовом скарне с кварцем и ассоциирует со спертинитом, малахитом, хризоколой, каолинитом, гетитом и фосфорсодержащим корнубитом. Новый минерал прозрачный, имеет небесно-голубой цвет, бледно-голубую черту и стеклянный блеск. Спайность не наблюдается. Твердость по шкале Мооса около 3. Измеренная плотность равна 3.18(2) г/см³, вычисленная – 3.196 г/см³. Химический состав ледневита (по данным электронно-зондовых анализов, мас.%; содержание H_2O рассчитано по стехиометрии): CuO 40.20, ZnO 3.92, P_2O_5 36.29, As_2O_5 4.80, H_2O 14.98, сумма 100.15. Эмпирическая формула, рассчитанная на 3 атома Н и 5 атомов О: $(\text{Cu}_{0.91}\text{Zn}_{0.09})_{\Sigma 1.00}[(\text{P}_{0.92}\text{As}_{0.08})_{\Sigma 1.00}\text{O}_3(\text{OH})]\cdot\text{H}_2\text{O}$. Кристаллическая структура уточнена методом Ритвельда до $R_p = 0.0042$, $R_{wp} = 0.0061$, $R_{obs} = 0.0354$. Ледневит моноклинный, пространственная группа $P2_1/a$, параметры элементарной ячейки равны $a = 8.6459(6)$, $b = 6.3951(4)$, $c = 6.8210(5)$ Å, $\beta = 93.866(2)^\circ$, $V = 376.28(4)$ Å³ и $Z = 4$. Наиболее сильные линии порошковой рентгенограммы [d , Å (I , %) (hkl): 5.135 (100) (110), 4.648 (33) (011), 3.241 (28) (21–1), 3.095 (49) (211), 2.891 (27) (11–2), 2.775 (53) (112), 2.568 (29) (220)]. Ледневит изоструктурен

синтетической фазе $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$. Часть оптических и спектроскопических данных, которые невозможно было получить на природном образце, получены на синтетическом материале. Кристаллическая структура синтетического аналога ледневита решена на монокристалле и уточнена до $R_1 = 0.0173$ для 1159 независимых рефлексов с $I > 2\sigma(I)$. Определены все позиции атомов водорода. Ледневит назван в честь Владимира Сергеевича Леднева, минералога-любителя из Барнаула (Алтайский край), нашедшего образец с новым минералом.

Ключевые слова: ледневит, новый минерал, синтетический аналог, химический состав, кристаллическая структура, Мурзинское золоторудное месторождение, Алтайский край