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GEOLOGY

Zincolivenite $CuZn(AsO_4)(OH)$: A New Adamite-Group Mineral with Ordered Distribution of Cu and Zn

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A new mineral, zincolivenite $CuZn(AsO_4)(OH)$, the cation-ordered analogue of olivenite $Cu_2(AsO_4)(OH)$ and adamite $Zn_2(AsO_4)(OH)$, was found in samples from the Lavrion deposit, Attika Prefecture, Greece. The new mineral species and its name were approved by the Commission on New Minerals and Mineral Names of the Russian Mineralogical Society and accepted by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association on January 31, 2007.

The development of the Lavrion deposit commenced with the mining of lead and silver approximately 5000 years ago. Zincolivenite was identified in samples taken recently from the large dump accumulated in Kamariza mining area (hereafter, Kamariza dump) in the years 1864–1977 owing to resumption of mining in attic adits and processing of old wastes. Together with other wastes, barren rocks from the interconnected Hilarion, Serpieri, and Christiana mines were piled in the large Kamariza dump.

Zincolivenite forms prismatic crystals (up to 0.7×2 mm) and their radial intergrowths (Fig. 1) in association with jarosite, conichalcite, alumopharmacosiderite, arseniosiderite, and scorodite in the cavities of limonite ores.

The crystals of zincolivenite are composed of prismatic faces {120} (main form) and {101}. They are observed as green or greenish blue translucent crystals with vitreous luster, white streaks, and conchoidal fracture. The mineral is brittle (Mohs' hardness is 3.5). Cleavage is perfect on (010) and imperfect on (101). The density measured by hydrostatic weighing is 4.34(15) g/cm^3, which is close to 4.330 g/cm^3 calculated from empirical formula and unit cell parameters.

The IR spectrum of zincolivenite (Fig. 2) shows maximums with the following wavenumbers (cm^{-1}): 3480 (O–H stretching vibrations); 1070 (shoulder); weak 1020 band (P–O stretching vibrations); 865, 833, 819, 788 (As–O stretching vibrations); 529, 465 (stretching vibrations of Zn- and Cu-centered polyhedrons). The region of O–H stretching vibrations (3000–3800 cm^{-1}) contains a single band of the OH group coordinated by the CuCuZn atomic triplet. This is a distinctive feature of the studied sample as compared to intermediate members of the

Fig. 1. Aggregate of zincolivenite crystals from Lavrion.

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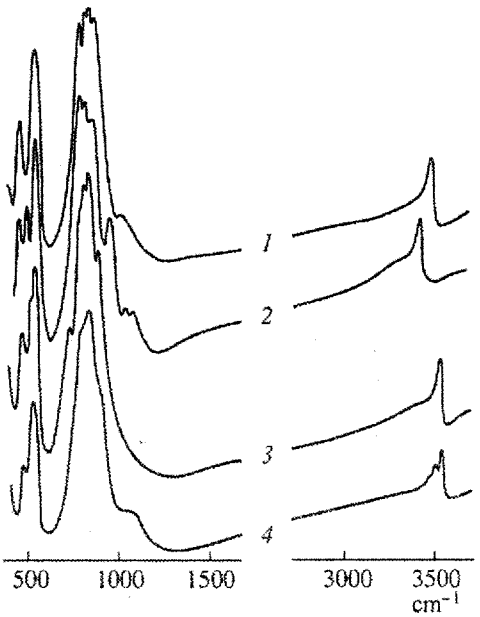

Fig. 2. (*1*) IR spectra of zincolivenite, (*2*) low-Zn olivenite from Tsumeb, Namibia, (*3*) pure Zn-adamite from the Ojuela Mine, Mexico, and (*4*) Cu-adamite from Dal'negorsk, Russia.

isomorphic olivinite–zincolivenite and zincolivenite–adamite series. In the O–H stretching vibration region indicated above (Figs. 2, 3), IR spectra of these members contain two or more bands with maximums within 3420–3430 cm^{-1} (CuCuCuOH), 3470–3480 cm^{-1} (CuCuZnOH), 3490–3500 cm^{-1} (CuZnZnOH), and 3530–3540 cm^{-1} (ZnZnZnOH). It should be mentioned that the bands were assigned with the consideration of data in [1]. The IR spectrum of zincolivenite lacks bands of fragments (CuCuCu)OH, (CuZnZn)OH, and (ZnZnZn)OH. This fact confirms a high degree of Cu and Zn ordering in the new mineral and indicates that its composition corresponds to atomic ratio Cu : Zn = 1 : 1. The same conclusion was made by Chisholm who examined the IR spectrum of synthetic solid solutions of $Cu_2(AsO_4)(OH)$–$Zn_2(AsO_4)(OH)$ series [1]. The IR spectrum of the new mineral lacks the absorption bands of water molecules (1500–1700 cm^{-1} region).

Zincolivenite is biaxial negative: $\alpha = 1.736(2)$, $\beta = 1.784(2)$, $\gamma = 1.788(2)$; $2\vartheta_{meas} = -30(5)°$, $2\vartheta_{calc} = -31.5°$. Dispersion is very strong ($r > v$). Orientation: $X = b$, $Y = a$, $Z = c$. Pleochroism is very weak: light bluish green along X, light blue along Y and Z. Parallel extinction.

The chemical composition of zincolivenite was studied by local microprobe analysis on a VEGA TS 5130MM digital electron scanning microscope (accelerating voltage 15.7 kV, beam current 0.5 nA). The water content was analyzed by the Alimarin method in an oxygen current at 1000°C using absorbing pipes filled with calcined $Mg(ClO_4)_2$. Based on five local microprobe analyses, the average content of major components is as follows, wt % (range is given in parentheses): CuO 26.33 (25.60–27.35), ZnO 29.62 (28.48–30.43), FeO 0.55 (0.42–0.67), As_2O_5 39.94 (39.55–40.42), P_2O_5 0.41 (0.29–0.56), H_2O 3.83 ± 0.30, total 100.68 wt % (no other elements with atomic number >8 were found).

The empirical formula of zincolivenite based on $(AsO_4,PO_4)_{1.00}$ taking into account charge balance is

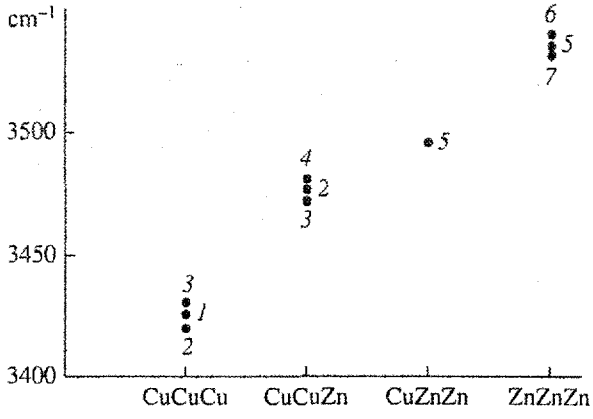

Fig. 3. Wavenumbers of bands of O–H stretching vibrations of hydroxyl groups coordinated by different cation triplets in the IR spectrum of (*1*) low-Zn olivenite from Tsumeb, Namibia, (2) Zn-bearing olivenite from Tsumeb, Namibia, (*3*) Zn-bearing olivenite from Novoveska Huta, Slovakia, (*4*) zincolivenite from Lavrion, Greece, (*5*) cation-disordered Cu-adamite from Lavrion, Greece, (*6*) low-Cu adamite from Lavrion, Greece, and (*7*) pure Zn-adamite from the Ojuela Mine, Mexico.

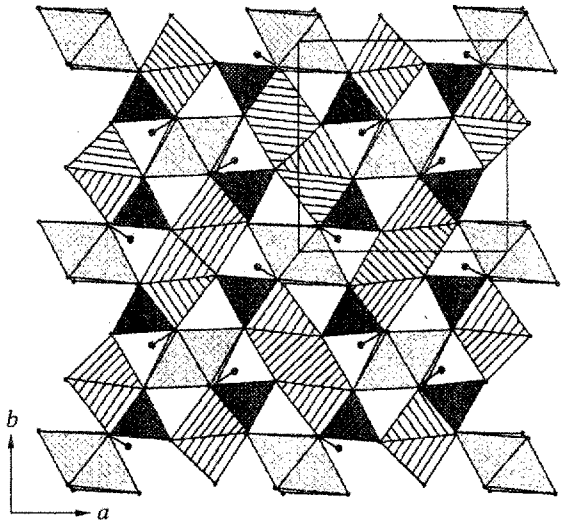

Fig. 4. Crystal structure of zincolivenite in the projection on plane (001). Cu octahedra are shown in gray, Zn bipyramides are hatched, and As tetrahedra are shown in black. Hydrogen atoms are designated by black spherules.

Table 1. Coordinates of atoms and parameters of thermal displacements in the zincolivenite structure

Atom	x	y	z	U^*_{equiv}
As1	0.24806(10)	0.23669(9)	0.5	0.01343(19)
Cu1	0	0	0.24940(15)	0.0174(3)
Zn1	0.12503(12)	0.36203(11)	0	0.0181(3)
O1	0.0798(3)	0.1304(3)	0.5	0.0151(6)
O2=OH	0.0997(3)	0.1202(3)	0	0.0159(6)
O3	0.3946(4)	0.1043(4)	0.5	0.0274(9)
O4	0.2610(3)	0.3528(3)	0.2729(3)	0.0232(5)
H	0.193(8)	0.067(11)	0	0.09(4)**

Note: (*) U_{equiv} values are calculated based on parameters of anisotropic atomic displacements.
(**) U_{iso}.

$Cu_{0.94}Zn_{1.03}Fe_{0.02}[(AsO_4)_{0.98}(PO_4)_{0.02}](OH)_{0.98}(H_2O)_{0.10}$. The idealized formula is $CuZn(AsO_4)(OH)$.

The correctness of determination of the chemical composition, refractive indexes, and density of zincolivenite is supported by good compatibility in terms of the Gladstone–Dale index: $1 - (K_p/K_C) = -0.037$ for measured density; $1 - (K_p/K_C) = -0.046$ for calculated density.

The 3D diffraction data were obtained for zincolivenite crystals ($0.10 \times 0.15 \times 0.15$ mm in size) on a Xcalibur S CCD single crystal diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å) at room temperature. The refined unit cell parameters for the orthorhombic structure are as follows: $a = 8.5839(15)$, $b = 8.5290(13)$, $c = 5.9696(9)$ Å, $V = 437.05(12)$ Å^3 ($Z = 4$). These values are close to the parameters of orthorhombic natural and

Table 2. Experimental and calculated X-ray powder diffraction pattern of zincolivenite

I_{exp}, %	d_{exp}, Å	I_{calc}, %	d_{calc}, Å	hkl
54	6.00	54	6.035	110
64	4.860	58, 52	4.893, 4.878	101, 011
42	4.219	51	4.240	111
40	3.805	33, 12	3.827, 3.807	210, 120
100	3.002	100	3.018	220
47	2.968	22	2.979	002
67	2.690	28, 16, 26	2.709, 2.692, 2.689	310, 221, 130
53	2.662	48	2.671	112
11	2.562	11, 19	2.577, 2.558	301, 031
94	2.456	56, 42	2.466, 2.451	311, 131
86	2.437	21, 46	2.446, 2.439	202, 022
18	2.340	21	2.351	212
3	2.148	4	2.144	400
3	2.124	0.2	2.120	222
3	1.997	2, 3	2.004, 1.996	312, 132
6	1.951	6, 8	1.962, 1.949	411, 141
3	1.928	4, 6	1.935, 1.934	103, 013
7	1.898	8	1.906	331
4	1.878	3	1.887	113
4	1.848	4, 4	1.855, 1.851	322, 232
2	1.810	2	1.813	241
8	1.729	11, 5	1.739, 1.730	402, 042
10	1.660	18, 4, 4	1.667, 1.667, 1.659	332, 150, 223
49	1.604	15, 39, 11	1.605, 1.604, 1.602	151, 242, 313
7	1.509	21	1.509	440
14	1.500	18	1.490	004
7	1.484	3	1.480	342
4	1.397	2, 5	1.397, 1.396	160, 252
12	1.342	10, 4	1.346, 1.345	442, 260
5	1.331	14	1.336	224
2	1.313	4, 1, 5	1.316, 1.312, 1.312	532, 261, 352
3	1.301	5, 5, 2, 2	1.305, 1.303, 1.302, 1.300	314, 134, 541, 451
6	1.278	6, 7, 5, 9	1.288, 1.283, 1.279, 1.277	602, 513, 062, 153

Table 3. Minerals and synthetic compounds with a general formula M_2XO_4OH structurally similar to adamite

Mineral	Formula	Sp. gr.	Source
Libethenite	Cu_2PO_4OH	*Pnnm*	[5]
Zincolibethenite	$CuZnPO_4OH$	*Pnnm*	[6]
Zn-rich zincolibethenite	$(Zn_{1.06}Cu_{0.94})(P_{0.98}As_{0.02})O_4OH$	*Pnnm*	[7]
Adamite	Zn_2AsO_4OH	*Pnnm*	[8]
Paradamite	Zn_2AsO_4OH	*P*–1	[8]
Eveite	Mn_2AsO_4OH	*Pnnm*	[9]
Sarkinite	Mn_2AsO_4OH	$P2_1/‡$	[10]
Tarbuttite	Zn_2PO_4OH	*P*–1	[11]
Synthetic	Zn_2PO_4OH	*Pnnm*	[12]
Synthetic	Co_2PO_4OH	*Pnnm*	[12]
Synthetic	Co_2AsO_4OH	*Pnnm*	[5]
Olivenite	Cu_2AsO_4OH	$P2_1/n$; *Pnnm*(?)	[13]
Zincolivenite	$CuZnAsO_4OH$	*Pnnm*	Present paper
Synthetic	$(Mg_{2-x}Ni_x)AsO_4OH$ ($x = 0$; $x = 0.45$)	*Pnnm*	[14]

synthetic adamite-type compounds with a general formula $M_2^{2+}XO_4OH$. The correction for absorption was made with consideration of the crystal shape (μ = 17.777 mm^{-1}).

The crystal structure of zincolivenite was defined independently based on direct methods in space group *Pnnm* using the SHELX-97 software package [2]. The structure was further refined with the JANA2000 software [3] with allowance made for anharmonicity of thermal vibrations of As, Cu, and Zn (third and fourth orders). Final $R_{hkl} = 0.0626$ for 2033 reflections with $I > 2\sigma(I)$. Table 1 shows coordinates of atoms and parameters of their thermal displacements in the zincolivenite structure.

The X-ray powder diffraction pattern of zincolivenite (Table 2) was obtained on a RIGAKU diffractometer using monochromatic Cu$K\alpha_1$ radiation. All reflections are indexed in space group *Pnnm* with unit cell parameters found for single crystal.

Adamite-type minerals with a general formula $M_2^{2+}XO_4OH$ (M = Cu, Zn, Mn; X = P, As) are structurally close to andalusite Al_2SiO_5 and often disposed to polymorphism (Table 3). A transition from monoclinic to orthorhombic symmetry is observed in the $(Cu_xZn_{1-x})_2AsO_4(OH)$ solid solution at an adamite content more than 20 mol %. A space group *Pnnm* was determined for Cu-adamite with composition $(Cu_{0.42}Zn_{0.58})_2AsO_4OH$ [4].

Figure 4 shows the crystal structure of zincolivenite. As with other minerals of the adamite group, its structure is mainly composed of a framework of $CuO_4(OH)_2$ octahedra, $ZnO_4(OH)$ trigonal bipyramids, and AsO_4 tetrahedra. Interatomic distances in coordination polyhedra of zincolivenite are close to standard values: As–O from 1.682(2) to 1.706(3) Å (average 1.690 Å); Zn–O from 1.998(4) to 2.074(3) Å (average 2.031 Å). Atoms of Cu form hexahedrons with distance ranging from 1.986(2) to 2.409(2) Å. Similar polyhedrons (4 + 2) are typical of Cu and related to the Jahn–Teller distortion, where two Cu–O(4) distances (2.409(20 Å)) are significantly higher than four other distances: two distances Cu–O(1) = 1.986(2) Å and two distances Cu–[O(2) = OH] = 2.000(2) Å.

Zincolivenite is an isostructural As-predominating analogue of the recently found Cu–Zn ordered zincolibethenite $CuZn(PO_4)(OH)$ of the phosphate series [6] (Table 4). This analogy is reflected in the name of the new mineral reported in this paper: cognation of zincolivenite with olivinite is similar to that of zincolibethenite with libethenite. The most important diagnostic characteristics of zincolivenite are its chemical composition, IR-spectrum (in the OH stretching vibration region), and optical constants (in particular, low 2ϑ value).

Taking into consideration specific features of isomorphism in these minerals, we suggest the following compositional ranges for the zincolivenite mineral species: $Cu_{0.5}Zn_{1.5}(AsO_4)(OH)$–$Cu_{1.5}Zn_{0.5}(AsO_4)(OH)$. In particular, the bright green intermediate zone in the studied zoned crystals of Cu-adamite from the oxidation zone of the Dal'negorsk base metal deposit (Primorye, Russia) corresponds to low-Cu zincolivenite with the following composition (wt %): MgO 1.01, CuO 16.67, ZnO 40.00, As_2O_5 41.47, total 99.15.

Table 4. Comparative data on zincolivenite and cognate minerals

Mineral	Zincolivenite	Adamite	Olivenite		Zincolibethenite
Formula	$CuZn(AsO_4)(OH)$	$Zn_2(AsO_4)(OH)$	$Cu_2(AsO_4)(OH)$		$CuZn(PO_4)(OH)$
Crystal system	orthorhomb.	orthorhomb.	monoclin.	orthorhomb.	orthorhomb.
Sp. gr.	*Pnnm*	*Pnnm*	$P2_1/n$	*Pnnm*	*Pnnm*
Unit cell parameters:					
a, Å	8.584	8.386	8.5894	8.5894	8.326
b, Å	8.529	8.552	8.2073	8.2076	8.260
c, Å	5.9696	6.036	5.9285	5.9286	5.877
β, deg			90.088		
Strong bands on the powder XRD pattern *d*, Å (*I*, %)	6.00 (54)	4.893 (70)	5.940 (58)		5.868 (39)
	4.860 (64)	2.975 (100)	4.885 (78)		4.794 (100)
	3.002 (100)	2.700 (70)	4.816 (63)		3.699 (22)
	2.690 (67)	2.469 (65)	4.199 (64)		2.935 (33)
	2.662 (53)	2.458 (60)	2.976 (100)		2.632 (47)
	2.456 (94)	2.448 (55)	2.656 (59)		2.405 (19)
	2.437 (86)	2.415 (65)	2.464 (62)		2.304 (18)
Optical data:					
optical sign	–	+	+		–
2θ, deg°	Approximately 30	Approximately 90	Approximately 90		49
α	1.736	1.708–1.722	1.747–1.780		1.660
β	1.784	1.732–1.744	1.785–1.820		1.705
γ	1.788	1.756–1.773	1.829–1.865		1.715
Density, g/cm^3	4.34	4.35–4.45	4.30–4.46		3.972
Strong bands of O–H stretching vibrations in the IR spectrum, cm^{-1}	3480	3530–3540	3420–3430		3510
Source	Present paper	[8, 15]; ICDD 39–1354; Present paper	[13, 15]; ICDD 42–1353; Present paper		[6]

Empirical formula is $Cu_{0.58}Mg_{0.07}Zn_{1.36}(AsO_4)(OH)_{0.98}O_{0.02}$.

The holotype specimen of zincolivenite is deposited in the Mineralogical Collection, Technische Universität, Bergakademie Freiberg, Germany (inventory no. 81475).

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