

Zdenekite, $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$, a new mineral from the Cap Garonne mine, Var, France

PIERRE-JACQUES CHIAPPERO ⁽¹⁾ and HALIL SARP ⁽²⁾

⁽¹⁾ BRGM - Avenue de Concyr, B.P 6009, 45060 Orléans cedex 2, France

⁽²⁾ Département de Minéralogie du Muséum d'Histoire Naturelle de Genève
B.P 434, 1211 Genève 6, Switzerland

Abstract : Zdenekite occurs as single tetragonal tabular crystals (up to 0.1 mm) flattened on {001}, or as spherulites and aggregates up to 0.3 mm across. The crystal forms observed are {001}, {100} and {110}. The mineral is fragile and soft, has an irregular fracture and a perfect cleavage along (001). Megascopically, the mineral is translucent with a vitreous lustre and an intense blue colour with a pale blue streak. It is not fluorescent in the ultra-violet range. Zdenekite is optically uniaxial negative; $\omega = 1.770(5)$, $\epsilon = 1.710(5)$, measured at 590 nm; it is pleochroic with O = intense turquoise blue and E = pale blue to light green. The measured specific gravity is 4.1(1) g/cm^3 . Zdenekite is tetragonal, possible space groups $P4_122$ or $P4_322$, unit-cell parameters $a = 10.066(1)$, $c = 39.39(4)$ Å, $V = 3991.41(4)$ Å³, $Z = 8$, $D_{\text{calc}} = 4.08$ g/cm^3 . The strongest lines in the powder pattern are [I, d(Å), (hkl)] : 100, 9.83, (004); 60, 4.925, (008); 50, 4.482, (204) (211); 90, 3.132, (226) (1.0.12); 40, 2.772, (308) (317); 50, 2.515, (400) (401); 40, 1.778, (440) (441). The average of 16 electron-microprobe analyses gave (in wt%) : Na₂O 2.92; CaO 0.62; PbO 16.79; CuO 32.97; As₂O₅ 36.66; Cl 3.54; H₂O (by TGA) 7.2; Cl ≡ O - 0.80; total 99.90. The empirical formula calculated on the basis of 22(O + Cl) is Na_{1.15}Ca_{0.13}Pb_{0.92}Cu_{5.09}As_{3.90}H_{9.82}Cl_{1.23}O_{20.77}, or ideally NaPbCu₅(AsO₄)₄Cl·5H₂O. Zdenekite is the tetragonal lead analogue of lavendulan. It was found in the northern part of the Cap Garonne mine. It is associated with anglesite, an unknown mineral of the tsumcorite group, and olivenite in a quartz conglomerate mineralized in tennantite and covellite. The name honours Dr Zdenek Johan (1935-), mineralogist and Director of Scientific Affairs of the Bureau de Recherches Géologiques et Minières (BRGM), France.

Key-words : zdenekite, new mineral, sodium copper lead arsenate, Cap Garonne, France.

Introduction

The mineralogy of the Cap Garonne deposit was studied by Guillemin (1952), Mari & Rostan (1986) and Chiappero (1993). More than one hundred mineral species have been recognized in this deposit. About two thirds are secondary minerals (principally copper arsenates and copper sulphates) among which zdenekite discovered by one of the authors (PJC) during his PhD thesis work. The description and name of this new mineral were approved by the Commission on New Minerals and Mineral Names of the I.M.A. in November 1992.

Occurrence

The " red-bed " type Cu-Pb deposit of Cap Garonne is located near Le Pradet, 12 km east of Toulon, Var department, France. It was mined during several periods from 1857 to 1917, producing a total of 25,000 tons of copper ore (average Cu content 5 wt%) and 500 tons of lead ore (Mari & Rostan, 1985). The mineralization impregnates 0.1 to 1.2 m of sandstone and conglomerate of the Lower Triassic near their basal contact with Permian sediments (Guillemin, 1952; Mari & Rostan, 1986). Two different mineralized horizons can be distinguished : a copper-bearing

horizon containing tennantite as the principal ore mineral, locally overlain by a lead-bearing horizon, less than 0.2 m thick, characterized by the presence of galena and cerussite.

The copper-bearing horizon shows in some places, cementation linked to the presence of joints (Chiappero, 1993) and characterized principally by the transformation of tennantite into chalcocite and covellite. These joints, together with the sandstone porosity have also favoured the circulation of oxidizing, low-temperature solutions, leading to the formation of almost all the secondary minerals recognized (Sarp *et al.*, 1992); these can be observed in the joints or in the sandstone pores. Zeunerite is one of the earliest mineral phases formed during this oxidation process, its $^{234}\text{U}/^{230}\text{Th}$ isotopic composition places the beginning of this oxidation period at 232^{+38}_{-28} thousand years (Chiappero, 1993).

Only those parts of the orebody free from oxidation or affected by cementative enrichment have been preferentially mined with the exception of some zones (generally kept as pillars). Zdenekite comes from one of these zones. The zone concerned consists of a pod of primary ore showing the two ore horizons described above. It was superficially oxidized after exposure during mining about 100 ± 20 years ago. Zdenekite is a neoformed mineral as shown by its formation directly on the mine wall. The new mineral comes from the northern part of the Cap Garonne mine, especially from pillars 78, 78b and 80 (Chiappero, 1993), where it forms blue crusts of several square centimetres on the tennantite-bearing horizon, near the contact with the lead-bearing horizon.

Mineral association

Zdenekite has been found in two distinct mineral associations where it is the latest mineral to appear. The first, most common one, consists of the following minerals (the direction of the arrows indicates the chronology of apparition): tennantite \rightarrow covellite \rightarrow anglesite \rightarrow unknown Cu, Fe, Pb, As mineral of the tsumcorite group \rightarrow olivenite \rightarrow zdenekite. All the secondary minerals formed up to the unknown mineral of the tsumcorite group belong to an acidic sequence (Keller, 1977). Olivenite may belong to the acidic or basic sequence as its pH formation field is very large (Magalhaes *et al.*, 1988). Zdenekite

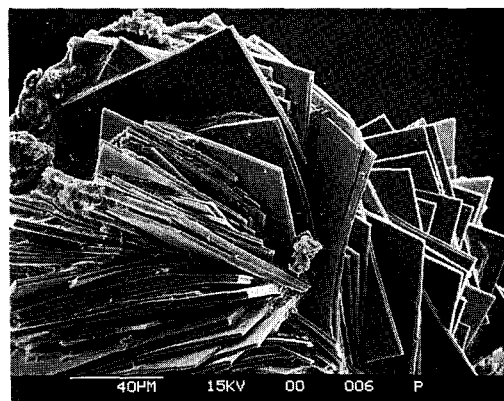


Fig. 1. Scanning electron microscope picture of zdenekite crystals (Cambridge Stereoscan 250).

could belong to a basic sequence, given that lavendulan and zdenekite are related and that the synthesis of lavendulan has been carried out in neutral or slightly basic pH (Guillemin, 1956). The second association is tennantite \rightarrow covellite \rightarrow antlerite \rightarrow geminite (Sarp & Perroud, 1990) \rightarrow zdenekite. All the secondary minerals up to geminite belong to the acidic sequence and were formed at a $\text{pH} \leq 3$ as suggested by the geminite synthesis conditions (Guillemin, 1956). The lead in both these associations comes from the leaching of the lead-bearing horizon immediately overlying the copper-rich level.

Table 1. Chemical composition of zdenekite.

	1	2	3	4
Na ₂ O	2.92	2.29 - 3.36	0.3	2.52
CaO	0.62	0.10 - 0.95	0.2	--
PbO	16.79	15.19 - 18.40	1.2	18.15
CuO	32.97	31.50 - 33.66	0.86	32.36
As ₂ O ₅	36.66	35.01 - 37.90	1.2	37.40
Cl	3.54	3.20 - 3.88	0.2	2.88
H ₂ O*	7.2			7.34
Cl=O	- 0.80			- 0.65
total	99.90			100.00

1. Weight percentages, average of 16 microprobe analyses.
2. Range.
3. Standard deviation.
4. Theoretical composition for $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}_5\text{H}_2\text{O}$. (*) determined by T.G.A.

Table 2. X-ray powder pattern of zdenekite.

hkl	d(calc)	d(meas)	I	hkl	d(calc)	d(meas)	I
004	9.854	9.83	100	444	1.751	1.749	< 5
110	7.118	7.11	25	528	1.748		
104	7.042	7.02	< 5	530	1.726		
008	4.927	4.925	60	531	1.725	1.728	5
204	4.482	4.482	50b	600	1.678		
211	4.473			601	1.676	1.676	10
118	4.051	4.046	10b	448	1.674		
221	3.544	3.546	15b	613	1.642	1.642	< 5
300	3.355	3.556	< 5	605	1.641		
0012	3.285	3.283	10	0024	1.641	1.629	< 5
226	3.129	3.132	90	538	1.629		
1012	3.121			606	1.625	1.572	10
228	2.885	2.887	5	540	1.572		
307	2.882			624	1.571	1.492	5
308	2.773	2.772	40	541	1.571		
317	2.771			633	1.491	1.423	10
223	2.731	2.736	< 5	550	1.424		
309	2.663	2.657	< 5	704	1.423	1.409	5
400	2.516	2.515	50	551	1.423		
401	2.511			640	1.396	1.396	< 5
0016	2.462	2.458	5d	641	1.395		
405	2.397	2.399	5d	723	1.375	1.374	10
420	2.251	2.252	10	645	1.374		
424	2.194	2.193	5	559	1.354	1.353	< 5
426	2.129	2.127	< 5	726	1.353		
428	2.047	2.058	< 5	728	1.331	1.332	< 5
430	2.013	2.010	5	649	1.330		
500	2.013			652	1.286	1.283	10
431	2.011	1.973	< 5	653	1.283		
510	1.974			815	1.233	1.232	10
434	1.972	1.924	5	745	1.233		
511	1.972			816	1.227	1.227	< 5
0020	1.970	1.868	< 5	746	1.227		
436	1.925			749	1.201	1.201	5
515	1.915	1.836	5	826	1.200		
520	1.869			750	1.170	1.171	5
521	1.867	1.778	40	834	1.170		
524	1.836			440	1.779	1.778	5
518	1.832	1.778	40	441	1.778		
440	1.779			441	1.778		

Gandolfi camera, 114.6 mm diameter, CuK α radiation,
b = broad, d = diffuse. Intensities estimated visually.

Physical and optical properties

Zdenekite occurs as tetragonal tabular crystals (up to 0.1 mm) flattened on {001}, as individuals or forming spherulites and aggregates up to 0.3 mm across (Fig. 1). The crystal forms observed are {001}, {100} and {110}. Megascopically, the mineral is translucent with a vitreous lustre; its colour is turquoise blue and the streak is pale blue. It is not fluorescent in the ultra-violet wavelength range. Zdenekite crystals are soft and fragile, which prevented determination of the Mohs hardness. The crystals show an irregular fracture and a perfect cleavage along (001). Zdenekite is optically uniaxial negative with $\omega = 1.770(5)$ and $\epsilon = 1.710(5)$, measured at 590 nm, and no visible zonations. It is strongly pleochroic with O = turquoise blue and E = pale blue to light green. The specific gravity, determined using heavy-liquid immersion, is 4.1(1) g/cm³. The density calculated according to Mandarino (1981a) is 4.08(1) g/cm³.

Chemical composition

The microprobe analyses of zdenekite were obtained on the CAMEBAX microprobe in the BRGM-CNRS microprobe laboratory, Orléans. The following elements were detected by wavelength dispersive qualitative analysis: Na, Pb, Cu, As, Cl, Ca. The operating conditions for the quantitative analysis were: accelerating voltage 15 kV, incident current 5.5 nA, beam diameter 6 μ m and the standards used were albite (NaK α), vanadinite (ClK α), galena (PbM α), clinoclase (CuK α , AsL α) and andradite (CaK α). The water content was determined by thermogravimetric analysis (Mettler TA2 balance).

The average and range of 16 microprobe analyses are given in Table 1. The empirical formula calculated on the basis of 22(O + Cl) is:

$\text{Na}_{1.15}\text{Ca}_{0.13}\text{Pb}_{0.92}\text{Cu}_{5.09}\text{As}_{3.90}\text{H}_{9.82}\text{Cl}_{1.23}\text{O}_{20.77}$
or, ideally, $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$. The compatibility index calculated with the Gladstone-Dale constants of Mandarino (1981b) is excellent with a value of 0.037.

Chemically, zdenekite is thus a Pb analogue of lavendulan, $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$, which was described as orthorhombic (Guillemin, 1956). In the case of the sample analysed, the little variation of the CaO concentration precludes the existence of important zonations, con-

firmed the optical examination. It is clear that, for the moment, only a limited solid solution exists between zdenekite and a hypothetical tetragonal dimorph of lavendulan.

X-ray crystallography

The single-crystal study was carried out using a precession camera. Zdenekite is tetragonal with possible space groups $P4_122$ and $P4_322$. The unit-cell parameters refined by least-squares from the X-ray powder pattern are: $a = 10.066(1)$, $c = 39.39(4)$ Å; $V = 3991.41(4)$ Å³; $Z = 8$. The X-ray powder pattern (Table 2) was obtained using a Gandolfi camera (114.6 mm diameter) and CuK α radiation. The c/a ratio calculated from the unit-cell parameters is $c/a = 3.9132$.

Nomenclature and conservation

The new mineral has been named in honor of Dr Zdenek Johan (born 1935), Director of Scientific Affairs of the BRGM, France, for his important contributions to Mineralogy. As johannite already exists and a complex name formed by contraction of name and surname could have led to confusion, we chose to use only Dr Johan's first name to form the mineral name. Type specimens are preserved in the Department of Mineralogy of the Natural History Museum of Geneva, Switzerland and in the collection of Mineralogy of the National Museum of Natural History in Paris, France.

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