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PRELIMINARY DATA OF ERYTHRITE FROM CIECHANOWICE (MIEDZIANKA DEPOSIT, SUDETES MTS.)

Abstract: Erythrite, $Co_3(AsO_4)_2 \cdot 8H_2O$, with an unexpectedly high content of ZnO and also CuO was found in the dump of the polymetallic ore deposit in Rudawy Janowickie, Sudetes Mts. Some of the crystals, viz. those of which the structural formula is: $(Zn_{0.69}, Co_{0.49}, Cu_{0.41}) (As_{0.97}O_4) * 4(H_2O)$, can be named neither erythrite nor kottigite ($Zn_3(AsO_4)_2 \cdot 8H_2O$).

Keywords: erythrite, solid solution, kottigite, Ciechanowice.

INTRODUCTION

Erythrite is one of the secondary minerals formed in the oxidation zone of cobalt-bearing deposits. The bright red-purple colour of the mineral is so characteristic that erythrite is easily noticed among these secondary minerals and therefore is an important marker of the ore.

The first author of the present contribution obtained specimens of red-purple mineral from the dump of the old polymetallic mine located at the road Miedzianka – Ciechanowice. The complex ore deposit in the Rudawy Janowickie is known as a hydrothermal ore of a chlorite copper system. It was formed in the tectonised zones of basic rocks as a result of the main Intra-Sudetic faulting, and of contact metamorphism due to the Karkonosze granitic body (Zimnoch 1978, Mochnacka 1982).

The presence of secondary minerals, including erythrite, formed in the oxidation zone of the Miedzianka ore deposit was noticed already in early publications (a.o. Traube 1888). Precise characteristics of them were collected by Lis and Sylwestrzak (1986), and published by Pieczka et al. (1988), Holeczek (1990), Holeczek, Janeczek (1991) and Ciesielczuk, Bzowski (2003). As the deposit contains a wide variety of ore minerals, the chemical composition of some secondary minerals is unusual. Ciesielczuk and Bzowski (2003) found Zn- bearing copper phosphate and arsenate minerals in Miedzianka. On the basis of the mineral phase, of which the chemical composition is intermediate between pseudomalachite and cornwallite, they proved the existence of a pseudomalachite-cornwallite solid solution. Because large amounts of zinc and legrandite were also

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detected, they postulated the possible existence of a solid solution between pseudomalachite, cornwallite and legrandite.

Two types of erythrite are common among the samples from Miedzianka: pure erythrite (sample ER2), and erythrite with a higher concentration of zinc and even copper (sample ER1).

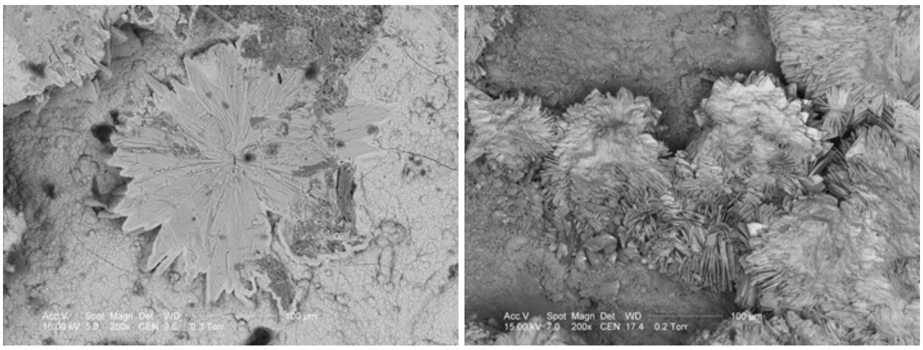
The purpose of the present contribution is to characterise the erythrite from Miedzianka ore deposit in Rudawy Janowickie, which is new proof of existence of solid solutions among minerals forming during the oxidation stage of the ore.

METHODS OF INVESTIGATIONS

The samples of erythrite were first examined using a scanning microscope Philips XL 30 ESEM/TMP (Faculty of Earth Sciences, University of Silesia). A qualitative EDS method was used for checking their chemical composition. XRD patterns were recorded by an INEL CPS-120E diffractometer with a DSH system (Institute of Geological Sciences, Polish Academy of Sciences). The quantitative chemical composition was determined with an electron microprobe CAMECA SX-100 (Faculty of Geology, Warsaw University).

RESULTS

Erythrite, $Co_3(AsO_4)_2 \cdot 8H_2O$, found in the dump in Ciechanowice forms small (up to 50μm) radial crystals (Fig. 1). The red-purple crystals of "cobalt bloom" are translucent. Apart from them, a second generation of erythrite is present. The crystals are smaller (up to 10μm).



a) b)

Fig. 1. Erythrite from Ciechanowice. a – sample ER1, b – sample ER2. Scanning microscope.

X-ray data of the ER2 sample indicate the presence of pure erythrite (JCPDS 33-413). The location of peaks in the XRD pattern of sample ER1 is slightly shifted towards higher theta values. As Zn^{2+} and Co^{2+} have ionic radii of similar sizes, the conformity of their XRD patterns was expected (tab. 1).

Table 1. XRD data for erythrite from Ciechanowice (samples ER1 and ER2) in comparison with pure erythrite (JCPDS 33-413).

sample ER1		sample ER2		erythrite 33-413	
d	I	d	I	d	I
8.028	35	7.949	35	7.937	25
6.755	100	6.738	100	6.711	100
4.969	9	4.976	9	4.950	9
4.419	15	4.404	20	4.405	15
3.928	12	3.924	12	3.922	12
3.234	30	3.226	30	3.226	40
3.005	20	3.014	30	3.003	45
2.735	20	2.745	20	2.740	30
2.712	15	2.718	15	2.710	20
2.656	12	2.666	12	2.660	12
2.471	12	2.467	12	2.463	15
2.327	10	2.326	12	2.326	15
2.077	8	2.082	7	2.083	9
1.915	7	1.919	6	1.916	8

The erythrite present in sample ER2 is chemically pure. Apart from CoO and As_2O_5, the following elements (in oxides) are present in traces (less than 0.3%): CaO, SO_3, ZnO, CuO, NiO, FeO and MnO.

Erythrite from sample ER1 contains higher amounts of ZnO and CuO. The chemical composition of the center differs from that in the rim of crystals. The rims are enriched in Zn and also in Cu, so that they have a similar composition as the small grains of the second generation (tab. 2).

Table 2. Representative microprobe analyses of erythrite present in sample ER1 from Ciechanowice. 90 and 19 – analyses of smaller grains, 5 and 27 – analyses of the outer parts of grains, 15 and 4 – analyses of the inner parts of grains, 68 – analysis of homogeneous grain, 53 – analysis of erythrite formed in a calcitic vein.

No analysis	90	19	5	27	15	4	68	53
	smaller grains		rim		center			vein
As_2O_5	41.91	40.88	42.34	43.50	44.46	43.93	43.29	37.01
CaO	0.00	0	0.06	0.14	0.20	0.65	0.29	0.94
SO_3	0.14	0.17	0.14	0.08	0.17	0.21	0.15	0.03
P_2O_5	0.09	0.06	0.17	0.13	0.10	0.18	0.22	0.09
CoO	**17.01**	**13.64**	**22.70**	**7.68**	**27.71**	**31.94**	**31.45**	**6.23**
ZnO	**22.80**	**21.06**	**17.39**	**23.98**	**10.77**	**6.41**	**6.52**	**24.62**
CuO	**3.07**	**12.10**	**0.81**	**8.47**	**0.34**	**0.82**	**0.71**	**14.06**
NiO	0.11	0	0.25	0.13	0.14	0.24	0.28	0.00
FeO	0.19	0	0.11	0.13	0.03	0.11	0.09	0.06
MnO	0.31	0.11	0.43	0.28	0.52	0.44	0.23	0.30
total	85.64	88.02	84.38	84.50	84.43	84.93	83.22	83.34

DISCUSSION

Grains of the mineral present in sample ER1 have an unusual chemical composition (tab. 1). According to XRD data the mineral is monoclinic. The only mineral containing Co, Zn and As present in mineralogical data-bases is cobaltkoritnigite (Co, Zn)(AsO_3)(OH)·H_2O, a triclinic mineral with the following chemical composition: ZnO 9.31%, CoO 25.72%, As_2O_5 52.60% and H_2O 12.37% (www.webmineral.com, www.mindat.org). Cobaltkoritnigite contains, however, a higher amount of As_2O_5 and has different cell dimensions than the mineral investigated from sample ER1.

Erythrite is isostructural with the rare mineral kottigite, $Zn_3(AsO_4)_2 \cdot 8H_2O$. The inner part of the grains from sample ER1 can confirm the existence of a limited solid solution between these minerals.

The chemical composition of the fluid percolating through the oxydised zone of the ore must have had an input of Zn and Cu ions. It caused the consecutive enrichment in Zn and Cu within the rims of the then existing Zn-erythrite, and also caused the crystallisation of small grains and vein filling.

The unusual erythrite confirms the possible existence of a limited solid solution between Cu-, and Zn-oxyminerals, as postulated by Ciesielczuk and Bzowski (2003), and extended it with cobalt.

On the other hand, sample ER1 can represent a mineral that has not been identified as yet.

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