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The origin of copiapite from chlorite pyritic schist (Wieściszowice, Lower Silesia, Poland) in the light of Mössbauer analysis

Z. Adamczyk · J. L. Komraus

Abstract This work presents the results of the analysis of copiapite, formed from weathering and oxidation of pyrite in pyritic schist from Wieściszowice, Lower Silesia (Poland). The pure phase of copiapite was found in secondary minerals after pyrite and identified by optical microscopy, XRD and Mössbauer spectroscopy. In the analyzed copiapite major cations appear to be Fe^{2+} and Fe^{3+}. Some Fe^{3+} is substituted by other cations, mainly Al^{3+}. Al^{3+} probably comes from leaching of chlorite from which hydrated sulphates of iron, mainly szomolnokite, form followed by hydrated sulphates fibroferrite, which is replaced by copiapite.

Keywords Mössbauer spectroscopy · Copiapite · Pyrite · Sulfate minerals · Pyrite weathering

1 Introduction

The deposit of pyrites is localized in proterozoic schist, which form part of the eastern cover of a granite intrusion in the Karkonosze Mountains (Rudawy Janowickie, Lower Silesia, Poland). The study area is located in the town Wieściszowice (Fig. 1). A detailed description of this deposit [1–4] shows that chlorite–sericite, sericite, chlorite and quartz–sericite ore-bearing schists occur among chlorite schist (in the roof) and quartz schist (in the floor). These ore-bearning rocks are composed of chlorite, sericite, quartz and on occasion epidote, orthoclase and plagioclases,

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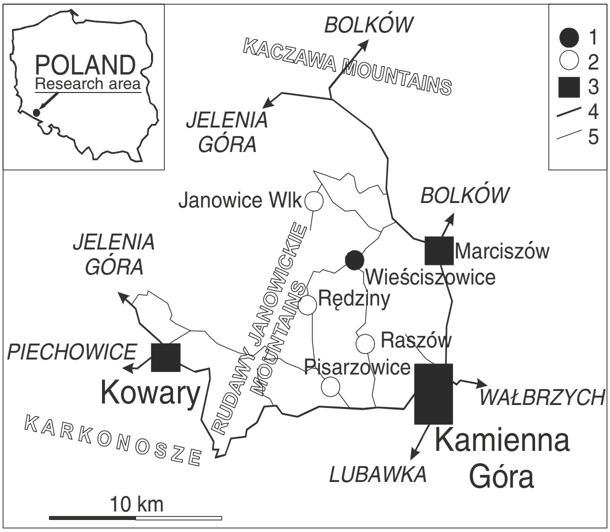
Z. Adamczyk (✉)
Institute of Applied Geology, Silesian University of Technology,
ul. Akademicka 2, 44-100 Gliwice, Poland
e-mail: zdzislaw.adamczyk@polsl.pl

J. L. Komraus
Institute of Physics, University of Silesia, ul. Uniwersytecka 4,
40-007 Katowice, Poland
e-mail: komraus@us.edu.pl

Fig. 1 Location map of the Wieściszowice. *1* research area, *2* village, *3* town, *4* road, *5* local road



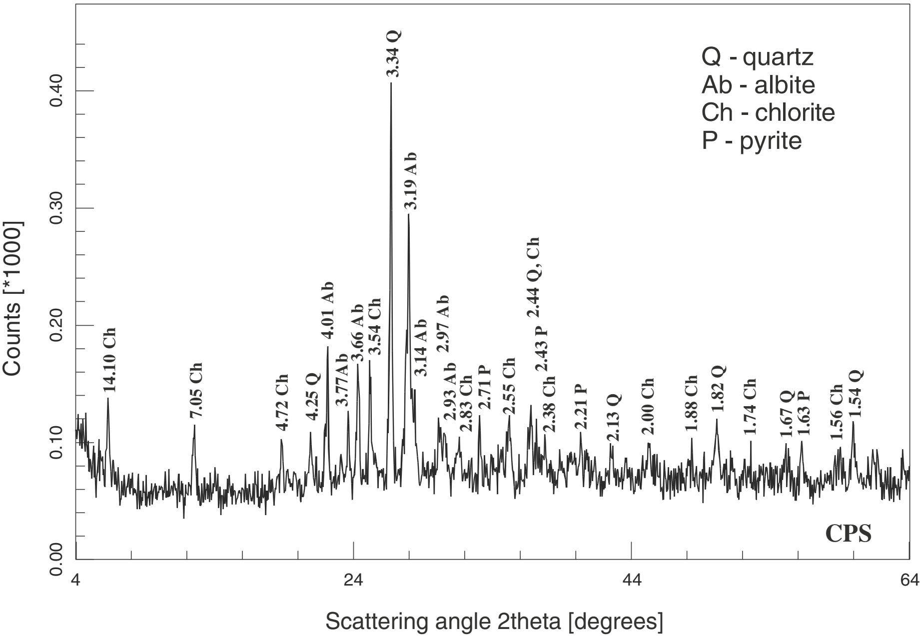


Fig. 2 X-ray diffractogram of sample CPS from Wieściszowice

carbonates, biotite, actinolite, leucoxene, ilmenite, titanite and iron oxides. The dominant ore mineral is pyrite, whose proportion in the rock ranges from a few to tens of percent [1]. Pyrite is accompanied by small amounts of chalcopyrite, galena and sphalerite [2] as well as pyrrhotite, chalcocite, siderite; marcasite [3].

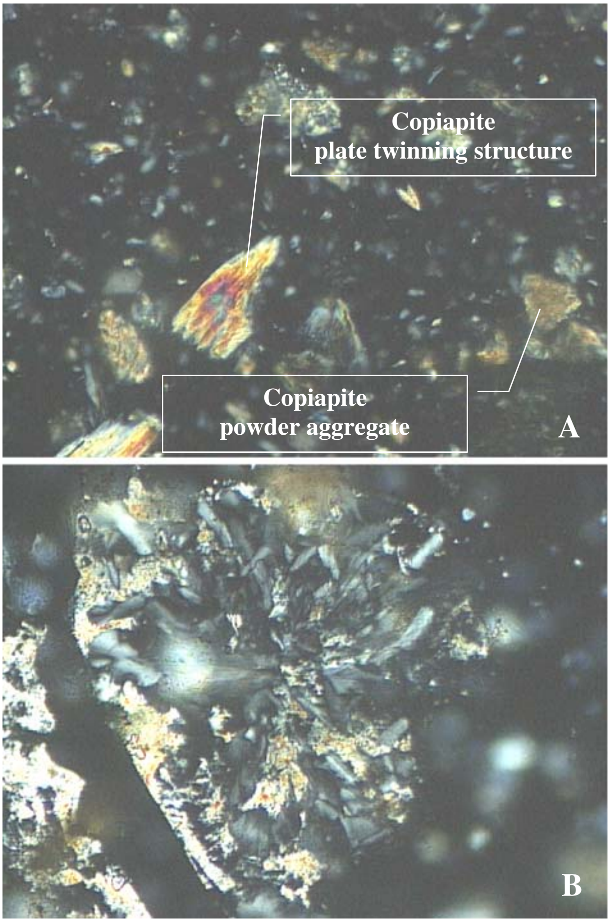


Fig. 3 Microscopic image of tabular crystal habit (**a** magnification, ×100) and concentric crystal in aggregate (**b** magnification, ×200) of copiapite, transmitted light, crossed polars

The pyrite deposit belongs to metamorphosed sedimentary deposits [1, 3, 4] and pyrite mineralization, which took place together with effusive—exhalative activity of undersea volcanism [2]. These deposits had been exploited since the eighteenth century and the exploitation ceased in 1925. The workings were then flooded and the result of this drainage is secondary mineralization of hydrated iron sulphates. Secondary sulphate minerals occur as a result of transformations of pyrite.

2 Experimental

The sample of the chlorite pyritic schist (CPS) and secondary sulphate minerals (SSM) was examined mineralogically by the means of optical microscopy in transmitted light, X-ray diffraction (XRD) and Mössbauer spectroscopy.

Microscopic observations were made on thin sections of rock and minerals. XRD analysis was performed using a HZG-4 X-ray diffractometer, with the use of a $\mathrm{Cu}_{\mathrm{K}\alpha}$ X-ray tube in the following conditions: voltage 30 kV, intensity 20 mA, 2 theta angle

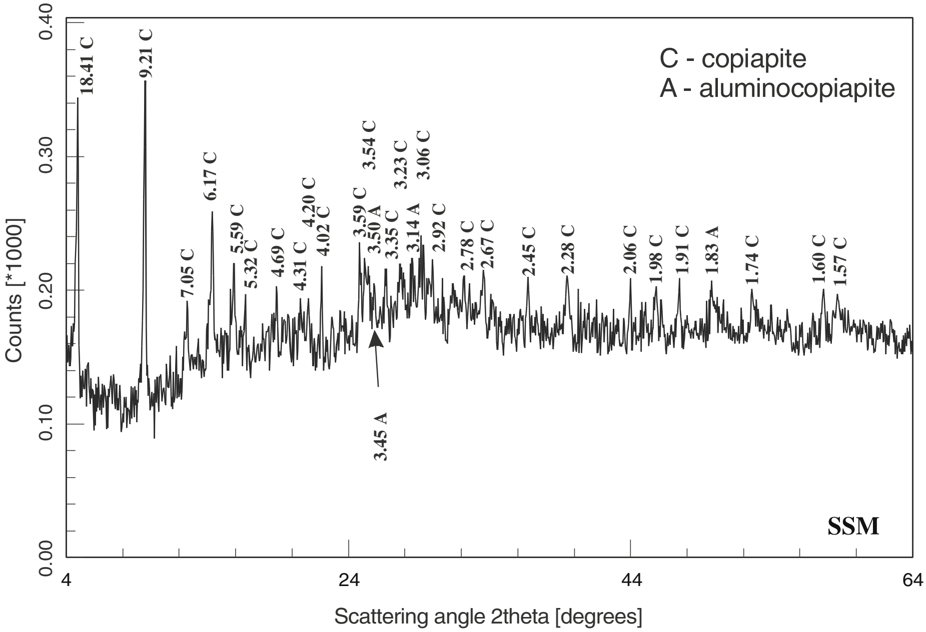


Fig. 4 X-ray diffractogram of sample SSM from Wieściszowice

Table 1 X-ray powder patterns of copiapite (sample SSM) from Wieściszowice according to Fig. 3

Mineral	d_{hkl}(**Å**)
Copiapite	18.41, 9.21, 7.05, 6.16, 5.69, 5.32, 4.69, 4.31, 4.20, 4.02, 3.59, 3.54, 3.35, 3.23, 3.06, 2.92, 2.78, 2.67, 2.45, 2.28, 2.06, 1.98, 1.91, 1.74, 1.60, 1.57
Aluminocopiapite	3.50, 3.45, 3.14, 1.83

range 4–64°, step 0.02°. Mössbauer spectroscopy was performed in the transmission mode. As a source of γ radiation the isotope ^{57}Co/Cr was used, with initial activity of 20 mCi. Calibration of apparatus was done with the use of sodium nitroprusside and α-Fe.

3 Results and discussion

A chlorite pyritic schist (CPS) is of a greenish grey colour. The rock is of a slate-type texture. The mineral components of the rock are quartz and feldspars (represented mainly by albite), chlorites and pyrite (Fig. 2). Sometimes plates of sericite appear. Pyrite is present mainly on the surfaces of separate pieces of slate.

Secondary sulphate minerals (SSM) occur as a conglomerate mixture on the chlorite pyritic schist outcrop. The schist outcrop is cementation of secondary sulphate minerals. Main sulphate mineral is copiapite.

Table 2 Mössbauer spectra parameters of iron compound from chlorite pyritic schist (CPS) and copiapite (SSM) from Wieściszowice, with relative content of iron from these compounds (in atomic %)

Sample	IS [mm/s]	QS [mm/s]	Contents [%]	Minerals
CPS	1.127 ± 0.002	2.645 ± 0.005	52	Chlorite Fe^{2+}
	0.319 ± 0.002	0.594 ± 0.004	48	Pyrite Fe^{2+} , chlorite Fe^{3+}
SSM (Copiapite)	0.405 ± 0.004	0.439 ± 0.031	51	Fe^{2+}
	0.410 ± 0.003	0.888 ± 0.020	49	Fe^{3+}

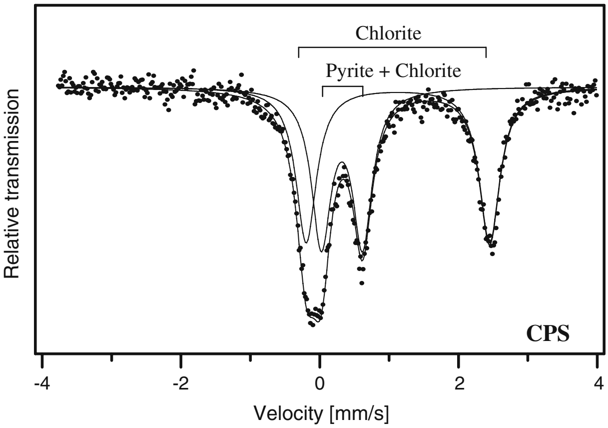


Fig. 5 The Mössbauer spectra of sample CPS

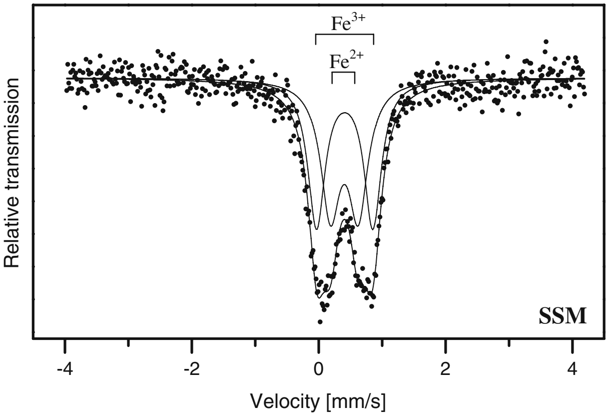
Copiapite occurring in the pyrite deposits in of Wieściszowice is yellow orange in color and has a pearly lustre. Like other hydrated sulphates of iron occurring here, grape-like, aggregate incrustations occur on outcrops of pyrite ore-bearing rocks [5]. Most often, on incrustations, after breaking, one can see powdery aggregate accumulations, of sizes not bigger than 1 mm of diameter.

In transmitted light, copiapite shows platy structure (Fig. 3a) with colourless to pale yellow pleochroism. Concentric accumulations of crystals were often seen in powdery aggregates (Fig. 3a). Sometimes a concentration of copiapite, also in plate structure, would form spherical aggregate (Fig. 3b). Perfect cleavage in one direction is visible.

By means of the X-ray diffraction the monomineralic character of the sample SSC was confirmed (Fig. 4). The presence of copiapite is shown by the presence of interplanar distances d_{hkl} which are characteristic of this mineral (Table 1). Moreover, reflections at d_{hkl} values 3.50, 3.45, 3.14 and 1.83 Å occur on the diffraction pattern (Table 1), which may show the variety containing admixture of aluminum [6, 7]. They were ascertained in chemical analyses [5].

On the basis of Mössbauer spectroscopy the occurrence of two minerals containing iron in a CPS sample was found: chlorite and pyrite (Table 2, Fig. 5). In the Mössbauer spectrum of this sample two quadrupole doublets are visible. The parameters of the first of them (IS = 1.127 mm/s, QS = 2.645 mm/s) correspond with Fe^{2+} in chlorite [8–11]. The second quadrupole doublet comes from Fe^{3+} in chlorite and Fe^{2+} in pyrite [8, 12].

Fig. 6 The Mössbauer spectra of sample SSM



In the Mössbauer spectrum of sample SSM two quadrupole doublets are visible (Table 2, Fig. 6). A similar spectrum for copiapite was shown in a recent study concerning oxidation of pyrite in bituminous coal [13]. However no parameters of doublets coming from iron cations were given. The measurements carried out for the analyzed sample from Wieściszowice show that the parameters of the first doublet are: IS = 0.410 mm/s and QS = 0.888 mm/s (Table 2). The parameters of the second doublet are: IS = 0.405 mm/s and QS = 0.439 mm/s. The values of the parameters for the first doublet are similar to values typical of Fe^{3+} in complex iron sulphates containing a hydroxyl groups e.g. butlerite, jarosite. It can therefore be concluded that the first of the doublets corresponds with Fe^{3+} in the structure of copiapite showing a structure that consists of infinite chains [14]:

$$\left[Fe_2^{3+}\,(OH)\,(H_2O)\,4\,(SO_4)_3\right]_2 Fe^{2+}\,(H_2O)_6\}\,(H_2O)\,6$$

Fe^{3+} is coordinated in the structure of copiapite by sulphate tetrahedrons, water and a hydroxyl group. The second of the doublets, correspond to Fe^{2+} in the structure of copiapite and is coordinated only by water.

The structural formula of copiapite indicates that the contribution of the field coming from Fe^{3+} should be much bigger than Fe^{2+}. However, the contributions of the quadrupole doublet fields coming from Fe^{2+} and Fe^{3+} are similar and amount to about 50% of the field of the whole spectrum. It is therefore suggested that part of the Fe^{3+} is substituted with other cations. As indicated by XRD, this cation is likely Al^{3+}. It probably comes from leaching chlorites by water solutions, of which hydrated iron sulphates crystallize then.

4 Conclusion

Copiapite is a typical secondary mineral arising during weathering and oxidation of pyrite. The basic chemical reaction describing the decomposition of pyrite, resulting in crystallization of secondary sulphates containing iron [15] is as follows:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

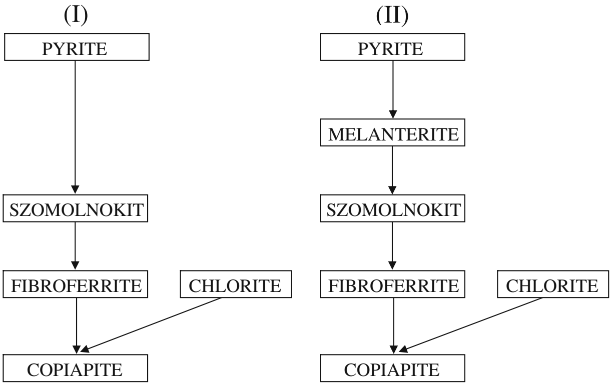


Fig. 7 Diagrams of transformations of pyrite to copiapite with part of chlorite ([15, 19] modified)

In anaerobic conditions, szomolnokite arises in the deposit in Wieściszowice, according to the reaction:

$$Fe^{2+}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + H_2O \rightarrow Fe^{2+}SO_4{}^{*}H_2O \tag{2}$$

This mineral can also form as a result of melanterite dehydration [16]. The product is therefore hydrated sulphate containing Fe^{2+}.

In aerobic conditions oxidation of Fe^{2+} takes place according to the reaction [15]:

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \tag{3}$$

The presence of Fe^{3+} ions can induce crystallization of fibroferrite and butlerite. Simultaneously copiapite can crystallize. Nordstrom [16] concludes that copiapite can form as a result of oxidation of rozenite and szomolnokite, whose formation results from melanterite dehydration. Zodorow and others [17] suggest copiapite formed from melanterite through the medium of rhomboclase or fibroferrite.

Copiapite, identified by XRD, contains substitutions of Al^{3+}.

Al^{3+} cation would substitute for Fe^{3+} in the position X of the general formula [18]:

$$X\,(OH)_2\,R^{3+}{}_4\,(SO_4)\,6^{*}nH_2O$$

where X can be $2/3R^{3+}$, $1R^{2+}$or $2R^+$: R^{3+}=Fe^{3+}, Al^{3+}; R^{2+}=Fe^{2+}, Mg^{2+},Mn^{2+}, Cu^{2+}, Zn^{2+}, Ca^{2+}; R^+=K^+, Na^+.

Based on the results of research by Mössbauer spectroscopy it is suggested that the reaction resulting in the crystallization of copiapite, is as follows:

$$3Al^{3+}_{(aq)} + Fe^{2+}{}_{(aq)} + Fe^{3+}{}_{(aq)} + 6SO_4{}^{2-}{}_{(aq)} + 21H_2O + 0.5O_2 \rightarrow$$
$$\rightarrow \left(Fe^{2+}\right) Fe^{3+}Al^{3+}{}_3\,(SO_4)_6\,(OH)_2\,{}^{*}20H_2O_{(s)} \tag{4}$$

There are possible variants of its formation, which are schematically presented in Fig. 7. The crystallizing mineral is copiapite with substitutions of Al^{3+}. Therefore its presence in the group of secondary minerals arising from pyrite in Wieściszowice can explain leaching of Al^{3+} from chlorites, one of the main minerals in the schist. It seems that the crystallization of the analyzed copiapite occurs according to the scheme (*I*), because in the analyzed sample of the secondary minerals no presence of melanterite was found.

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