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MINERALS OF THE BRAVOITE – VILLAMANINITE SERIES AND CUPRIAN SIEGENITE FROM KARNIOWICE, POLAND

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ABSTRACT

Copper-bearing Ni–Co–Fe disulfides with a pyrite-type structure and cuprian siegenite have been recognized in galena from a minor occurrence of Pb–Cu mineralization in Permian travertine from Karniowice, Poland. The pyrite-type phases occur as minute, optically and compositionally zoned crystals. The composition of individual zones varies from cuprian pyrite with 2.9 wt.% Cu through cuprian bravoite to villamaninite $Cu_{0.36}Ni_{0.46}Co_{0.14}Fe_{0.04}S_2$. Cuprian siegenite $Cu_{0.31}Ni_{1.46}Co_{1.18}Fe_{0.05}S_4$ probably formed by transformation of the disulfides.

Keywords: villamaninite, cuprian pyrite, cuprian bravoite, cuprian siegenite, electron-microprobe analysis, Poland.

SOMMAIRE

On a découvert des disulfures cuprifères de Ni–Co–Fe à structure du type pyrite et de la siegenite dans la galène provenant d'un indice de minéralisation en Pb–Cu dans du travertin permien de Karniowice (Pologne). Les disulfures se présentent en grains minuscules qui montrent une zonation en propriétés optiques et en composition. D'une zone à une autre, la pyrite cuprifère (2.9% Cu en poids) passe à la bravoïte cuprifère et celle-ci à la villamaninite $Cu_{0.36}Ni_{0.46}Co_{0.14}Fe_{0.04}S_2$. La siegenite, cuprifère elle aussi ($Cu_{0.31}Ni_{1.46}Co_{1.18}Fe_{0.05}S_4$), serait le produit d'une transformation des disulfures.

(Traduit par la Rédaction)

Mots-clés: villamaninite, pyrite cuprifère, bravoïte cuprifère, siegenite cuprifère, analyse par microsonde électronique, Pologne.

INTRODUCTION

During the course of investigations of trace Pb–Cu mineralization in the Permian travertine of Karniowice, 20 km west of Kraków, Poland, anomalous Co and Ni contents (0.1–1 wt.%) were found as a result of the spectrographic analysis of galena (Lipiarski & Zakrzewski 1971). Observations in reflected light showed very small grains of a mineral tentatively identified as linnaeite. Electron-microprobe analysis revealed the mineral to be a member of the siegenite–fletcherite isomorphous series. Numerous small zoned crystals with compositions in the bravoite–villamaninite series were also observed.

The investigated occurrence of sulfides is an example of polymetallic mineralization in Paleozoic rocks in close spatial proximity to the Triassic Zn–Pb deposits of "Mississippi Valley type" of southeastern Silesia. The mineralization occurs as two assemblages: one rich in chalcopyrite, with marcasite, pyrite and products of their oxidation, and another rich in galena , with rare sphalerite, pyrite and the cuprian Ni–Co–Fe minerals described in this paper. Galena forms crystals and irregular grains up to 5 mm in diameter in porous, soft calcareous travertine. All the grains are covered with a layer of cerussite up to 300 μm thick. Anglesite occurs but is rare. Small flakes of covellite commonly occur at the contact between galena and cerussite. Cerussite also occurs with covellite around the cuprian Ni–Co–Fe minerals.

The original polished section investigated by Lipiarski & Zakrzewski (1971) contains only a few grains of galena. A second section was prepared from a crushed sample preconcentrated by hand picking. Electron-microprobe analyses were performed with a Cambridge Instruments Microscan MK-9. Natural and synthetic compounds were used as standards. Apparent concentrations were corrected by ZAF with the MK-9 on-line program.

CUPRIAN BRAVOITE - VILLAMANINITE

The cuprian disulfides having the pyrite structure and compositions in the bravoite–villamaninite series occur exclusively as a idiomorphic zoned crystals included in galena. In places, the concentration reaches a few hundred crystals per mm^2; isolated crystals were found in almost every grain of galena. The average size of the individual crystals is about 10 μm, rarely up to 30 μm.

The individual zones in the crystals of disulfide reach up to 10 μm across, but in most cases they vary between 1 and 3 μm. Because of the small size, differences in hardness and reflectivity could only be characterized qualitatively. Observations on the pyrite - cuprian bravoite - villamaninite solid-solution series from Karniowice support the conclusions of Vaughan (1969) with regard to the relationship between the physical properties and the chemical composition in the pyrite–bravoite series. In reflected light, the pyrite end-member is yellow and hard; increasing Ni and Cu contents result in a lowering of hardness, a pinkish grey color and a lowering of reflectance. The crystals are relatively resistant to oxidation and generally remain unaltered in cerussite, but in places they are limonitized; their primary compositional zonality is then reflected by the intensity of brown internal reflections in individual zones.

The presence of copper in pyrite-group minerals is rare and has only been described from a few localities, the most important being the Providencia mine near Villamanin (Léon, Spain), the type locality of villamaninite. Villamaninite has been redefined as a Cu–Ni–Co–Fe mineral having the pyrite structure and containing CuS_2 in the range between 25 and 75 mol. % (Ypma *et al.* 1968). Shimazaki & Clark (1970) proposed the name for compositions close to the join CuS_2–NiS_2, whereas for compositions close to the join CuS_2–FeS_2, the name *fukuchilite* was proposed. Moh & Kullerud (1982) also designated villamaninite as an intermediate member of the CuS_2–NiS_2 series, with a compositional range between $CuNi_2S_6$ and $CuNiS_4$, and thus between 33 and 50 mol. % CuS_2. According to this the "villamaninite" of Ypma *et al.* (1968) as well as the copper-rich disulfide from Lubin, Poland (Moh & Kucha 1980) should be classified as fukuchilite. It is interesting to note that compositions similar to the fukuchilite from Villamanin were not found by Maaskant (1968), who performed 29 analyses and obtained the range of compositions indicated by the dotted field in Figure 1. The villamaninite investigated by La Iglesia *et al.* (1974) from the same locality also plots within this field.

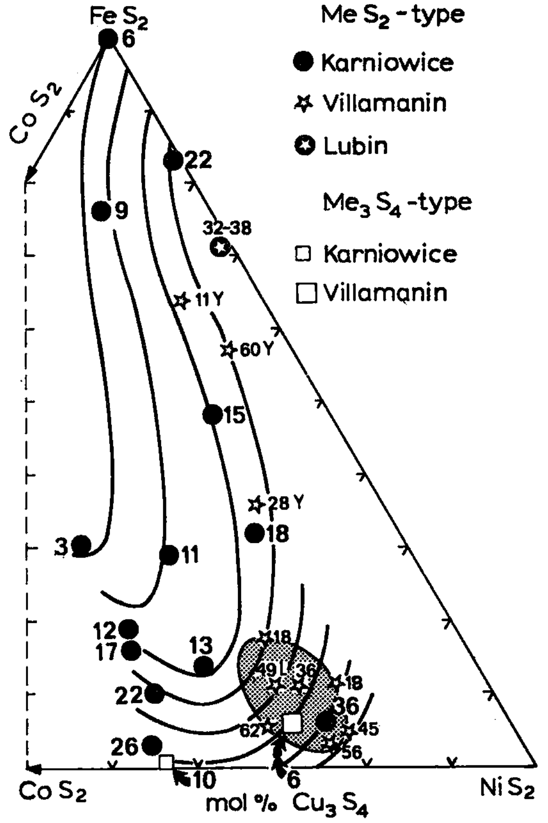

FIG. 1. Compositions of the Cu–Ni–Fe–Co disulfides. Numbers and contours indicate CuS_2 content calculated on the bases of Cu + Ni + Fe + Co = 1 and Ni + Fe + Co = 1. Sources: Karniowice: this study, Lubin: Moh & Kucha (1980), Villamanin: (dotted field) Maaskant (1968), (Y) Ypma *et al.* (1968), (L) La Iglesia *et al.* (1974).

In this paper the Ni-rich disulfide phases with more than 25 mol. % CuS_2 are designated as villamaninite (Table 1, #1,2), those with CuS_2 in the range between 25 and 5 % (arbitrary) as cuprian bravoite (#3–11) or cuprian pyrite (#12), and those with less than 5 % as bravoite (#13). The composition of the iron-rich bravoite (#4) is very close to fukuchilite. Considering the results of the electron-microprobe analyses as given in Table 1, it should be borne in mind that they only approximate the real composition, as the 3–4 μm diameter of the X-ray spot often exceeds the thickness of individual zones. The results obtained are projected onto the FeS_2–NiS_2–CoS_2 plane, and the CuS_2 content is shown by numbers and contours. The proportions of Ni, Fe and Co in the cuprian disulfides from Karniowice resemble those from Villamanin; their Cu content, however, reaches only 36 mol. % CuS_2. The shape of the CuS_2 contours can be interpreted as a result of two trends: firstly, the Cu content is related to the Ni/Fe ratio (Fig. 1, points 3, 12, 17, 22, 26 and 9, 15, 18, 36); secondly, for a given Ni/Fe ratio, Cu shows an antipathetic relation to Co (points 3, 11, 18). The sympathetic relationship between Ni and Cu and the antipathetic one between Ni and Fe

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF VILLAMANINITE, CUPRIAN BRAVOITE AND CUPRIAN SIEGENITE FROM KARNIOWICE, UPPER SILESIA

		Weight %						Atomic proportions				
	Mineral	Cu	Fe	Co	Ni	S	Total	Cu	Fe	Co	Ni	S
1	Villamaninite	18.1	2.0	6.5	21.6	51.4	99.6	0.36	0.04	0.14	0.46	2.01
2		13.4	1.3	15.1	18.5	51.1	99.4	0.26	0.03	0.32	0.39	1.98
3	Bravoite	11.1	3.3	14.6	18.0	50.7	97.7	0.22	0.08	0.31	0.39	2.00
4		11.1	29.2	0.7	5.5	52.2	98.7	0.22	0.65	0.01	0.12	2.02
5		9.4	11.9	7.5	19.7	50.5	99.0	0.18	0.26	0.15	0.41	1.91
6		8.9	6.3	15.2	17.8	51.5	99.7	0.17	0.14	0.32	0.37	1.97
7		7.7	17.9	5.7	14.8	51.4	97.5	0.15	0.14	0.12	0.32	2.03
8		6.6	4.9	13.6	22.1	49.4	96.6	0.13	0.11	0.29	0.47	1.93
9		6.4	7.9	16.8	18.0	49.0	98.1	0.12	0.17	0.34	0.37	1.83
10		5.6	11.9	12.9	18.0	52.6	101.0	0.11	0.26	0.26	0.37	1.98
11		4.3	30.5	5.8	4.6	50.6	95.8*	0.09	0.69	0.12	0.10	2.00
12	Pyrite	2.9	42.6	0.1	-	53.2	98.8	0.06	0.94			2.05
13	Bravoite	1.6	13.6	18.6	14.9	52.3	101.0	0.03	0.29	0.38	0.30	1.94
14	Siegenite	6.4	1.4	21.6	25.2	40.9	95.5	0.33	0.08	1.19	1.40	4.16
15		6.1	0.6	21.9	27.0	40.8	96.4	0.30	0.04	1.19	1.47	4.08
16		5.9	0.4	21.4	27.4	40.4	95.5	0.30	0.02	1.17	1.51	4.08

* includes 3.4 wt. % Pb from adjacent galena.

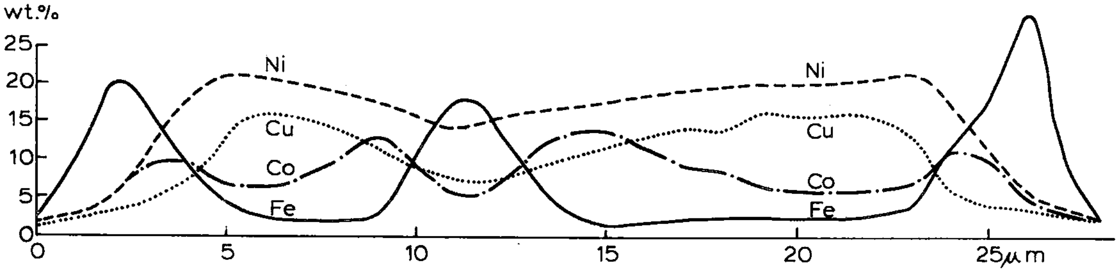

FIG. 2. Concentration profile across zoned crystals of disulfide from Karniowice.

can also be observed on a concentration profile through a zoned crystal (Fig. 2). The behavior of Co is more complex; in the central zones a maximum of Co is related to a minimum of Fe, whereas on the edges, high Co is correlated with a high Fe content.

CUPRIAN SIEGENITE

The only grain of cuprian siegenite found in Karniowice is enclosed in galena. It is an elongate (150 × 30 µm), somewhat porous grain. The cuprian siegenite is optically isotropic, with a white color and a reflectance higher than that of galena. The pores are filled with cerussite and, in a single case, with covellite. Cerussite also occurs with flakes of covellite around the grain at the contact with galena. There are no intergrowths with disulfide minerals, but at a distance of 10 µm, a concentration of several zoned crystals occurs, also surrounded by cerussite with minor covellite.

Results of electron-microprobe analyses from three points on the grain are given in Table 1. The low total of about 96 wt.% is probably due to the porous nature of this mineral. The composition corresponds to an intermediate member between Ni-rich siegenite, $CoNi_2S_4$, and fletcherite, $Cu(Ni,Co)_2S_4$, and is designated as cuprian siegenite. Minerals of this series are only known from the Viburnum Trend, U.S.A. (Craig & Carpenter 1977), the type-locality of fletcherite, and from the Shinkolobwe and Kambowe deposits in Zaire (Riley 1980). The "unusual white linnaeite" from Villamanin has a composition $Ni_{1.92}Co_{0.72}Fe_{0.18}Cu_{0.18}S_4$ (Ypma *et al.* 1968), and should be classified as cuprian Ni-rich siegenite.

DISCUSSION

The cuprian Ni–Co–Fe minerals from Karniowice occur only as isolated inclusions in galena, suggesting that galena formed a microenvironment in which the Ni–Cu–Co–Fe–S system could remain poor in iron. An iron-rich environment contributed to the formation of the chalcopyrite assemblage with marcasite and pyrite. Considering the pyrite-group minerals and siegenite, iron and copper are preferentially concentrated in pyrite-type phases.

There is general agreement that copper-bearing minerals with the pyrite-type structure are metastable (Shimazaki & Clark 1970, Vaughan & Craig 1978). The occurrence of cuprian siegenite in Karniowice suggests that it was formed from the pyrite-type disulfides. This is indicated by 1) the shape of the siegenite grain which is reminiscent of a row of several crystals of disulfide, 2) its porous nature, 3) the presence of covellite and 4) its chemical composition. The projection of the composition of siegenite in the FeS_2–NiS_2–CoS_2 diagram (Fig. 1), recalculated on the bases of Ni + Co + Cu + Fe = 1 and Ni + Co + Fe = 1, shows low Fe and Cu values, whereas the Ni/Co ratio resembles that of the disulfides. The analysis of the cuprian siegenite from Villamanin plots within the iron-poor part of the villamaninite field (Fig. 1).

It is interesting to note the presence of compositions of the pyrite-type phases in which all four cations (Ni,Co,Cu,Fe) are present in major quantities (Table 1, #5–10). The composition of siegenite is typified by the presence of only three cations, which is in agreement with the observation of Riley (1980) that no member of this group has been reported with four cations in major quantities.

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