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SPHALERITE-CHALCOPYRITE-STANNITE ASSEMBLAGE  
FROM A MINERALIZATION ZONE IN RĘDZINY  
AND ITS SIGNIFICANCE IN ORE-GENESIS EXPLANATION

**Abstract:** A sphalerite-chalcopyrite-stannite assemblage has been found within arsenopyrite-chlorite-quartz veins in ore-mineralized contact zones of amphibolite and mica schists with dolomite marble of the Kowary-Czarnów Unit in the Rędziny quarry. The composition of the minerals allowed estimation of the physico-chemical conditions under which the mineralization formed. Based on the sphalerite-stannite geothermometer and the chalcopyrite composition, the temperature range was estimated at 320-290°C, pressure below 1 kb, and sulphur fugacity expressed as log  $f_{S_2}$  between -9.5 and -8.5.

**Keywords:** sphalerite, chalcopyrite, stannite, thermobarometric condition, Rędziny, the Western Sudetes

INTRODUCTION

The eastern metamorphic envelope of the Variscan Karkonosze granite intrusion, represented by the Rudawy Janowickie range in the Western Sudetes, is known for many ore occurrences of post-magmatic origin. Some of them were recurrently exploited in the past, *e.g.* in the Miedzianka-Ciechanowice area, in Czarnów and Kowary. Ore mineralization is generally associated with the Kowary granitogneisses and Czarnów schists of the Kowary-Czarnów Unit, directly contacting with the Karkonosze granite.

Next to the area of the abandoned „Szczęście Eweliny” mine of arsenic ores in Czarnów, there is localized in Rędziny the active quarry of dolostone marbles (also within the Czarnów schists horizon). The dolostone lens, approximately 1000x200 m large, was fragmented into several parts during Hercynian orogeny and enclosed within micaceous schists and amphibolites repeatedly entering the dolostone body. The distance between the walls of the quarry upper levels and the outcrops of the Karkonosze granite from NW is only some tens of metres, while from S micaceous schists with the enclosed dolostones border the pinching out Kowary granitogneisses. In many places, particularly on the W side of the quarry, the schist zones contain ore mineralization, very often strongly altered by weathering (Domański, Piotrowicz 1972; Wołkowicz 1984; Gołębiowska, Pieczka 2002; Parafiniuk, Domańska 2002; Gołębiowska 2003). Primary mineralization is

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usually disseminated in schists and also dolostones immediately contacting with schists and amphibolites, less frequent are found ore vein fragments or small nests. In the last years the authors collected samples with polymetallic mineralization, in which arsenopyrite and cassiterite predominate and are accompanied by pyrite, pyrrhotite, chalcopyrite, galena, sphalerite, tetrahedrite, tennantite, chalcocite, digenite, bornite, native bismuth, joseite, bismuthinite, hematite, Bi-sulphosalts, *etc.* Within this set of minerals was recognized a sphalerite-chalcopyrite-stannite paragenesis, that can indicate the conditions under which the polymetallic mineralization formed not only in Rędziny but also, in a wider context, in the whole eastern metamorphic envelope of the Karkonosze granite.

#### METHODS OF INVESTIGATIONS

Optical observations in the reflected light were carried out using a OLYMPUS BX-12 microscope. Chemical compositions of sphalerite, chalcopyrite and stannite were analysed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the Warsaw University with a Cameca SX-100 electron microprobe operating in the WDS mode under the following conditions: excitation voltage 15 kV, beam current 10 nA, peak count-time 20 s, background time 10 s. The following standards, analytical lines and crystals were used: Zn – sphalerite ( $K_{\alpha}$ , LIF), Cu – chalcopyrite ( $K_{\alpha}$ , LIF), Fe – chalcopyrite ( $K_{\alpha}$ , LIF), Mn – rhodonite ( $K_{\alpha}$ , LIF), As – GaAs ( $L_{\alpha}$ , TAP), Se – ZnSe ( $L_{\alpha}$ , TAP), S – chalcopyrite ( $K_{\alpha}$ , PET), Ag – metallic Ag ( $L_{\alpha}$ , PET), Cd – greenockite ( $L_{\alpha}$ , PET), In – InSb ( $L_{\alpha}$ , PET), Sn – cassiterite ( $L_{\alpha}$ , PET). Data were corrected with ZAF procedure. Formula units were obtained on the basis of  $(S+Se+Te) = 4$ , or 2, or 1 apfu for stannite, chalcopyrite and sphalerite, respectively.

#### RESULTS AND DISCUSSION

The paragenetic assemblage sphalerite-chalcopyrite-stannite was found under the microscope, studying dark brownish sphalerite. It occurs as the grains up to 1 cm, accompanied by chalcopyrite, galena and Bi-sulphosalts in fragments of arsenopyrite-chlorite-quartz veins. In the grains of dark sphalerite, both chalcopyrite and stannite occur as inclusions and indicate that all the minerals originated from a high-temperature, homogenous  $(Zn,Cd,Cu,Fe,Sn)S$  sulphide. According to Kojima & Sugaki (1984), ZnS dissolves substantial amounts of Fe and Cu at temperatures above 600°C. At temperatures below 500°C the amount of dissolved CuS is small and shows no link with the FeS amount. In this context, the high-temperature sulphide mentioned must have broken down on cooling into Zn-enriched stannite, chalcopyrite, and Fe- and Cd-enriched sphalerite.

Stannite was rarely observed as euhedral crystals with sizes reaching 250-300  $\mu\text{m}$ , but more frequently disseminated within sphalerite as drop-like, sometimes diffused exsolutions up to several tens of micrometers, and equally frequent „clouds” of fine, lamellar inclusions with sizes of single micrometers and smaller. In the reflected light the stannite is always olive-grey. Chalcopyrite is frequent in some sphalerite grains, where it usually occurs as drop-like exsolutions of various sizes, from single micrometers to some tens of micrometers. Rare are anhedral

chalcopyrite grains with sizes exceeding even 200  $\mu\text{m}$ . Sphalerite is not always homogenous, also in the grains without visible exsolutions of stannite and chalcopyrite. Within the same grain it is possible to observe zones of homogenous, inclusion-free sphalerite, without the presence of Sn in its composition, and also the zones with a distinct olive tint, in which the Sn content reaches even 2-3 wt.%. A presence of Sn, atypical component in sphalerite, indicates cryptoinclusions of stannite, whose content can be estimated at 10-12 mol.%.

The sphalerite-stannite-chalcopyrite system could be successfully applied in preliminary evaluation of physico-chemical conditions under which the polymetallic mineralization in the Rędziny area formed; the results obtained can be projected into the whole eastern, metamorphic envelope of the Karkonosze granite. The partition of Fe and Zn between the coexisting sphalerite and stannite was used to construct a sphalerite-stannite thermometer (Nakamura, Shima 1982; Shimizu, Shikazono 1985). According to Nakamura & Shima (1982), the partition coefficient  $K_d$  of Fe and Zn between sphalerite and stannite  $(X_{\text{Cu}_2\text{FeSnS}_4}/X_{\text{Cu}_2\text{ZnSnS}_4})_{\text{in stannite}}/(X_{\text{FeS}}/X_{\text{ZnS}})_{\text{in sphalerite}}$  is temperature-dependent. This dependence is expressed by the equation:  $\log K_d = 2800T^{-1} - 3.5$ . Calculations carried out for some pairs of coexisting zincian stannite (according to classification of Petruk 1973) with the Fe/Fe+Zn ratio equal to 0.66-0.77 and dark brownish sphalerite from Rędziny indicate that the pairs formed at temperatures 320-290°C. For this temperature range, an additional projection of  $X_{\text{Fe}}$  in sphalerite (0.09-0.11 apfu) vs  $X_{\text{Fe}}$  in stannite (0.68-0.92 apfu) points to sulphur fugacity slightly increasing with the drop of temperature, expressed as a change of  $\log f_{\text{S}_2}$  from -9.5 to -8.5. A projection of the compositions of both phases in the system  $\log(X_{\text{Cu}_2\text{FeSnS}_4}/X_{\text{Cu}_2\text{ZnSnS}_4})_{\text{in stannite}}$  vs  $\log(X_{\text{FeS}}/X_{\text{ZnS}})_{\text{in sphalerite}}$  (Shimizu & Shikazono, 1985) corresponds rather to the vein-type than skarn-type mineralization. Sugaki *et al.* (1975) showed that at 300°C chalcopyrite has a small solid solution field, ranging from almost stoichiometric  $\text{CuFeS}_2$  towards compositions more enriched in Fe, with the (Cu+Fe)/S ratio close to 1. Maximum dissolution of Zn in such a chalcopyrite is estimated to be 0.6 at.% (Kojima, Sugaki 1985). An intermediate solid solution present in the Cu-Fe-S system can contain slightly higher amounts of dissolved Zn, dependable on the Cu and Fe amounts and pressure, reaching a maximum of 1.2 at.% at 2kb and 300°C. Chalcopyrite exsolutions in the crystals of brownish-black sphalerite from Rędziny projected in the CuS-FeS-ZnS triangular system have their compositions located slightly outside the field bordered by the 300°C isotherm and pressure of 0.5 kb, suggesting a more substantial effect of pressure. This conclusion is corroborated by earlier, direct measurements of thermobarometric conditions, carried out on gaseous-liquid inclusions from yellow-brownish cassiterite from Rędziny (Mochnacka *et al.* 2000): they indicated pressure of 0.8-0.9 kb.

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