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**THE ARSENOPYRITE GEOTHERMOMETER – A DIFFICULT  
APPLICATION TO ARSENOPYRITE FROM THE RADZIMOWICE  
ABANDONED Au-As-Cu DEPOSIT (KACZAWA MOUNTAINS)**

**Abstract:** Application of arsenopyrite geothermometer despite its limits allowed to obtain crystallization temperatures of various type arsenopyrites from the Radzimowice abandoned Au-As-Cu deposit. Early two types arsenopyrites (*Asp I* and *Asp II*) represent mesothermal stage of the primary ore crystallization. *Asp I* in comparison to the other types characterised by high admixtures of Co (<7 %wt) and Au (“invisible gold” or “refractory gold”) what limits its application to arsenopyrite geothermometer, dramatically. Used of international standards and very precise measurements allowed calculate that *Asp II* (Co admixture < 1wt%) formed at 455 to 345°C along the arsenopyrite-pyrrhotite-loellingite buffer after Kretschmar, Scott (1976), modified by Shap *et al.* (1985) and late arsenopyrite *Asp III* crystallized below 370°C along the arsenopyrite-pyrite buffer.

**Keywords:** arsenopyrite geothermometer, Radzimowice Au-As-Cu deposit, Kaczawa Mountains

#### INTRODUCTION

The As/S ratio of the arsenopyrite coexisting with other phases in the system As-S-Fe has been experimentally calibrated as a geothermometer (*e.g.* Kretschmar, Scott 1976; modified by Shap *et al.* 1985). However, simple application is often rather problematic. Among the main problems is the widespread presence of significant amounts of other elements in arsenopyrite. Furthermore, arsenopyrite is often zoned with respect to arsenic content and true-buffered assemblages are often hard to find (*op. cit.*). An application of the elaborated diagrams request use of the international arsenopyrite standards (ASP 57 and/or ASP 200) and a very precise selection of materials before the microprobe measurements.

The primary ore mineralizations at the Radzimowice Au-As-Cu deposit have been subject of several authors' studies (*e.g.* Manecki 1965; Zimnoch 1965; Paulo, Salamon 1974; Sylwestrzak, Wołkowicz 1997; Pająk 1997; Mikulski 1999, 2003, 2005a, 2005b; Machowiak, Weber-Weller 2003). Recently, also secondary minerals of the weathered primary ore mineralization were investigated (Siuda 2005). The Radzimowice deposit is now days classified as transition from the porphyry to the epithermal type (Mikulski 2005a). The economic ore mineralization has resulted from several hydrothermal stages. Early mesothermal quartz – Fe with As sulfides and refractory gold was cataclastically deformed and followed by epithermal base-metal sulfides of low sulfidation character with non-refractory gold and carbonates (Mikulski 1999, 2005a). Co-rich arsenopyrite with *refractory gold* and pyrite are the most abundant minerals of the early stage of sulfide precipitation. *Non-refractory gold* associated with base-metal sulfides and with Bi-Te-Ag-

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fractionation Pb-S mineral assemblages are represented by electrum of two generations, and minor maldonite (*Au<sub>2</sub>Bi*). According to the result of the sulfur isotope fractionation geothermometer the temperature of base metal crystallization was in the range from 322 to 289°C (Mikulski 2005a). Low temperatures of late hydrothermal solutions from 207 to 177°C are also indicated by chlorite geothermometry on chlorite from altered peraluminous rocks as estimated by Machowiak, Weber-Weller (2003).

## METHODS OF INVESTIGATION

Detailed microscopic studies in reflected light were complemented by microprobe investigations using an EDX Link ISIS System coupled with a JEOL JSM-35 electron microscope at the Polish Geological Institute in co-operation with E. Starnawska (Mikulski 2001). Operating conditions were 20 kV, 2 µm spot size, and 10 nA sample current for arsenopyrite. Calibration was on international standards of arsenopyrite (ASP-200 and ASP-57), and the ZAF-4 correction program was used for semi-quantitative data reduction.

## ARSENOPYRITE GEOTHERMOMETRY

Three groups of arsenopyrites with different contents of As and S from the Radzimowice deposit have been recognized (Fig. 1). Arsenopyrite of the first group (*Asp I*) occurs minor as fractured single big grains of a columnar habit from 0.3 mm up to a several mm in size and major as massive aggregates. In some samples loellingite forms intergrowths with arsenopyrite. Beside, that inside arsenopyrite, it is possible to find fine remnants of loellingite or inclusions of pyrrhotite. These arsenopyrites also may contain inserts of younger association minerals such as gold, bismuth and tellurium minerals. Arsenopyrite I, especially from richest in gold sulfide ores from the northern part of deposit, revealed a constant cobalt admixture from 0.48 up to 6.36 atom.% Co (arithmetic mean  $x_{n=28} = 3.3$  atom.% Co). These Co-bearing arsenopyrites show compositional variation ranging from 34.81 up to 37.45 atom.% As with an arithmetic mean of 35.81 atom.% As, ( $\sigma = \pm 1.43$ );  $n=28$  measurements. They have from 2 up to over 3 atom. % deficiencies of sulfur.

Arsenopyrites of II type (*Asp II*), form single grains of rhomboedric shapes up to 1 mm in size or crystalline aggregates intergrown with gangue minerals (quartz). They may contain also Co admixtures what make them similar to arsenopyrites of the first type. However, arsenopyrite II contains usually lower Co admixture, <1 atom.%. The composition of arsenopyrites II is ranging between 32.01 and 34.13 wt.% As. Arithmetic mean of these arsenopyrites is 33.11 atom.% As ( $\sigma = \pm 1.21$ ) close to stoichiometric value. Meanwhile, their sulfur content, like arsenopyrites of the first type, characterized by a decrease of sulfur from 1 up to 2 atom.%. Conditions close to arsenopyrite-pyrrhotite-loellingite buffer  $fS_2$  have been assumed only for these arsenopyrites that contain Co admixture less than 1 atom.% Co, (As content varies from 32.21 to 33.81 atom.% As).

Arsenopyrite of the third type (*Asp III*) is different from previous. Arsenopyrites III occur as fine-grained euhedral crystals in narrow quartz veinlets cut dacite porphyries that are associated with pyrite or/and galena veinlets and sulfosalts. Arsenopyrites of 3<sup>rd</sup> type are of thinly rhomboedric or acicular habits and may form cross twins of crystals. These arsenopyrites are representing youngest generation. They contain below 31 atom.% As and

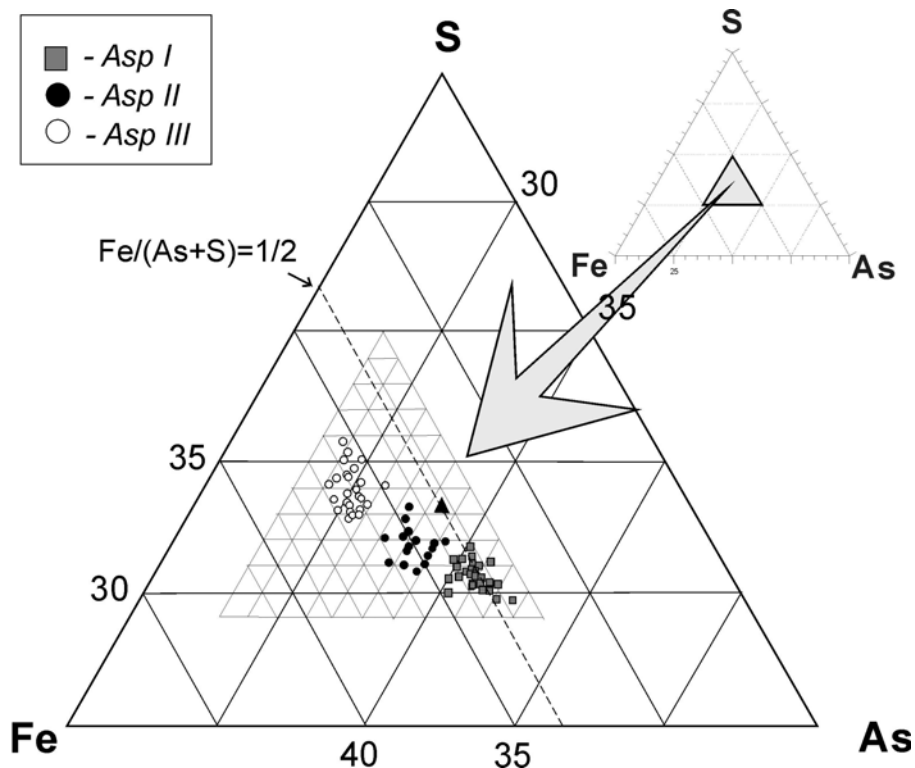


Fig. 1. Plot of the atomic percent composition of arsenopyrites from the Radzimowice deposit. *Abbreviations: Asp I* - arsenopyrite of the first type with high Co-admixture; *Asp II* of the second (intermediate) type; *Asp III* – arsenopyrite of the third (youngest) type.

have an arithmetic mean value of 29.95 atom.% As ( $\sigma = \pm 0.58$ );  $n=25$  and are free of admixtures. These arsenopyrites composition range from 28.75 to 30.98 atom.% As.

#### DISCUSSION

Arsenopyrites of the first type (*Asp I*) characterised by a high cobalt admixture and they are not suitable for geothermometry except only a several found arsenopyrite grains that have Co-admixture below 1 atom.% (As content varies 34.81-35.49 atom.% As). To establish a temperature range for these arsenopyrites, it should be assume that the beginning of this crystallization took place at the arsenopyrite-pyrrhotite-loellingite buffer  $fS_2$  due to pyrrhotite appearance and loellingite intergrowths. However, the presence of pyrrhotite is limited only to small inclusions in arsenopyrites. According to the isopleths of arsenopyrite composition in the  $\log fS_2 - T$  from Kretschmar, Scott (1976), modified by Sharp *et al.* (1985), the temperature ranges between 495 and 535°C. Taking into consideration that these arsenopyrites contain high Co and Au admixtures obtained crystallization temperatures seems to be questionable.

Arsenopyrite II (*Asp II*) contained much less admixtures of Co ( $\ll 1$  atom.%) and characterised by more homogenous composition. *Asp II* could have originated at temperatures of 345 to 455°C (arithmetic mean = 400°C) along the arsenopyrite-pyrrhotite-loellingite buffer. Obtained temperatures of *Asp II* crystallization from 345 to 455°C are in good agreement with data presented by Machowiak, Weber-Weller (2003). According to

them the crystallization temperature of arsenopyrite-pyrite assemblage range from 368 to 428°C calculated on the basis of the fractionation of S isotopes between these minerals. According to Kretschmar, Scott (1976) the most common association of arsenopyrites in nature is with pyrite.

Arsenopyrite III (*Asp III*) has composition range from 28.75 to 30.98 atom.% As, equivalent to temperature ranges between 370°C and below 300°C using the arsenopyrite-pyrite buffering curve after Kretschmar, Scott (1976), modified by Sharp *et al.* (1985).

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