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CONDITIONS OF CASSITERITE FORMATION IN THE RĘDZINY AREA (WESTERN SUDETES, POLAND)

Abstract: Thermochemical conditions under which cassiterite formed in the Rędziny area have been determined on the basis of compositions and texture relations among coexisting sulphides and sulphosalts as well as homogenization temperatures of liquid inclusions present in cassiterite. Cassiterite precipitated from medium-saline (13-5 wt.% NaCl equivalent), acidic hydrothermal solutions (pH \approx 3-4) under 0.8-0.9 kb and at 412-285°C simultaneously with crystallization of base-metal sulphides and the youngest arsenopyrite. Sulphur and oxygen fugacities, expressed as $\log f_{S_2}$ and $\log f_{O_2}$, changed progressively during this stage from -6.5 to -10.5 ± 0.5 and from < -38 to at least -25, respectively. Reducing character of the ore-forming hydrothermal solutions is emphasised by Ti-enrichment in crystals of the earliest cassiterite.

Key-words: Rędziny, cassiterite, temperatures, sulphur fugacity, oxygen fugacity.

INTRODUCTION

The presence of cassiterite in Rędziny was first mentioned by Gołębiowska, Pieczka (1997). Ore mineralization containing cassiterite is associated there with a contact zone of dolostones with schists and amphibolites of the Kowary-Czarnów Unit that surrounds from E the Karkonosze granite intrusion. Arsenopyrite, cassiterite, base-metal sulphides and sulphosalts occur as disseminated grains mostly in schists and amphibolites, and less frequently as fragments of small ore veins and nests, which can be found especially in the W and NW walls of the active dolostone quarry. Primary ore mineralization has been strongly altered by weathering giving a wide spectrum of hipergenic minerals (Gołębiowska 2003).

METHODS OF INVESTIGATIONS

Thermochemical conditions under which the cassiterite mineralization formed have been established from some mineral assemblages containing cassiterite with coexisting arsenopyrite, base-metal sulphides, haematite, pale-coloured mica and chlorite on the basis of compositions of those minerals and texture relations among coexisting phases as well as homogenization temperatures of liquid inclusions in cassiterite.

Optical observations were carried out using an OLYMPUS BX-12 microscope. Chemical compositions of sulphide minerals, cassiterite, micas and chlorite 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. Conditions under which the large assemblage of sulphides and sulphosalts

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crystallized (temperature and sulphur fugacity fS_2) have been described in details by Pieczka *et al.* (2005). The temperature and pH of ore-forming hydrothermal solutions have been established from the stability fields of pale-coloured mica and chlorite (Patterson *et al.* 1981) using an X-ray chlorite geothermometer (Battaglia 1999), while oxygen fugacity fO_2 from thermochemical data of Afifi *et al.* (1988) and Simon, Essene (1996) describing stabilities of many sulphide phases, hematite, and barite coexisting with selenides and tellurides.

RESULTS AND DISCUSSION

In the quarry of dolostones in Rędziny cassiterite can often be found in the NW walls, although its traces were also observed on the E side of the quarry. Cassiterite accumulations reaching some millimetres occur in the fragments of quartz-arsenopyrite-chlorite veins, where it especially coexists with arsenopyrite, and also in the fragments of mineralized amphibolites in the E wall, where is accompanied not only by arsenopyrite, but also by pyrrhotite, glaucodot, pyrite and chalcopyrite. Textural relations between cassiterite and sulpharsenides indicate that the cassiterite crystallization overlapped the final stage of arsenopyrite formation. It is unequivocally corroborated by the homogenization temperatures of fluid inclusions, indicating for the cassiterite from Rędziny crystallization at 412-285°C and $p = 0.9-0.8$ kbar (Mochacka *et al.* 2001). Thus, the upper temperature of this range corresponds with the medium stage of arsenopyrite crystallization, established at around 500-370°C (Pieczka *et al.* 2005). Small intergrowths of prismatic crystals of cassiterite were also observed inside the grains of dark brownish sphalerite with inclusions of ferrokesterite and Zn-bearing chalcopyrite. Being older than this mineral assemblage, they must have crystallized at the temperatures higher than 320°C, determined as the lower temperature of such a sphalerite formation (Pieczka *et al.* 2004). Larger accumulations of cassiterite occur in relicts of mineralized quartz veins (or nests), in which most of primary ore minerals have been oxidized and altered into goethite, hematite, farmacosiderite, yukonite, arseniosiderite, conichalcite, hemimorphite, malachite, chrysocolla, *etc.* (Gołębiewska 2003). Cassiterite was also found in accumulations of talc, and even in the dolomite overgrowing accumulations of secondary Fe and Cu minerals. It forms there single grains even 2-3 cm large or string-like intergrowths, usually yellowish-brownish, yellow or yellow-green, with strong vitreous lustre, mostly poorly zoned, with weak, yellowish pleochroism. In one point a very rich cassiterite accumulation was found, with cassiterite making up even >50 vol. % of the species up to 20 cm in diameter. Distinctly prismatic crystals of this cassiterite are dark steel with metallic lustre in hand specimens and reveal under the microscope excellent oscillatory zoning, composed of dark-brown (Fe-rich) and light (Fe-poor) bands.

Cassiterite from Rędziny is heterogeneous in its composition. Practically it does not concentrate Mn, Nb and Ta and the amounts of these elements are usually below the detection limits of the WDS mode (0.0X wt.%). The same can be said on W, although sometimes its amounts in the range 0.X wt.% and, in single cases, even exceeding 1 wt.% were noted. The main admixtures are Fe (up to 2.0-2.5 wt.%) and Ti. The ratio of Fe/W \approx 2:1 indicates that W in the structure of this cassiterite appears as a result of limited miscibility between SnO₂ and Fe₂WO₆, as it was noted by Möller *et al.* (1988) and Serranti *et al.* (2002). The amount of Ti is an important factor in establishing conditions of cassiterite crystallization. Since Ti is a mobile element under strongly reducing conditions, its presence in some of the cassiterite grains of Rędziny proves their forming from hydrothermal solutions with just such a character. The content of Ti changes from about 2.5 wt.% TiO₂ in cassiterite inclusions in dark sphalerite crystallizing above 320°C to around

1.5 wt.% TiO₂ in cassiterite younger than the arsenopyrite-pyrrhotite aggregates from the E wall of the quarry to about 0.X, and usually even 0.0 wt.% in cassiterite from strongly oxidized ore-accumulations containing only relictic grains of chalcopyrite, pyrite and haematite. It indicates that Ti activity in hydrothermal solutions decreased during crystallization of various cassiterite generations.

Tin in acid hydrothermal environments is transported as reduced alkali-bearing chloride and hydroxy-chloride stannous complexes, *eg.* SnOHCl, SnCl₂, KSnOHCl₂, NaSnOHCl₂, KSnCl₃, NaSnCl₃, *etc.*, and precipitation of SnO₂ is favoured by decreasing fluid acidity as well as aqueous alkali/acid and K/Na ratios, and by oxidizing conditions (Taylor and Wall 1993). The hydrothermal solutions, from which the cassiterites of Rędziny formed, contained mainly dissolved NaCl with small admixtures of CaCl₂. An initial salinity about 13 wt.% of NaCl equivalent dropped in final stages to almost 5 wt.%. The pH of mineralizing solutions can be evaluated at around 4 from the stability conditions of chlorite and light mica around 180-220°C (X-ray chlorite geothermometer). Under these conditions the precipitation of cassiterite involves an oxidation of Sn²⁺ to Sn⁴⁺ according to the reaction $\text{SnCl}_2^0 + \text{H}_2\text{O} + 0.5\text{O}_2 = \text{SnO}_2 + 2\text{H}^+ + 2\text{Cl}^-$, and the process depends critically on the $f(\text{O}_2)$ (Patterson *et al.* 1981, Heinrich, Eadington 1986, Taylor, Wall 1993). It is difficult to determine the oxygen fugacity $f(\text{O}_2)$ in initial stages of cassiterite precipitation at about 400°C, but it can be assumed to be exceptionally low. The lowering of $f(\text{O}_2)$ in this stage resulted from earlier precipitation of rutile and titanite, and the earliest cassiterite is characterized themselves by a content of several percents of TiO₂. A tendency of $f(\text{O}_2)$ changes can be assessed in medium and final stages of cassiterite precipitation, from the formation of the assemblage: dark sphalerite – stannite – Zn-bearing chalcopyrite till the end of its crystallization at about 285°C, and even slightly lower. If 300±20°C is accepted as the mean temperature of this stage, the $f(\text{O}_2)$ values can be determined from the diagrams of stabilities of sulphides, selenides and tellurides (Afifi 1988, Simon, Essene 1996). The assemblage dark sphalerite – stannite – Zn-bearing chalcopyrite occurs in Rędziny in arsenopyrite-chlorite-quartz veins. In the central parts they contain a disseminated mineralization of Cu(Ag)-Pb-Bi(Sb)-sulphosalts (mainly aikinite) that crystallized at the temperature about or slightly above 300°C, Bi-sulphides (mainly ikunolite, in which S is usually replaced by Se up to 50 at.%) intergrown with chalcopyrite, and bismuth (the temperatures around 320° down to about 260°C); the ore minerals mentioned are embedded in quartz that contains in places crystals of barite, relicts of chalcopyrite and pyrite grains and haematite flakes. It can be concluded that the crystallization sequence: arsenopyrite → cassiterite → Cu(Ag)-Pb-Bi(Sb)-sulphosalts → sphalerite–stannite–Zn-chalcopyrite → chalcopyrite–ikunolite–bismuth → barite(?) → haematite → quartz combined with the lack of barite among the grains of arsenopyrite and cassiterite may point to the crystallization of cassiterite slightly above 300°C (up to about 350°C) at the oxygen fugacity expressed by the $\log f(\text{O}_2) < -38$, at which BaS is oxidized to barite (oxygen fugacity around $\log f(\text{O}_2) \approx -38$ has been attained later during filling central parts of such veins). At 350°C the stability of cassiterite in the SnS/SnO₂ system is described at the $\log f(\text{O}_2)$ about -36 (Patterson *et al.* 1981). The flakes of haematite often form garlands around earlier-crystallized aggregates of quartz and ore minerals and indicate a progressive increase of $f(\text{O}_2)$ up to the value of $\log f(\text{O}_2)$ close to -(31-30). Bismite Bi₂O₃ in the most frequent form of grape-like rims up to few millimetres overgrowing the core of bismuth has been observed in the assemblage of Bi-sulpho-tellurides. Although the formation of bismite is usually attributed to the hypergenic stage, one must consider the fact that Bi is refractory to chemical alterations. It means that at temperatures lower than about 260°C, *i.e.* after the crystallization of cassiterite, the oxygen fugacity expressed as

$\log f(\text{O}_2) \approx -25$ must have been at least locally reached, as it is the value initiating oxidation of Bi to Bi_2O_3 .

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