

Complex tin-bearing sulphides of the South Chinese ore type

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Abstract: In the Chinese skarn deposits of Dachang and Shizhuyuan unusual mineral associations include: silver-enriched stannites containing mercury and arsenic producing stannite-kesterite-velikite mixed crystals with transitions to stannite-luzonite.

Traces of bivalent tin replace lead in jamesonite and bournonite. Teallite was observed, and franckeite with tin in two valency state has constant amounts of Sn^{2+} and varying concentrations of Sn^{2+} as substitute for Pb^{2+} .

In Shizhuyuan, manganese-bearing stannite was found to react with wolframite producing normal stannite and Mn-enriched wolframite. Mn-bearing stannite was found to be unstable with pyrrhotite, as the mineral phases would react to produce normal stannite and alabandite.

The mineral phases pyrite, pyrrhotite, bismuthinite and native bismuth were found to occur closely associated, partly intergrown, displaying either formation temperatures around 200°C (invariant reaction) or preserved disequilibria which remain after stages of mineral formation and/or metamorphism.

Asian tin-tungsten deposits are mostly exploited as placers. Of these, cassiterite, wolframite are the heavy minerals of commercial interest but none or very little information is available on the primary sulphides which occur in the unweathered country rocks below. Also, hardly any attention has been paid to varlamoffite, a common break down product of tin-bearing sulphosalts. Drill cores of the hard rocks and information of their opaque minerals are only rarely available, except in cases of underground mining.

Some of the ore mineral associations have been studied employing techniques such as reflected light microscopy, X-ray spectrometry, electron probe, AAS and spectrochemical analytical procedures. Such studies were contemporaneous with experimental studies. The detailed investigations revealed very complex mineral assemblages and present many similarities to the Bolivan ore type.

The occurrences discussed here mainly concern the polymetallic skarn deposits at Dachang, Guangxi province, and Shizhuyuan, Hunan province, in China. These are compared with the tin deposits in Malaysia.

In all these mines and localities, several stages of mineralization and/or metamorphism took place, and the ore minerals of interest contain sulphides and sulphosalts, of which stannite is the most common. During the last few decades a number of stannite-type minerals have been described (Moh, 1975; Moh, 1984).

Besides stannite ($\text{Cu}_2\text{FeSnS}_4$) and kesterite ($\text{Cu}_2\text{ZnSnS}_4$) and their mutual solid solution members, the silver-rich end-members hcartite ($\text{Ag}_2\text{FeSnS}_4$) and pirquitasite ($\text{Ag}_2\text{ZnSnS}_4$) were found elsewhere as naturally occurring minerals while cernyite ($\text{Cu}_2\text{CdSnS}_4$) and velikite ($\text{Cu}_2\text{HgSnS}_4$) belong to the thio-stannates.

Microprobe analyses of the stannites of selected Dachang ores revealed distinctly silver-enriched stannite-kesterite-velikite mixed crystals, similar to that mentioned in a Peruvian occurrence by Burkart-Baumann & Amstutz (1982). Other observed trace elements were Cd, As, and In. The mercury enrichment in the stannites can be attributed to the relatively high Hg-concentration within and particularly around the Dachang mining area. Silver on the other hand is a commercial extract of the ores, and diaphorite ($\text{Pb}_2\text{Ag}_3\text{Sb}_3\text{S}_8$), pyrargyrite (Ag_3SbS_3) as well as native silver traces were observed in the polished sections with stannite. Indium has been analyzed as a common trace element in many stannites all over the world (Gmelin, 1936; Moh 1984). The stannite lattice however, takes approximately 1 wt% As, indicating a solid solution towards luzonite (Cu_3AsS_4) or stanno-luzonite, respectively (Wang, 1982 and Moh, 1984).

Since varlamoffite is known as a common stannite alteration product, semi-quantitative analyses of different Malaysian varlamoffite occurrences could give some evidence for the original tin-bearing sulfosalts and complex stannite compositions with respectable silver-contents (Traub & Moh, 1978).

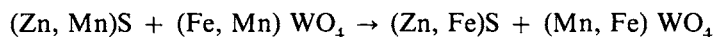
In sulphosalts, tin commonly occurs in its tetravalent state as, for instance, in the 'stannite group'. Minerals with mixed valencies of Sn^{4+} and Sn^{2+} or minerals with only bivalent tin e.g., teallite (Pb Sn S_2) which was recognized by Ramdohr in some of the Dachang polished sections (Heidelberg collection No. 12633 and 12641) has bivalent tin substituting for Pb^{2+} in an unusual jamesonite (Ramdohr, Moh & Bernhardt, 1982). The tin contents of 0.14 wt%, was fairly low, but arsenic was also found replacing antimony in jamesonite up to 1 wt% As.

A peculiarity was the observation of traces of tin in bournonite. At first one could think of contamination caused by impurities of either cassiterite or stannite which, of course, cannot be excluded. This led to experimental investigations resulting in the finding of a limited substitution of Sn^{2+} for Pb^{2+} up to a maximum of no more than 5 wt% in the bournonite lattice. This could account for the observed tin traces in the mineral (Cai, 1984).

The rare mineral franckeite has been found only in a few localities, mostly in Bolivia, in the Soviet Union, and in Canada. It is also interesting to note the observation of franckeite in respectable amounts in the Dachang ores, which justifies detailed research. Two microprobe analyses, one with 0.46 wt% Ag and one silver-free, were compared with numerous other franckeite occurrences and discussed with respect to crystal-chemical considerations (compare Bernhardt, 1984). Systematically performed experiments on franckeite resulted in findings of a fairly large solid solution range with the general formula $(\text{Pb, Sn})_{6-x}^{2+} \text{Sn}_2^{4+} \text{FeSb}_2\text{S}_{14-x}$ ($x = 0 - 1$) for silver-free franckeite: from lead-rich potosiite through intermediate incaite up to a lead-free composition which has not yet been found as a mineral in nature. Obviously in the

presently recognized franckeite, tin occurs in two valency states, with a constant amount of Sn_2^{4+} in addition to a variable amount of bivalent tin replacing Pb^{2+} in the franckeite structure (Li, 1984).

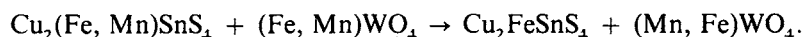
The varying distribution of tin, tungsten and other elements in silicates and oxides of skarns and pegmatites is of mineralogical interest, particularly as a result of chemical metamorphism, i.e. sulphidization. Considering Fe- and Mn-contents of wolframite and coexisting sphalerite, evidence of mutual reactions is obvious during or after formation at elevated temperatures. In this respect, reactions between manganese-bearing sphalerite and wolframite may take place, resulting in manganese-free but iron-enriched sphalerite and increased Mn-contents in the wolframite. The simplified reaction



was observed in ores of Russian origin (personal communication by Galina Ivanova, 1981).

Quite similar observations have been made in the Shizhuyuan skarn ore, and the sequence of reactions becomes clear when comparing the transition elements ^{25}Mn up to ^{30}Zn of the periodic table. For instance, ^{25}Mn has the highest affinity to oxygen and a very low affinity to sulphur. With increasing atomic numbers the chemical properties of the elements change gradually. The element ^{30}Zn is characterized by a high affinity to sulphur and a much lower one to oxygen. This change can be simply expressed as: $\text{MnS} + \text{ZnO} \rightarrow \text{ZnS} + \text{MnO}$. In the following simplified equation the element pair ^{25}Mn and ^{26}Fe has to be considered which shows the same tendency of reactions: $\text{MnS} + \text{FeO} \rightarrow \text{FeS} + \text{MnO}$.

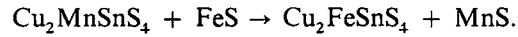
Shizhuyuan is recognized as a large tungsten-tin-molybdenum-bismuth skarn deposit with respectable beryllium enrichments and an intensive sulphide mineralization at the last stage. Tin cannot be extracted economically due to the finely dispersed cassiterite and intergrowths throughout the metamorphosed country rocks. In addition these minute cassiterite grains show commonly thin incrustations of stannite under the microscope. However, at least some of these secondary tin sulphosalts are manganese enriched although pure Mn-stannite, $\text{Cu}_2\text{MnSnS}_4$, has not been found yet in nature. These Mn-contents have reacted with wolframite, probably after sulphidization, as a result of heat during metamorphism. The simplified reaction is



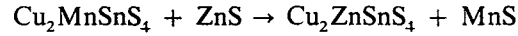
Wolframite isolated stannites remain unaffected, only stannite-wolframite intergrowth formation proceeded following the affinity tendency as discussed above. Besides traces of cassiterite, stannite, wolframite and molybdenite, no other ore minerals were observed in the analyzed polished section.

The manganese concentration in the Shizhuyuan ore body is considerable. In addition to numerous Mn-bearing silicates, rhodonite, rhodochrosite and alabandite were reported. Thus, the existence of Mn-enriched stannite becomes obvious. The stannite—kesterite—Mn-stannite stability relations were studied in some detail and

applied to known natural occurrences by Jang (1984a). In this connection it should be noted, that intergrowths of pyrrhotite and Mn-stannite are unstable as they would react to form normal stannite and alabandite as follows:



Similar reactions involving sphalerite and kesterite occurring as



or

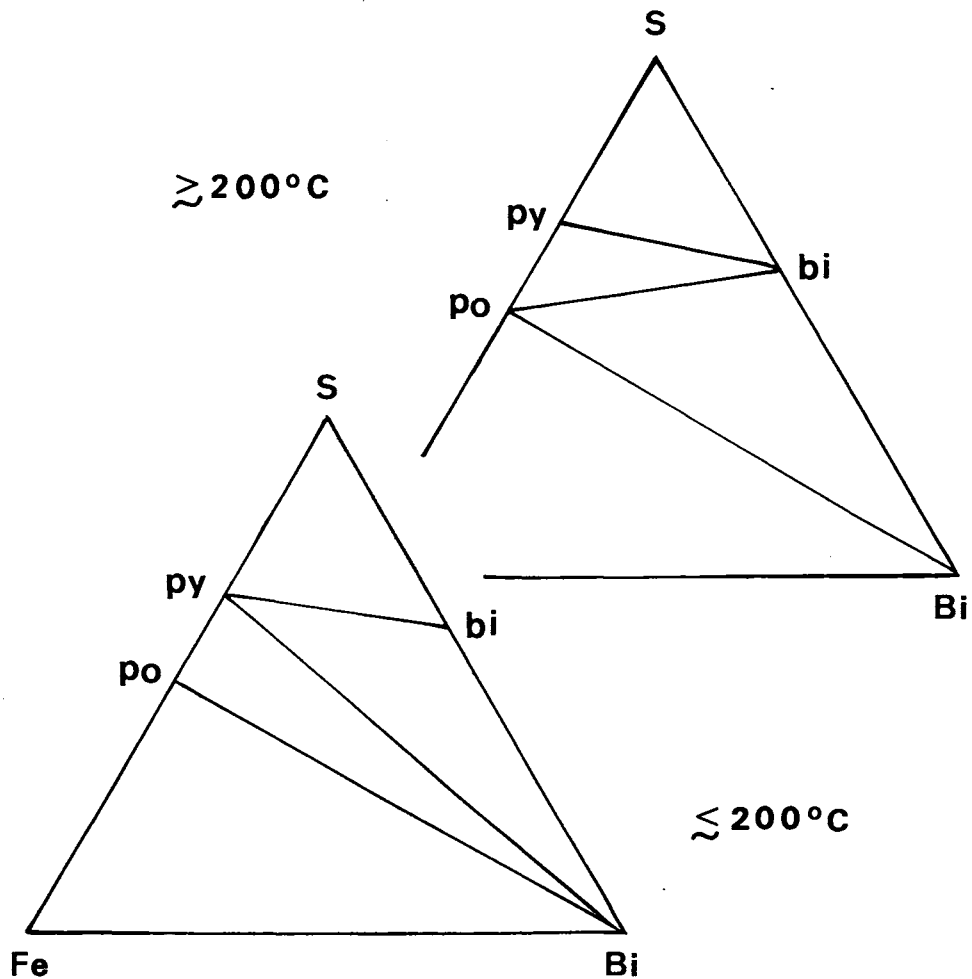
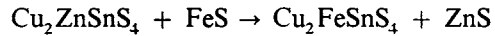
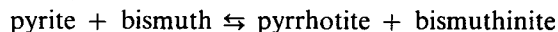


Fig. 1. Schematic illustration of phase relations within the ternary system iron-bismuth-sulfur showing two different isotherms above and below approx. 200°C. Abbreviations: py = pyrite, po = pyrrhotite, bi = bismuthinite.

were observed and are directly applicable to the respective mineral associations (Jang, 1984b).

Another interesting observation of the Shizhuyuan ores are mineral associations involving pyrite, pyrrhotite, bismuthinite, and native bismuth in one and the same specimen. With regard to calculations by Bente (1982), the invariant reaction:



can be deduced as taking place in the presence of vapour at 197°C. The resulting simplified phase relations given in figure 1 indicate that the following stable mineral associations occur at low temperatures, pyrite + bismuth + bismuthinite, and pyrite + pyrrhotite + bismuth, but above approximately 200°C pyrite + pyrrhotite + bismuthinite, and pyrrhotite + bismuthinite + bismuth. In the ore specimen concerned, mixtures of all four mineral phases were found closely associated and partly intergrown, indicating either formation temperatures around 200° or preserved disequilibria which probably remain after stages of mineral formation and/or metamorphism.

Laboratory experiments with mixtures of pyrite and bismuth heated for extended time periods far above the variant temperature and even beyond the melting point of bismuth (271°C) up to 375°C were without any visible reaction, probably due to sluggish reaction kinetics of pyrite. Quench products of charges heated above 400°C revealed under the microscope (oil immersion), seams of bismuthinite and pyrrhotite mixtures surrounding metallic bismuth, showing that pyrite partly started to decompose (Neukirch, 1983). The presently discussed unusual coexisting mineral assemblages were also observed elsewhere (personal communication by G. Kullerud, 1982).

Be-minerals are often common in tin-tungsten deposits. In Shizhuyuan the minerals beryl, chrysoberyl, taaffeite, phenakite, bertrandite, and helvite have already been described (Mining-Report Shizhuyuan, 1980).

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Manuscript received 1st Sept. 1984