

THE PSEUDOINARY SYSTEM $\text{Cu}_2\text{FeSnS}_4$ - $\text{Cu}_2\text{ZnSnS}_4$ AND ITS MINERALOGICAL SIGNIFICANCE

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ABSTRACT

The phase relations in the pseudobinary system $\text{Cu}_2\text{FeSnS}_4$ - $\text{Cu}_2\text{ZnSnS}_4$ (stannite-kesterite) were determined between 300°C and the melting and decomposition temperatures that range from 878 to 1002°C. Quenching and DTA experiments were employed using silica tubes as sample containers. Unlimited solid solubility was found to occur above about 680°C, but below this temperature there are two different stannite-kesterite phases separated by a miscibility gap. Natural stannite-kesterite exsolutions are explained in the light of the experimental results. It is pointed out that zincian stannite can serve as a geological thermometer.

INTRODUCTION

Intergrowths of stannites of varying chemical compositions and optical properties have occasionally been reported in the literature (e.g. Ramdohr 1960; Oen 1970). A good example of an apparent exsolution of one kind of stannite from another has recently been found in an ore from British Columbia (Harris & Owens 1972), and has initiated an investigation into the phase relations of the synthetic system $\text{Cu}_2\text{FeSnS}_4$ - $\text{Cu}_2\text{ZnSnS}_4$. Although this system is not strictly binary, but part of a more complicated phase relationship (Moh 1960, 1963, 1969), it was nevertheless hoped that even a restricted experimental study could shed light upon some of the many problems that are connected with the stannite group of minerals.

METHOD OF INVESTIGATION

The phase equilibrium study was carried out using the customary evacuated and sealed silica tubes as sample containers. Both quenching experiments and differential thermal analyses were conducted. For the latter purpose, the tubes were provided with a coaxial thermocouple well.

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The capsules were charged with either pure elements mixed in appropriate proportions or with mixtures of previously synthesized Cu_2FeSn_4 and Cu_2ZnSn_4 . High-purity sulphur (99.999%) was supplied by the American Smelting and Refining Company, New York, spectrographically standardized zinc, iron, and copper in rod form (total metallic impurities less than 10 ppm) came from Johnson, Matthey and Co., London, and tin pellets (99.999%) were purchased from the Consolidated Mining and Smelting Company of Canada, Montreal. A powder was produced from the metal rods by filing.

In the case of the DTA runs, Brazilian quartz was added to provide a calibration temperature (α - β inversion at 573°C). 30 mg of quartz was used together with 100 mg of sulphide to make the heat effects quantitatively comparable.

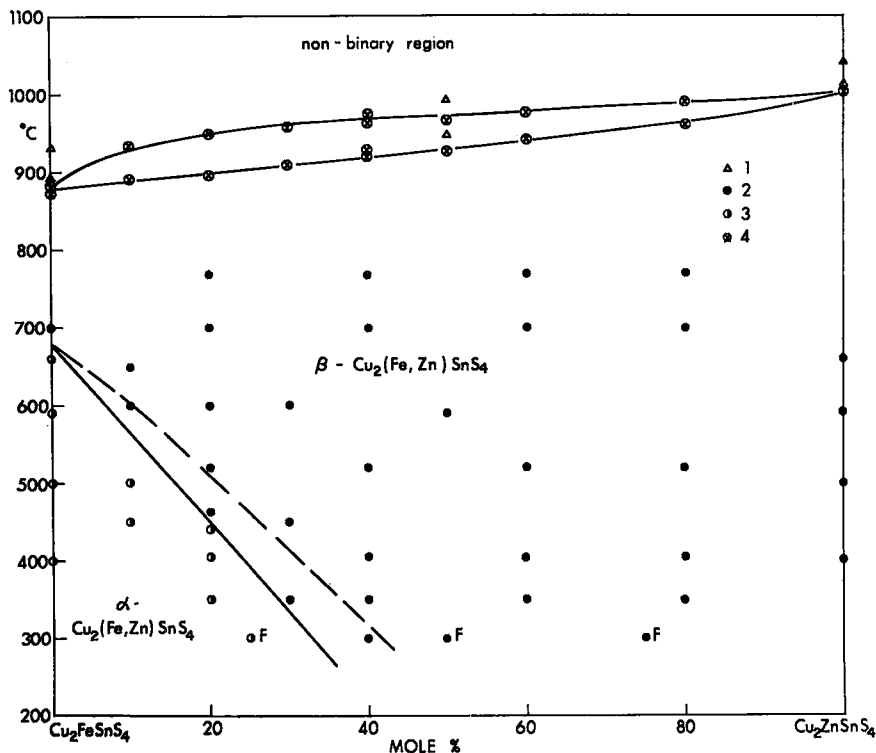


FIG. 1. Experimental points and phase relations in the pseudobinary system Cu_2FeSn_4 - Cu_2ZnSn_4 . 1 = partially or completely molten charges (see text). 2 = stannite-kesterite solid solution with no absences in *x-ray* powder pattern. 3 = stannite-kesterite solid solution with absences in *x-ray* powder pattern. 4 = maxima of endothermal peaks on DTA heating curves. F denotes that a flux was used. Vapour was present with all phases.

For the quenching experiments the capsules were inserted into horizontal tube furnaces and heated for periods of several days or weeks. Since it was found that at 300°C not even runs of 3-month duration could produce complete equilibrium, a flux was added to some of the charges. This consisted of a eutectic mixture of 44 wt % NH_4Cl and 56 wt % LiCl which has a melting point of 265°C . The sulphide:salt weight ratio was 1:4 and the reaction time at 300°C had to be kept in excess of 2 months for sufficient equilibration.

The quenched reaction products were investigated by reflected light microscopy of polished mounts and by x-ray powder diffraction analysis using a Guinier focussing camera. Electron microprobe analyses were carried out on some samples.

EXPERIMENTAL RESULTS

The results of the quenching and DTA experiments are summarized in Figure 1. The salient features of the diagram are that $\text{Cu}_2\text{FeSnS}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ form a complete solid-solution series from about 680°C to the melting and decomposition points which range from 878°C upwards. Below about 680°C the solid solution series is broken due to a structural change observable in the iron-rich members.

The upper limit of stability of the stannite solid-solution series was determined by DTA. Endothermic peaks were recorded at $878 \pm 3^\circ\text{C}$ for the iron end-member, and at $1002 \pm 3^\circ\text{C}$ for the zinc end-member. Macroscopic inspection of charges held above these temperatures showed that at least partial melting had taken place. For the intermediate members the peaks occurred at temperatures between 878 and 1002°C and were split into two, thus indicating that the charges had not only melted but had reacted in a more complex way. The lower of the two peaks decreased in intensity with rising zinc content whereas the one at a higher temperature increased along this concentration gradient and reached a maximum for pure $\text{Cu}_2\text{ZnSnS}_4$. The peak temperatures are plotted in the graph and are those measured during heating of the samples at a rate of about 3°C per minute. There were corresponding peaks on the cooling curves, but these usually fell at about 20 - 50°C below those on the heating curve. Cooling was not controlled at a fixed rate but varied from 3 - $15^\circ\text{C}/\text{min}$ depending on the natural heat loss from the furnace after power cut-off. Therefore no particular quantitative significance was placed on the cooling-curve effects. The considerable discrepancy between the heating and cooling

signals might be accounted for by vapour condensation, delayed solidification and other retardations.

X-ray powder photographs of the charges quenched from above the temperatures indicated by DTA yielded the usual stannite pattern but with additional lines that could be attributed to herzenbergite (SnS). However, reflected-light microscopy of polished sections, aided by electron probe analysis, revealed a complex and diversified assemblage. The Fe-stannite apparently melted completely and the quenched melt consisted of $\text{Cu}_2\text{FeSnS}_4$ with minor amounts of SnS. The $\text{Cu}_2\text{Fe}_{0.5}\text{Zn}_{0.5}\text{SnS}_4$ charges were found to contain bluish grey, isotropic cores of a zinc-rich phase of approximate composition $\text{Cu}_2\text{SnFeZn}_8\text{S}_{10}$ surrounded by buff-coloured anisotropic rims consisting of two very closely intergrown phases with an average composition of $\text{Cu}_7\text{Fe}_2\text{Sn}_8\text{S}_{12}$. SnS and other metal-rich phases were present in small quantities and clearly constituted decomposition products. The iron-free $\text{Cu}_2\text{ZnSnS}_4$ charge also consisted of zinc-rich cores of $\text{Cu}_2\text{Zn}_3\text{SnS}_8$ composition surrounded by buff-coloured rims of two phases of which the predominant one had the composition Cu_2SnS_3 . In between the rim/core aggregates two whitish phases were concentrated that were identified as Cu_2SnS_2 and SnS.

Both the DTA and the quenching experiments show that at high temperatures the system $\text{Cu}_2\text{FeSnS}_4$ - $\text{Cu}_2\text{ZnSnS}_4$ can no longer be considered binary. A final elucidation of the phase relations under these conditions must wait until the complete Cu-Fe(Zn)-Sn-S system has been analyzed in detail.

At about 680°C, a phase transition appears to take place in $\text{Cu}_2\text{FeSnS}_4$. This transition, which is reached at corresponding lower temperatures as zinc increases, is evident through the absence of some of the diffraction lines which normally arise in the patterns of kesterite and high-temperature stannite. A list of the x-ray reflections of zincian stannite is given by Berry & Thompson (1962, p. 52, no. 70) and these data apply to pure kesterite and high-temperature zincian stannite as well. The list may be supplemented by reflections at 1.813 Å (222), 1.789 Å (301), and 1.720 Å (310) which are very weak but clearly discernible on the Guinier films. It was observed, however, that the low-temperature iron-rich member did not display the lines 011, 013, 121, 123, and 301. The abrupt appearance or absence of these reflections depending on temperature and composition is a very striking feature of the x-ray patterns. If the absences are systematic, they indicate that reflections hkl are present only if l is even, and this would be incompatible with the presently accepted structure of stannite as determined by Brockway (1934). Whatever the nature of the structural

change, its occurrence is clearly indicated and an explanation will ultimately have to be left to a single-crystal diffraction study.

The two structurally different stannite-kesterite phases — a low-temperature (α) form that exhibits absences and a high-temperature (β) form that does not — must be separated by a two-phase region on the phase diagram as shown on Figure 1. It is difficult to determine the exact limits of the two-phase field on the zinc-rich side since the two forms have almost equal lattice spacings and are only distinguishable by the above noted reflections. The x-ray pattern of a mixture of the high- and low-temperature phases closely resembles that of the high-temperature form alone. It was decided that the charges that displayed the critical lines weakly belonged to the two-phase assemblage, whilst material with these lines strong or absent were in the one-phase regions.

Apart from the above mentioned abrupt structural break in the solid-solution series, other properties seemed to vary continuously. The change in reflectivity between stannite and kesterite was found to be small (about 2%), yet gradual, with the general appearance of kesterite being greyish-white in comparison to the lighter, olive-green tint of stannite. More conspicuous, however, than the change in reflectivity is the variation in the anisotropic behaviour. Kesterite, although discernibly anisotropic is considerably less so than stannite.

According to Berry & Thompson (1962) stannite has the lattice parameters $a = 5.47 \text{ \AA}$, $c = 10.746 \text{ \AA}$ and zincian stannite has $a = 5.44 \text{ \AA}$, $c = 10.88 \text{ \AA}$. Due to the near equality of the lattice dimensions there are only slight shifts in the line positions on the powder films. However, while in zincian stannite the reflections 020 and 004, and 022 and 024 coincide since $a = c/2$, they are clearly separated for iron stannite. From the amount of separation of the 020 and 024 reflections the value of $2a-c$ can be determined. It was found to be 0.19 \AA which is in close agreement with the value derived from the data of Berry & Thompson. The degree of separation does not change linearly over the solid-solution range. The lines were found to be still merged for $\text{Cu}_2\text{Zn}_{0.4}\text{Fe}_{0.6}\text{SnS}_4$ and began to be noticeably separated only at a composition of $\text{Cu}_2\text{Zn}_{0.8}\text{Fe}_{0.2}\text{SnS}_4$. A strong non-linear relationship therefore exists between lattice spacing and composition.

GEOLOGICAL IMPLICATIONS

On the basis of the above experimental findings, an explanation of natural intergrowths such as those described by Harris & Owens (1972) can be offered. If a stannite-kesterite solid solution is cooled to the two-

phase region, a segregation of an iron-rich and a zinc-rich phase can be expected. The compositional and optical difference between the segregated phases will be greatest at low temperature and at approximately 40 to 50 mole per cent $\text{Cu}_2\text{ZnSnS}_4$ in the stannite molecule. Depending on the exact composition, there will be either a separation of iron-rich stannite from zinc-rich stannite or vice-versa, and it is the former kind of intergrowth that was observed in the British Columbian ore by Harris & Owens. In an accessory experimental study, samples of this ore were heated to 300°C and 350°C for 9 weeks. After the treatment at 300°C, only remains of the stannite exsolution were visible and after annealing at 350°C the samples appeared to be completely homogenized. This result is in agreement with the proposed phase diagram and lends support to the contention that the segregation process gave rise to the observed textures in the natural ore.

It is apparent that zincian stannite can serve as a geological thermometer. A temperature estimate can, for example, be made from the composition of two separated phases. Thus the ore from British Columbia with its two stannites of 40 and 65 mole per cent kesterite content must have equilibrated at a temperature of about 200°C or less. Alternatively, if a stannite with, say, 20 mole per cent kesterite is found in a natural assemblage and does not show the above mentioned absences in the x-ray pattern, it must have been formed at a temperature above about 500°C and then cooled rapidly.

A more precise determination of the boundaries of the two-phase region and an extension of the experimental work to lower temperatures would allow more accurate deductions to be made. The stannite geothermometer can be expected to be fairly intensive to pressure zinc phases of very nearly equal molecular volumes are involved.

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BASTNAESITE AFTER ALLANITE FROM ROUGH ROCK LAKE, ONTARIO

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The minerals described here come from Rough Rock Lake, located on the Winnipeg River 9 miles NNW of Minaki, in western Ontario. Geology of this Precambrian area was described by Derry (1930). The bedrock is mostly granitic with a few disseminated bands of amphibolite, biotite gneiss and derived migmatites.

The granitic rocks at the eastern end and on the southeastern shore of Rough Rock Lake contain numerous leucocratic, pegmatitic schlieren. Their rock-forming constituents are the same as those of the surrounding granites. Oligoclase (An_{18} - An_{25} , with both Γ and Δ functions indicating low structural state) and microcline-perthite (obliquity 0.94-0.97, 4-6% Ab_{ss} in potassic phase, 0-1% Or_{ss} in perthitic albite) are usually most abundant but the K-feldspar may be almost absent. Quartz is mostly subordinate but prevails occasionally in central parts. Iron-rich biotite ($\beta = 1.655$ - 1.660) is rather rare in the pegmatitic schlieren but is often concentrated around them. It is frequently chloritized. Magnetite ($a = 8.39_5$ Å) is the most common accessory mineral in irregular grains up to 15 mm in diameter ;