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SOLID SOLUTION RELATIONSHIPS BETWEEN WOLFRAMITE AND SCHEELITE

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ABSTRACT

In zoned crystals of ferberitic wolframite containing scheelite inclusions from near Alice Springs, North Territory, almost complete solid solution is recorded between these two components at elevated temperatures. Retention of very small amounts of scheelite component in solid solution under atmospheric conditions is deduced, and, due to the relatively large ionic radius of calcium, significant variations in (111) spacings result. Without chemical analyses these (111) spacings may give incorrect mineralization temperatures. Nevertheless it is shown that values closer to the theoretical may be obtained after maintaining crystals for prolonged periods under increased vapor pressures and temperatures.

INTRODUCTION

The most common tungsten minerals include members of two isomorphous series, the monoclinic huebnerite-ferberite ($MnWO_4$–$FeWO_4$) group, and the tetragonal scheelite-powellite ($CaWO_4$–$CaMoO_4$) group. Hess and Schaller (1914) observed very small amounts of calcium in some wolframite, but this they ascribed to microscopic scheelite inclusions. Others observing this association have suggested that wolframite may be replaced by later scheelite, or very rarely vice versa (Kerr (1946); Edwards and Lyons (1957); Williams (1958)). The possibility of a limited solid solution between the huebnerite-ferberite and scheelite end members therefore appears to have been overlooked.

Moreover as a direct relationship has been established between the huebnerite-ferberite ratios of wolframite and temperature of formation in the Saxon Erzgebirges (Oelsner (1944, 1952 and 1954); Leutwein (1952); Bolduan (1954); Bauman and Starke (1964 and 1965); and Bauman, Donath and Kretzschmar (1964)), the presence of a possible additional component in this isomorphous series is worthy of closer examination. This is especially relevant in that Starke (1959) has shown that in view of the differing unit-cell parameters of huebnerite and ferberite, these huebnerite-ferberite ratios may be determined by X-ray diffraction using measured 2θ values of the (111) interfacial plane calibrated against an NaCl standard.

An investigation of this problem was recently made possible through the acquisition of several zoned wolframite crystals from a pegmatite dike near Alice Springs, N. T. These crystals, which are equidimensional, up to one inch in diameter, and possess good crystal form, are enclosed by massive vein quartz, pink and white alkali feldspars, and a little muscovite. As seen under an ultraviolet "mineralite," these crystals are riddled with scheelite inclusions while most posses a thin superficial coating of the same. Scheelite contents are especially high where partial alteration of the ferberitic wolframite to hematite has occurred. However, although some scheelite is indisputably of deuteric origin, the data presented below suggest that much may have been exsolved from the ferberitic wolframite.

MICROSCOPIC DATA

Under the reflecting microscope the wolframite crystals, when tarnished, show fine concentric zoning with irregular inclusions and thin films of scheelite usually confined to the interzonal regions (Fig. 1 A and B). Although these latter textural relations are interpreted as of purely exsolution origin, the occurrence of cross-cutting scheelite veinlets, which protrude into the enclosing host rock, could possibly be regarded as deuteric. However as similar scheelite veinlets and superficial films have been observed to form during experimental heating and cooling, conclusions based purely on textural evidence are not always valid. Thus positive evidence for the deuteric origin of scheelite in wolframite is possible only where some corresponding alteration of the latter to hematite can be recognized. The crystals selected for detailed study below possess little or no secondary hematite and thus the scheelite was apparently predominantly of exsolution origin.

X-RAY DIFFRACTION DATA

In order to determine whether any compositional differentation in the ratio of huebnerite to ferberite existed within a single zoned wolframeite crystal from this concentrate, 114 mm. Debye-Scherrer powder patterns using KCl as a calibration standard were obtained for the near-homogeneous core, the mottled intermediate zone, and the clearer, outer margin of a crystal. From core to margin this crystal revealed an increasing degree of scheelite exsolution and accurate determinations of (111) spacings for these three successive zones revealed respective values of 2.954, 2.951, and 2.949 Å. As discussed below, this decrease towards the margin, although due in part to a slight decrease in huebnerite/ferberite ratios, largely results from a progressive exsolution of scheelite from the wolframite. These (111) spacings are distinctly higher than the theoretical values of 2.939–2.943 Å for this compositional range (this deduction being based on ASTM (111) d-values for the huebnerite-ferberite end-members of 2.956 and 2.936 Å respectively). Thus they indicate huebner-

FIG 1(A). Zoned wolframite crystal from near Alice Springs, N.T., showing interzonal exsolution of scheelite, ×13.

ite/ferberite ratios somewhat higher than determined by chemical analyses (Tables 1 and 2). This anomaly is apparently due to the presence of calcium in the ferberite structure, and not to the differing (*hkl*)-spacings adopted by Starke (1959) and the writer.

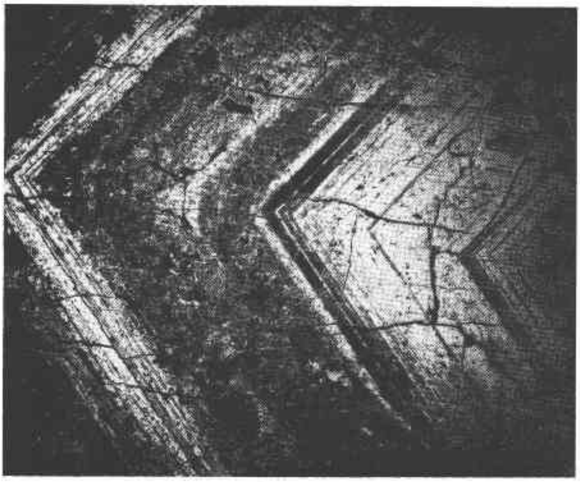

FIG. 1(B). Strongly zoned wolframite crystal after surface oxidation through heat treatment. Some fine interzonal scheelite exsolution lamellae again evident. ×13.

TABLE 1. CHEMICAL ANALYSIS OF A ZONED WOLFRAMITE CRYSTAL CONTAINING SOME EXSOLVED SCHEELITE

	Wt. %
WO_3	73.38
FeO	20.21
CaO	2.06
MnO	3.92
MgO	0.50
Total	100.07

Analyst: T. H. Donnelly.

CHEMICAL DATA

Chemical analyses. The zoned wolframite crystal described above was ground, and shaken in alcohol for 24 hours to ensure thorough mixing. The aggregate was analysed after fusing in sodium carbonate, the sodium ions being removed with an ion exchange resin (Table 1).

Spectrographic analyses. Due to the complicated tungsten spectrum, spectrographic analyses were of very limited use and only a few trace elements were observed. Semiquantitative analyses of the above described zoned crystal, however, revealed no apparent differences between the three successive zones for the observable elements: sodium, barium,

TABLE 2. POINT ANALYSES FOR TWO ELECTRON PROBE MICRO-SCANS ACROSS TWO SECTIONS OF A ZONED WOLFRAMITE CRYSTAL FROM NEAR ALICE SPRINGS, N.T.[1]

(a) Inner series of zones			(b) Outer series of zones		
Zone No.	Mn%	Fe%	Zone No.	Mn%	Fe%
1	4.85	13.5	1	3.95	14.5
2	5.0	13.4	2	4.7	13.5
3	4.9	13.5	3	4.25	14.5
4	4.9	13.4	4	4.3	14.5
5	5.4	13.0	5	4.3	14.5
6	4.9	13.8	6	4.4	14.1
7	5.15	14.0	7	4.5	14.1
8	6.05	12.5	8	4.5	15.0

[1] Analyst: P. K. Schultz, Australian Mineral Development Laboratories.

tantalum, niobium, tin, thorium, silica, aluminum, and magnesium. It can be concluded therefore that no other element present could have caused any detectable variation in the (111) spacings already noted.

Electron probe microanalyses. Calculated (111) d-values for three successive zones from core to margin of the above crystal show a progressive decrease suggesting some compositional zoning. To investigate this, a second similarly zoned crystal from the same locality was subjected to electron microprobe analyses (the first crystal having been destroyed for bulk analysis). Two scans, corresponding to inner and outer zones were made perpendicular to the zoning. The results (Table 2 (a) and (b)) show little variation in Mn:Fe ratios—apart from a slight decrease towards the crystal margin. This latter trend could only account for part of the decrease in (111) d-values; most of the disparity between recorded and theoretical values can only be due to the presence of a little scheelite in solid solution.

Also during the course of these microprobe analyses, it was observed that the greatest difference in Mn:Fe ratios between adjacent wolframite zones occurs where such zones are separated by films of scheelite. The exsolved scheelite contains relatively uniform Mn and Fe contents of:—$Mn = 0.17 \pm 0.03$ percent and $Fe = 0.40 \pm 0.04$ percent, with an Mn:Fe ratio significantly greater than that of the wolframite host.

EXPERIMENTAL WORK

Solid solution of scheelite in wolframite. The material used was the first wolframite crystal whose composition is listed in Table 1. An area of the specimen analyzed with a Swift automatic point counter. The chemical analysis of the same crystal in Table 1 shows that the modal analyses do not indicate the composition of the whole crystal. But since the same area was used throughout the following experiment, the results are clearly relevant for its purpose. The crystal was maintained at successive constant temperatures for a period of one week each, as indicated in Figure 2. After each run, the sample was quenched in water, gently repolished to remove surface oxidation, and immediately point-counted on the basis of 2000 counts per analysis using the same selected area traverse. By this means errors arising from re-exsolution of scheelite were maintained at a minimum.

As graphically illustrated in Figure 2, solid solution of scheelite in wolframite increases steadily with temperature up to 700°C but thereafter shows no apparent change. However, because the crystal had become finely fractured at this stage through repeated quenching (a feature

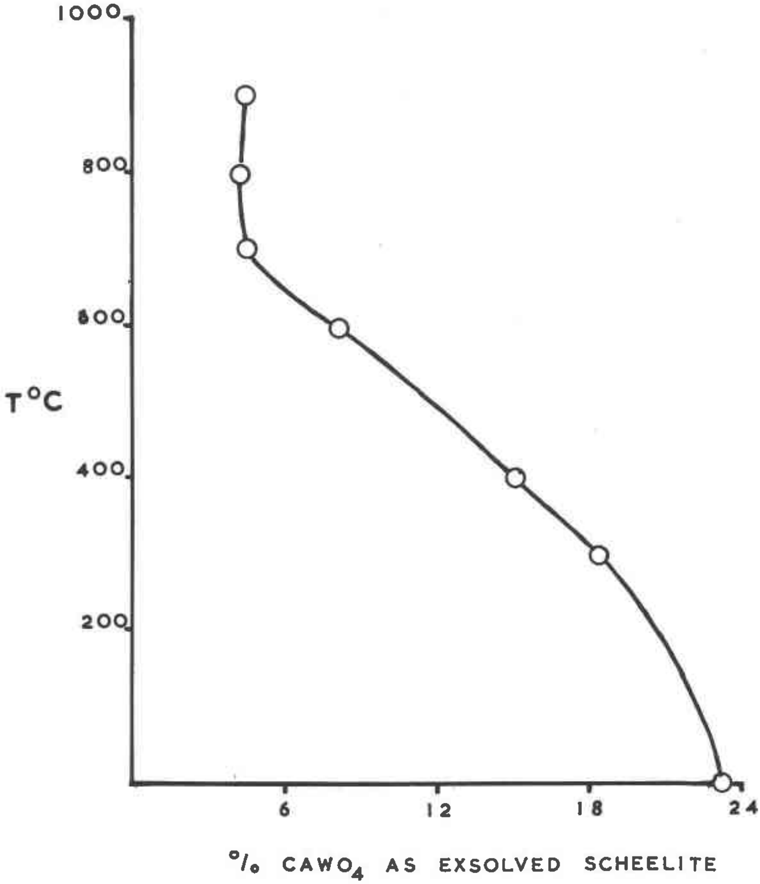

FIG. 2. Solid solution of scheelite in wolframite with increasing temperature.

which, as already demonstrated, induces increased exsolution of scheelite in wolframite), it is possible that the solid solution could, under more ideal conditions, continue to completion.

Effect of scheelite solid solution on (111) *spacings*. Owing to the large ionic radius of Ca^{2+} (0.99) relative to Mn^{2+} (0.80) and Fe^{2+} (0.74) solid solution of even small amounts of scheelite in wolframite may be expected to produce some significant changes in interplanar spacings. This has already been indicated by measurements obtained from the zoned crystal.

To confirm this, a wolframite crystal from the same concentrate containing an apparent abundance of associated scheelite, was encapsulated in a heavy-wall pyrex tubing at about 0.1 mm Hg pressure and heated for 18 days at 570°C. At completion, when much of the scheelite was assumed to have entered into solid solution with wolframite, the charge was quenched in ice, dried, finely ground and mixed with a weighed quantity of KCl standard. Recordings were made of (111) spacings at various set intervals using a Philips 1009 diffractometer unit at $\frac{1}{2}°$ 2θ per minute. A separate determination was made using a Debye-Scherrer 114 mm. powder pattern with KCl standard.

The results which are summarized in Table 3 show (111) spacings generally decreasing with time, and hence a tendency for the crystal to adjust to equilibrium conditions through exsolution of scheelite, this being accompanied by better resolution of the (111) peak from the initial broad slightly diffuse form apparent immediately after quenching. Yet even after 21 hours the (111) spacing of the crystal was still greater than the theoretical value at this composition. Hence to see whether complete exsolution of scheelite and thus closer approximation of the theoretical and actual (111) d-values can be obtained experimentally, two equal −150 mesh (B.S.S.) powder fractions of the above sample were encapsulated in heavy-wall glass tubing. One of these was sealed under a vacuum of approximately 0.1 mm. Hg. To the second, however, an HCl-KCl buffer solution of pH 1 was added, so that when both charges were heated at 145°C for five days this attained a total vapor pressure of between 50 and 100 bars. Measurement of (111) d-values against a KCl standard after completion of the run showed no change in the dry sample heated under vacuum, but in the solution this value had decreased to 2.946 Å, closer to the theoretical.

TABLE 3. (111) SPACING FOR A WOLFRAMITE CRYSTAL AT VARIOUS INTERVALS AFTER QUENCHING FROM 570°C

Hours after quenching	(111) Spacing values
0 hrs	2.960 ± .002 Å
$1\frac{1}{2}$ hrs	2.958 ± .002 Å
$3\frac{1}{2}$ hrs	2.956 ± .002 Å
21 hrs	2.949 ± .002 Å

DISCUSSION

The evidence indicates that whereas extensive solid solution between wolframite and scheelite predominates at elevated temperatures, at 0°C these end members are separated by a broad immiscibility region. Yet even under these latter conditions some limited solid solution may occur, with significant departures of wolframite (111) spacings from the theoretical values.

As the wolframite crystals examined here are essentially ferberite-rich, it is possible that the degree of solid solution between huebnerite and scheelite could be rather less extensive owing to the larger ionic radius of magnesium.

The existence of limited solid solution between wolframite and scheelite and its noteworthy effect on the unit cell parameters of the former, indicates that the use of assumed H/F coefficients in wolframite (where based entirely on X-ray diffraction data) should be treated with caution—particularly when scheelite is known to be present. In using the above H/F coefficient as a guide to mineralization temperatures, direct chemical analysis for manganese and iron is the only reliable method.

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