SOUTH AFRICAN SCHEELITES AND AN X-RAY METHOD FOR DETERMINING MEMBERS OF THE SCHEELITE-POWELLITE SERIES

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ABSTRACT

A detailed description of the physical and chemical properties of ten South African scheelites and of the synthetic $CaWO_4$-$CaMoO_4$ series is given. Three variation diagrams of values of 2θ with chemical composition of this series are also given, by means of which the MoO_3 content of a member can accurately be determined from its *x*-ray diffraction angles to within 1%.

INTRODUCTION

Powellite ($CaMoO_4$), although less common than scheelite ($CaWO_4$), is found at several localities in North America and also at Minusinsk, Siberia. Scheelite free from molybdenum is very rare in nature, the replacement of W by Mo being usually of the order from 1 to 15 per cent. The same range appears to apply to the replacement of Mo by W in natural powellites. These indications that scheelite and powellite may form an isomorphous series is strongly supported by the fact that the ionic radii of hexavalent W and Mo are both 0.68 Å (11, p. 167).

Scheelites from ten localities in South Africa were examined but not one contained more than 2 per cent MoO_3. Neither natural powellite nor other intermediate members of the postulated scheelite-powellite series were available. However, the end-members as well as some intermediate members were successfully synthesized.

The *x*-ray diffraction patterns, and hence also the crystal structures of synthetic $CaWO_4$ and $CaMoO_4$ are identical with those of natural scheelite and powellite, respectively. At the same time an *x*-ray method was devised for determining the composition of a member of the series in terms of its end-members to an accuracy of 2 per cent $CaMoO_4$, or about 1.5 per cent MoO_3 by weight.

The natural scheelites examined in this research came from the following South African localities:

Specimen Number	*Locality*
1	Gwelo dist., Southern Rhodesia.
2	Schurry's Claim, Natos Mine, South West Africa.
3	Joffe's Claim, Groendoorn River, Cape Province.
4	Boksputs, Gordonia, Cape Province.
5	Jackalswater, Namaqualand, Cape Province.
6	Leydsdorp, Transvaal.

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Specimen Number	*Locality*
7	"Altemooi," Steinknopf, Namaqualand, Cape Prov.
8	Stavoren Mine, Potgietersrust, Transvaal.
9	Forbes Reef, Swaziland.
10	Glynn's Reef, Vaalhoek, Pilgrimsrust, Transv.

CHEMICAL PROPERTIES

Samples from the localities listed above were analyzed chemically and spectrographically. Material used for these analyses was examined microscopically and no impurities or inclusions could be seen.

SPECTROGRAPHIC ANALYSES

No attempt was made to compare the intensities of the Ca-or W-lines as these constituents and Mo were determined chemically. When the intensities of the Mo-line (3,903 Å) for different scheelites were compared visually, variations in the intensity of this line were in very good agreement with the relative amounts of MoO_3 determined chemically.

The results obtained on other minor constituents and listed in Table 1, represent a rough semi-quantitative guide of the abundance of these minor constituents. It is considered that none of these is present in quantities exceeding 0.5 per cent. The intensity of each element-line has been visually estimated using an arbitrary scale from zero to 10. This allows a comparison vertically, but not horizontally, in Table 1.

TABLE 1. SPECTROGRAPHIC ANALYSES OF 10 SCHEELITES, SOUTH AFRICA

Sample No.	Si 2,882	Al 3,962	Mg 2,852	Sr 4,607	Ba 4,554	K 4,044	Na 3,302	V 3,184	Fe 3,581	Mn 4,031	Cr 4,275	Ti 3,235	Cu 3,274
1	10	10	8	tr.	0	3	0	8	0	0	2	4	2
2	8	10	6	2	10	0	0	4	0	0	0	0	10
3	10	8	0	tr.	0	0	0	9	2	10	0	0	4
4	7	1	0	1	0	2	0	6	0	0	0	10	1
5	0	5	4	4	2	0	10	10	1	0	0	2	0
6	10	9	7	10	3	10	6	3	0	2	6	8	4
7	4	6	0	2	4	0	1	0	0	1	0	0	0
8	6	4	tr.	1	0	6	0	10	8	10	10	0	0
9	2	1	10	0	1	0	0	6	6	8	8	2	0
10	7	10	0	0	0	1	0	10	10	3	0	1	0

Samples were arced in hollowed copper anodes, (the cathodes were slightly pointed) for 20 seconds at 5 amps (for Cu. analyses carbon electrodes were used). A large Hilger Littrow-type spectrograph was available.

The following elements were absent in all scheelites: Ta, Nb, Pb, As, Bi, Y, Yb, Ce, In, Sb, Li, Zr, B, Rb, Cs, Be.

TABLE 2. CHEMICAL ANALYSES OF 10 SCHEELITES, SOUTH AFRICA

Sample No.	Percentages by Weight of Components*							
	CaO	WO_3	MoO_3	SrO	CuO	Total	% $CaWO_4$	% $CaMoO_4$
1	18.96	77.00	$<.0004$	—	—	95.96	96.0	0
2	18.87	76.40	0.96	—	0.54	96.77	94.84	1.33
3	19.20	78.30	0.54	—	—	98.04	97.17	0.75
4	18.70	77.63	0.039	—	—	96.37	96.25	0.05
5	19.20	78.36	0.070	—	—	97.63	97.50	0.10
6	18.80	75.16	0.0062	0.46	—	94.43	93.30	0.09
7	19.68	77.08	1.87	—	—	98.63	95.67	2.62
8	19.60	78.84	0.0004	—	—	98.44	97.86	0
9	19.44	78.64	0.0023	—	—	98.08	97.61	0
10	19.36	78.68	$<.0004$	—	—	98.04	97.66	0

* Chemical analyses by C. J. Liebenberg, Division of Chemical Services, Pretoria.

From Table 2 it appears that all the specimens contain impurities. However, these were not visible under the microscope or ultra-violet lamp.

In the calculation of the norm, an excess of CaO was often found after all the WO_3 and MoO_3 had been allocated to CaO to form the scheelite and powellite molecules. This excess of CaO may be linked with the silica, alumina, or vanadium, the most common elements present in the scheelites. In sample No. 2 a small quantity of Ca was replaced by Cu, and in No. 6 Sr replaced some Ca. These minor replacements of Ca by Cu and Sr caused some deviations in many values of 2θ for many of the reflections in their *x*-ray diffraction patterns.

SYNTHESIS OF MEMBERS OF THE SCHEELITE-POWELLITE SERIES

Pure $CaWO_4$ and $CaMoO_4$ were synthesized by the Manross method (13) by fusing $Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$, respectively, with

$CaCl_2 \cdot 2H_2O$. The melting points of these substances, when they have lost their water of crystallization, are as follows:

$CaCl_2 = 772°$ C.
$Na_2WO_4 = 698°$ C.
$Na_2MoO_4 = 687°$ C. (1, p. 369)

Intermediate members containing 20%, 40%, 60% and 80% $CaMoO_4$ were synthesized as follows: pure $Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ were mixed in the required proportions to yield the aforementioned members of the series. These mixtures were then melted in an open crucible over a bunsen flame and thoroughly agitated to ensure a high degree of homogeneity before adding $CaCl_2 \cdot 2H_2O$. The mixture is then heated for another 15 minutes before cooling.

By grinding the product to about 200 mesh and boiling with water, all of the NaCl formed in the reaction as well as all excess reagents were removed. The final products were dried at 150° C.

The chemicals employed in the syntheses were analyzed reagents which contained alkalies as major impurities but in quantities not exceeding 0.2%. Other impurities were SO_4^{2-}, Pb, Fe, Ba and NH_4OH, but none was present in quantities greater than 0.005%. Spectrographic analyses proved that no Mn, V, Cr, Cu, Si, Sr, Ti, Be, Mg, or Al were present in the reagents, and tended to confirm the manufacturer's analyses.

FLUORESCENCE

Natural scheelites as well as all synthetic mixtures fluoresced when exposed to ultra-violet light ($\lambda = 2536$ Å), the synthetic material showing a somewhat brighter fluorescence than the corresponding minerals. The fluorescent colors of the minerals and their MoO_3 content are listed in Table 3.

TABLE 3. FLUORESCENCE COLORS, 10 SCHEELITES, SOUTH AFRICA

Specimen No.	% MoO_3 (Wgt.)	Fluorescent Color
1	<.0004	Pale blue
2	0.96	Yellow
3	0.54	White
4	0.039	Pale blue
5	0.070	Pale blue
6	0.0062	Pale blue
7	1.87	Yellow
8	0.0004	Pale blue
9	0.0023	Pale blue
10	<.0004	Pale blue

The fluorescence of the synthetic $CaWO_4$ was pale blue, similar to that of the seven samples poor in MoO_3 (Table 3), but all the other synthetic samples showed a yellow fluorescence. A sample containing about 0.5% MoO_3 was also synthesized, and it fluoresced white like the natural mineral of about the same composition (No 3).

R. S. Cannon, K. J. Murata and F. S. Grimaldi of the United States Geological Survey worked out the variation of fluorescence of scheelite with molybdenum content quantitatively with great success (14, p. 65). The variation in fluorescent color that they observed in the natural scheelites was confirmed by preparing synthetic samples of identical chemical composition, and the resulting method they suggested comprises the comparison of the fluorescent color of a scheelite of unknown molybdenum content with the fluorescent colors of a standard series containing scheelites with 0.05, 0.19, 0.33, 0.48, 0.72, 0.96, 1.4, 2.4, 3.4, and 4.8 per cent molybdenum. By employing this method the molybdenum content of scheelites containing less than 4.8 per cent of molybdenum can easily be determined to an accuracy exceeding any industrial requirements.

This pioneering work is of great importance in the industry, the only difficulty is that the molybdenum content cannot, according to this method, be determined accurately in samples containing more than about 5 per cent of molybdenum.

In a detailed study Greenwood (2, pp. 56–64) also noticed a change in fluorescence of scheelite from blue to yellow with increasing molybdenum content, but also related the fluorescence to some impurities, especially manganese. In view of his findings, and the presence of Mn, Fe, and especially V in some of the South African scheelites, some experiments were made by incorporating these components in some synthetic material. First, scheelites were prepared by adding quantities of Mn, Fe, and V varying from about 0.01% to 1% to $Na_2WO_4 \cdot 2H_2O$ and $CaCl_2 \cdot 2H_2O$. (These impurities were added in the form of FeO, $FeCl_2$, MnO, $MnCl_2$, and V_2O_5). However, the fluorescent pale blue color remained unchanged. The procedure was then repeated in the preparation of pure powellite; the fluorescent bright yellow color remained constant.

For MoO_3 percentages greater than about 1% the fluorescent color remains yellow but becomes somewhat brighter with increasing molybdenum content. Hence the intensity may serve as a rough guide to the content of MoO_3 in the scheelite-powellite series in this range of composition. However, this method must be considered unreliable not only because of difficulties in the direct measurement of intensities but also because other factors as yet unknown may influence the intensities. Marden and Meister (16) have studied the decrease in fluorescence intensity caused by various foreign elements when incorporated in synthetic scheelite.

SPECIFIC GRAVITY DETERMINATIONS

Two ordinary quartz specific gravity bottles of about 7 cc. capacity were employed. Triple distilled water which was freed from air was used. All possible precautions were taken to reduce evaporation to a minimum. Air bubbles adhering to the particles were completely removed by heating the bottle with the particles and about $\frac{3}{4}$ of its volume of water to about 60° C. under diminished pressure. Corrections were also made for the difference in the displacement of air by the volume of the contents of the pyknometers and the volume of the weights used with the balance.

Three determinations were made on different portions of each sample and the differences did not exceed 0.005. The results given below may therefore be considered correct to the nearest unit in the second decimal place.

TABLE 4. SPECIFIC GRAVITY, 10 SCHEELITES, SOUTH AFRICA

Sample No.	Specific Gravity (G_4^{25})	% MoO_3 (wgt.)
1	6.08	<0.0004
2	6.01	0.96
3	6.02	0.54
4	6.10	0.039
5	6.08	0.070
6	5.72	0.0062
7	6.00	1.87
8	6.09	0.0004
9	6.12	0.0023
10	6.06	<0.0004

The specific gravities of scheelites containing less than 0.5% MoO_3 are fairly constant, but that of sample No. 6, which contains 0.46% SrO is substantially different from the others. This reduction in specific gravity may be due to the expansion of the unit cell owing to the replacement of Ca with ionic radius of 1.06 Å by Sr with radius 1.27 Å (11, p. 168). On the other hand, this replacement should tend to increase the specific gravity because the atomic weight of Sr is more than twice that of Ca.

The following parameters are given in the literature:

Bragg (4, p. 133)		*Sillen and Nylander (5, pp. 1–27)*
$CaWO_4$: $a=5.24$ Å, $c=11.28$ Å	:	$CaWO_4$: $a=5.23$ Å, $c=11.348$ Å
$CaMoO_4$: $a=5.23$ Å, $c=11.44$ Å	:	$CaMoO_4$: $a=5.21$ Å, $c=11.426$ Å

If the specific gravities of scheelite and powellite are calculated from:

$$d = nM/Nv \cdots (1) \quad (3, \text{p. } 108)$$

where

$n=8$ for the scheelite group.
M = molecular weight.
N = Avogadro's Number $(6.0597 \pm .0016) \times 10^{23}$ Å
v = Volume of the unit cell.

the following values are found.

Bragg		*Sillen and Nylander*
$CaWO_4$: Sp. Gr. = 6.141	:	$CaWO_4$: Sp. Gr. = 6.125
$CaMoO_4$: Sp. Gr. = 4.231	:	$CaMoO_4$: Sp. Gr. = 4.253

Since the volumes of the unit cells of powellite and scheelite are practically the same, the variation of the density in this series will be a function of the molecular weight, or a function of the MoO_3 content.

Using the unit cell dimensions of two intermediate members of the powellite-scheelite series given by Ödman (7), their specific gravities were calculated according to formula (1). The results are:

(a) Sample with 22.1% MoO_3.	Sp. Gr. 5.56
(b) Sample with 59.3% MoO_3.	Sp. Gr. 4.60

The available specific gravity data suggest the simple relationship presented in Fig. 1.

The specific gravities of the South African scheelites are below 6.13 (calculated sp. gr. for pure $CaWO_4$), and thus may be due to the fact that all the natural scheelites contain impurities in the form of silica, alumina, and vanadium, causing the experimental values to be lower than the calculated ones.

REFRACTIVE INDICES

The refractive indices of natural and synthetic scheelites were determined according to a single variation method using phosphorus liquids as described by West (6, pp. 245–249). Grains were orientated on a Universal Stage and the indices matched at room temperature by adjusting the wavelength of a monochromator. All indices are given for Na-light at 22° C. and are correct to ±.003. The variation in refractive index from powellite to scheelite offers a fair method of determining the MoO_3 content of a member of this series. The refractive indices of the South African scheelites, except for samples Nos. 2 and 6 varied as follows.

ω from 1.914 to 1.926 and
ϵ from 1.931 to 1.939

The average of the refractive indices of the scheelites containing less than 0.5% MoO_3 are as follows:

$\omega = 1.921\ (\pm .003)$
$\epsilon = 1.938\ (\pm .003)$

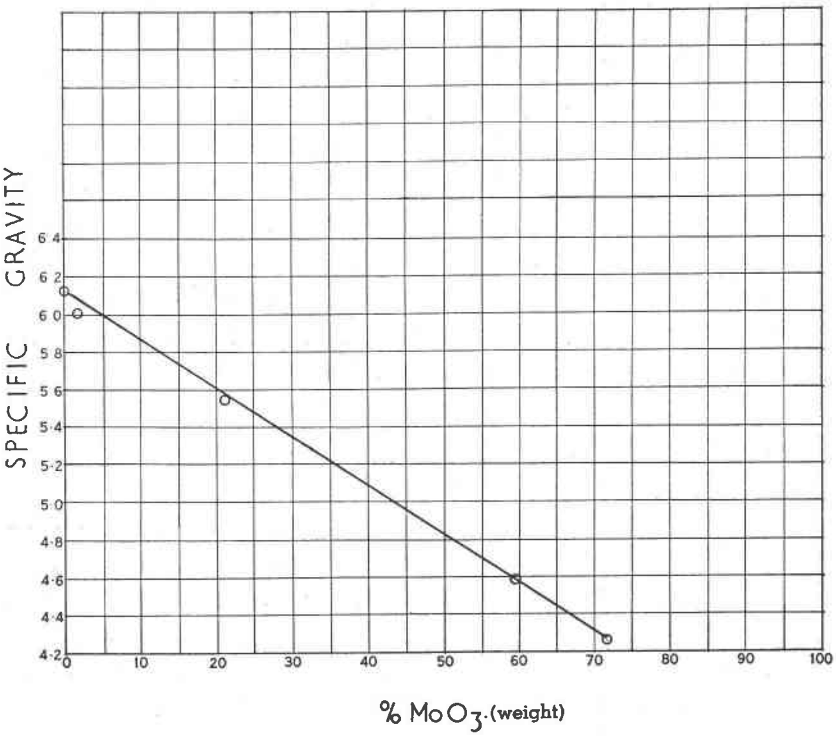

FIG. 1. Graphical representation of the variation of the specific gravity of members of the $CaWO_4$-$CaMoO_4$ series. No specific gravity determinations was attempted on the synthesized members because of their very fine grain size.

The following refractive indices were found for the synthetic material:

	100% $CaWO_4$	20% $CaMoO_4$	40% $CaMoO_4$	60% $CaMoO_4$	80% $CaMoO_4$	100% $CaMoO_4$
ϵ	1.935	1.946	1.954	1.967	1.973	1.984
ω	1.920	1.932	1.942	1.951	1.966	1.974

The refractive indices for natural and artificial scheelite are identical within the limits of errors viz. $\omega = 1.921$ and 1.920, respectively.

The birefringence (ϵ-ω) for the synthetic series decreases from 0.015 for $CaWO_4$ to 0.010 for $CaMoO_4$.

The refractive indices of sample No. 6 which contained 0.46% SrO was found to be:

$$\omega = 1.912\ (\pm .003)$$
$$\epsilon = 1.925\ (\pm .003)$$

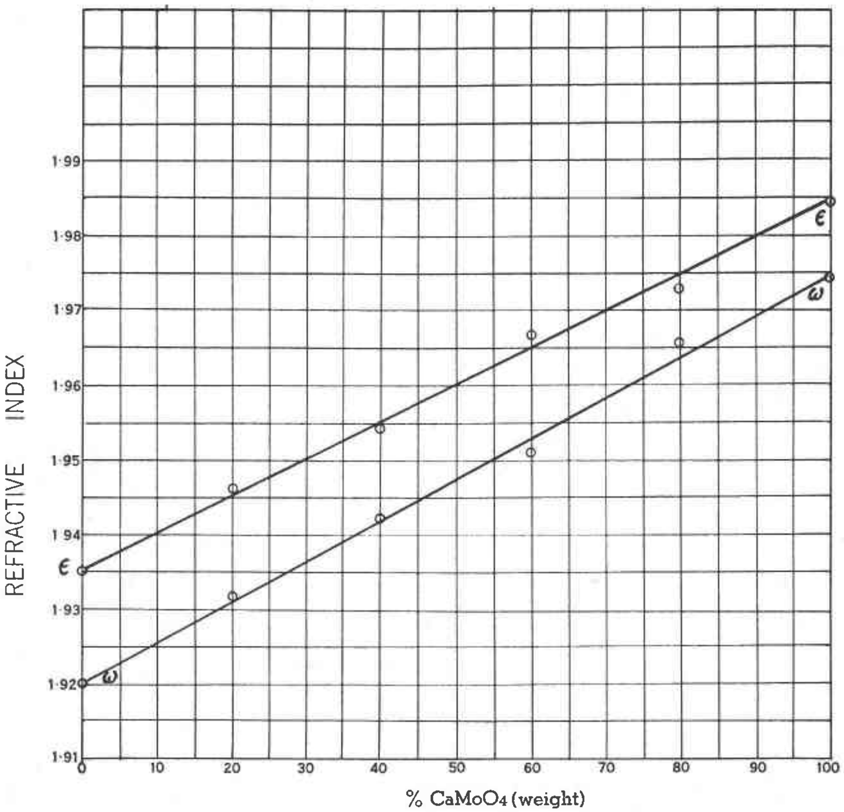

FIG. 2. Graphical representation of the variations of the refractive indices ω and ε with the chemical composition of the synthetic $CaWO_4$-$CaMoO_4$ series.

For sample No. 2 which contained 0.54% CuO the refractive indices are:

$$\omega = 1.930\ (\pm .003)$$
$$\epsilon = 1.947\ (\pm .003)$$

The specific refractive energies of WO_3 and MoO_3 were calculated according to Larsen and Berman (15, pp. 30–31) as 0.133 for WO_3 and 0.233 for MoO_3. It will be noticed that Larsen and Berman (15, p. 31) quoted exactly the same specific refractive energy for WO_3 but the calculated value for MoO_3 differs greatly from the 0.241 as given by them.

X-RAY EXAMINATION

X-ray powder diffraction patterns were obtained by using 114 mm. diameter cameras in which the film is mounted according to the Straumanis method (9, p. 726). The time of exposure was $2\frac{1}{2}$ hours using unfiltered Cu-radiation at 35 K.V. and 20 m.a. The temperature during the exposures did not vary more than 1° C. above room temperature (22° C). The variations in room temperature for different exposures did not exceed 3° C.

The films were allowed to dry for two weeks before measuring. The centers of the entrance and exit holes in the film were determined by the accurate measurement of the lines on either side of these holes in order to obtain "check points" from which a shrinkage correction factor was determined.

TABLE 5. *X*-RAY DATA ON 10 SCHEELITES, SOUTH AFRICA

No.	Int. (est)	Average of samples 1, 3, 4, 5, 8, 9 and 10		Sample No. 2 containing 0.54% CuO		Sample No. 6 containing 0.46% SrO	
		2θ (Cu)	d Å	2θ (Cu)	d Å	2θ (Cu)	d Å
1	10	29.01	3.08	29.05	3.07	28.99	3.08
2	8	47.30	1.923	47.41	1.918	47.30	1.923
3	9	58.05	1.589	58.19	1.585	58.08	1.588
4	8	59.71	1.549	59.75	1.547	59.58	1.552
5	9	76.41	1.247	76.42	1.246	76.30	1.248
6	8	90.76	1.082	90.70	1.083	90.70	1.082
7	7	99.43	1.010	99.41	1.010	99.27	1.011
8	8	117.02	0.9033	116.90	0.9039	117.02	0.9033
9	8	142.99	0.8122	142.97	0.8123	142.85	0.8127
10	9	150.91	0.7958	150.92	0.7957	150.74	0.7961
11	8	152.13	0.7936	152.01	0.7938	151.87	0.7941
12	8	165.53	0.7764	165.80	0.7762	165.50	0.7765

All reflections with $2\theta > 90°$ are α_1 reflections.

The measuring of the films was carried out as described by Wasserstein (8, p. 106). The films were measured four times using different parts of the scale in order to eliminate any possible errors due to incorrect calibration of the measuring scale or vernier. Each line was measured 5 times at the four different positions in which the film was placed on the scale. The more prominent lines were measured 10 times. The variations in 2θ did not exceed 0.05 degrees for different positions along the scale and all values given in Tables 6 and 7 are hence considered correct to 0.03 degrees.

The variations in 2θ of corresponding lines for those scheelites containing less than 1% MoO_3 never exceeded 0.06 degrees, but larger devia-

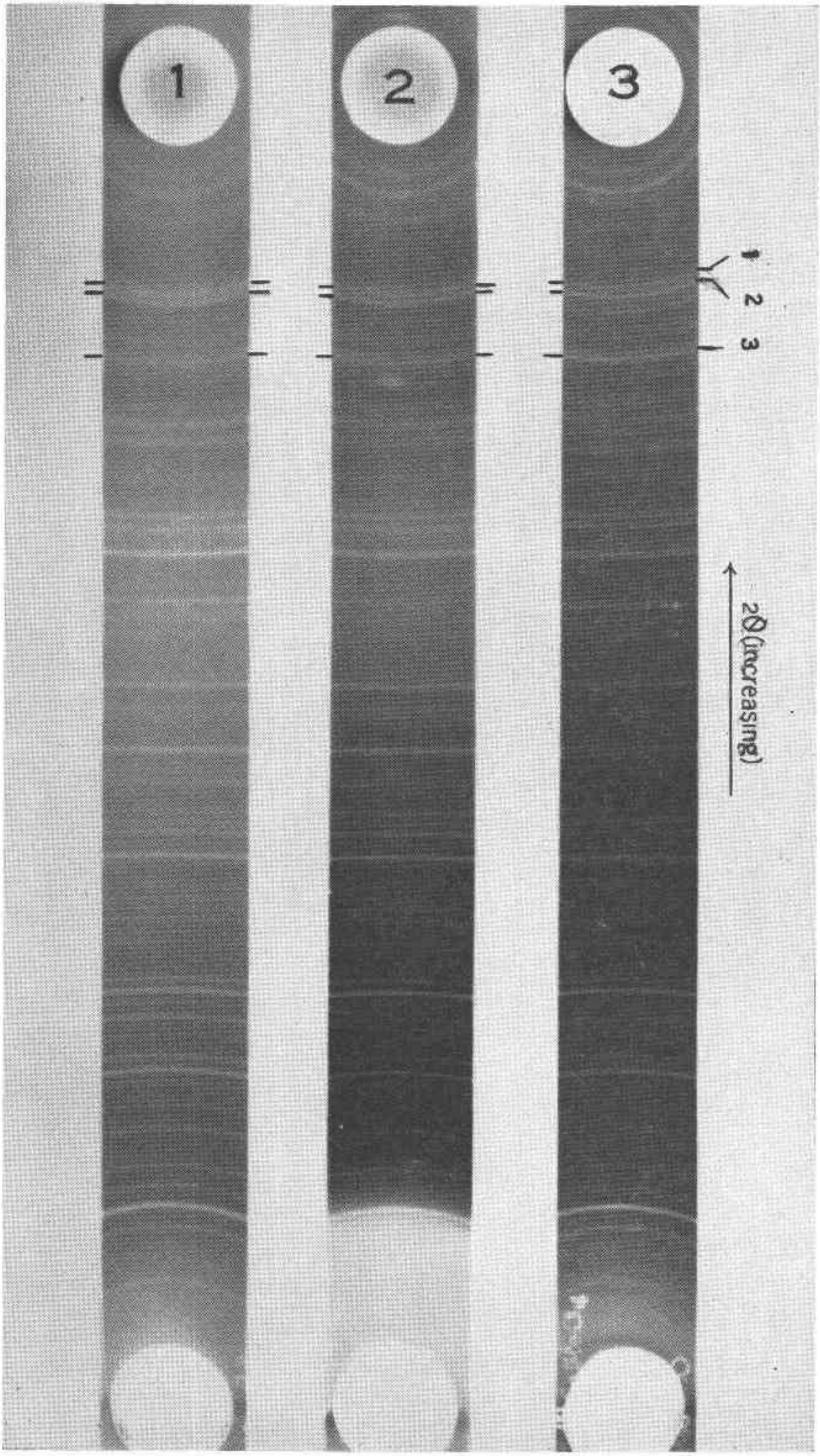

FIG. 3. *X*-Ray powder patterns of: 1. Natural scheelite, 2. Synthetic $CaWO_4$, 3. Synthetic $CaMoO_4$.

tions from these values of 2θ for corresponding lines were found in samples Nos. 2 and 6, which contained CuO and SrO, respectively. X-ray diffraction angles were converted into interplanar spacings by using suitable tables (10).

The above mentioned deviations of 2θ for the more prominent reflections for samples Nos. 2 and 6 form the 2θ values for scheelites containing little MoO_3 are listed in Table 5.

Table 5 illustrates that the partial replacement of Ca by Cu and Sr causes definite line shifts, but these are irregular. Although both samples contain some MoO_3 it is clear that this deviation in 2θ is not due to the MoO_3 content. The replacement of W by Mo causes a systematic shifting of lines as will be pointed out below. A detailed study of the Sr and Cu-bearing scheelites seems desirable.

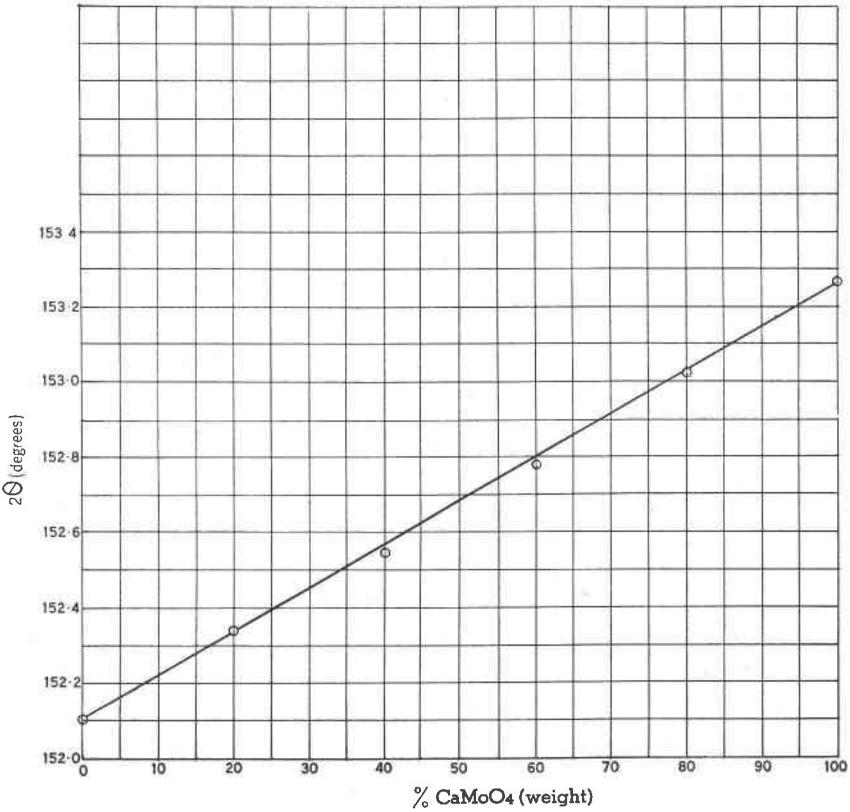

FIG. 4. Variation of 2θ for line No. 1 with variation in the chemical composition of the scheelite-powellite series.

AN X-RAY METHOD FOR DETERMINING THE CHEMICAL COMPOSITION OF MEMBERS OF THE SCHEELITE-POWELLITE SERIES

Members of this series may be considered to form solid solutions with complete solubility between the end-members $CaWO_4$ and $CaMoO_4$.

With the usual limitations the composition of any member of the series can be determined fairly accurately from its specific gravity or its refractive indices (Figs. 1 and 2, respectively). More accurate determinations can be made by means of x-ray diffraction analyses, with advantages inherent in this method. For this purpose diagrams have been prepared (see Figs. 4, 5 and 6) based on synthetic material and verified with available natural scheelite containing up to 2.62 per cent of $CaMoO_4$

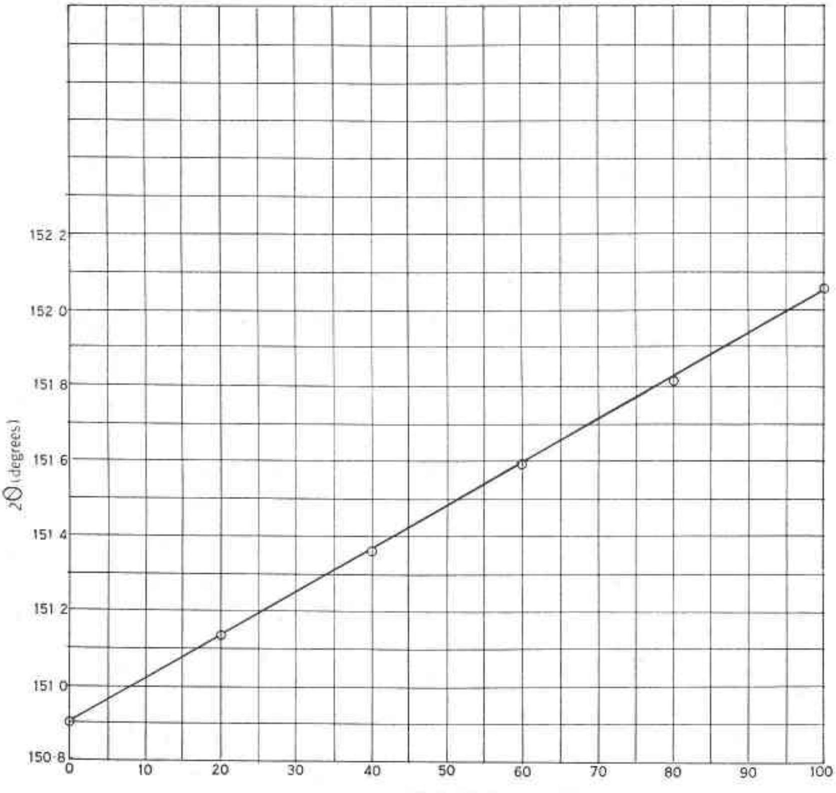

FIG. 5. Variation of 2θ for line No. 2 with variation in the chemical composition of the scheelite-powellite series.

TABLE 6. X-RAY DATA FOR $CaWO_4$ AND $CaMoO_4$

(The *d* values were derived from the measured 2θ values through the use of the tables of Ref. 10)

No.	Int. (obs.)	Natural Scheelite		Synthetic $CaWO_4$		Synthetic $CaMoO_4$	
		2θ (Cu)	d (Å)	2θ (Cu)	d (Å)	2θ (Cu)	d (Å)
1	6	18.82	4.72	18.86	4.71	18.87	4.71
2	4	26.04	3.42	26.10	3.41	26.11	3.41
3	10	29.01	3.08	28.96	3.08	29.00	3.08
4	4	34.42	2.605	34.39	2.608	34.48	2.601
5	4	39.41	2.286	39.39	2.287	39.59	2.276
6	3	42.50	2.127	42.55	2.125	42.49	2.128
7	1	43.48	2.081	43.53	2.082	—	—
8	1	44.29	2.045	44.37	2.042	44.42	2.041
9	3	45.60	1.989	45.65	1.987	45.79	1.982
10	8	47.30	1.923	47.32	1.921	47.34	1.920
11	6	49.31	1.848	49.33	1.847	49.54	1.840
12	4	52.10	1.755	52.04	1.757	52.18	1.753
13	1	53.40	1.716	53.28	1.719	53.57	1.711
14	4	54.48	1.684	54.52	1.683	54.42	1.686
15	2	56.60	1.626	56.53	1.626	56.46	1.630
16	9	58.05	1.589	58.07	1.588	58.06	1.589
17	8	59.71	1.549	59.68	1.549	59.75	1.545
18	4	64.91	1.437	64.94	1.436	65.00	1.435
19	4	67.80	1.382	67.84	1.382	67.83	1.382
20	4	69.34	1.355	69.54	1.355	69.59	1.351
21	4	70.64	1.333	70.64	1.333	70.73	1.332
22	2	72.30	1.309	72.24	1.308	72.57	1.303
23	2	75.29	1.262	75.36	1.261	—	—
24	9	76.41	1.247	76.41	1.247	76.32	1.248
25	1	78.16	1.223	78.07	1.224	—	—
26	6	79.52	1.205	79.55	1.205	79.80	1.202
27	6	80.86	1.1887	80.87	1.1886	81.07	1.1862
28	6	82.30	1.1715	82.40	1.1703	82.68	1.1671
29	1	86.19	1.1283	86.19	1.1283	86.08	1.1297
30	1	88.18	1.1080	88.25	1.1072	89.72	1.0927
31	8	90.76	1.0822	90.79	1.0819	91.00	1.0799
32	2	95.12	1.0437	95.02	1.0445	95.57	1.0400
33	2	96.51	1.0323	96.53	1.0322	96.47	1.0326
34	7	99.43	1.0097	99.41	1.0098	99.80	1.0070
35	2	—	—	100.86	.9992	—	—

Table 6 (*Continued*)

No.	Int. (obs.)	Natural Scheelite		Synthetic $CaWO_4$		Synthetic $CaMoO_4$	
		2θ (Cu)	d (Å)	2θ (Cu)	d (Å)	2θ (Cu)	d (Å)
36	2	106.22	.9631	106.29	.9626	106.22	.9631
37	2	108.16	.9511	108.17	.9511	108.44	.9493
38	2	—	—	110.61	.9368	110.30	.9386
39	8	117.02	.9033	116.99	.9034	117.24	.9022
40	6	120.41	.8876	120.41	.8876	121.05	.8848
41	6	122.05	.8805	122.00	.8807	122.59	.8782
42	3	—	—	127.38	.8593	—	—
43	5	131.90	.8435	131.86	.8436	131.90	.8435
44	6	134.68	.8347	134.70	.8346	135.20	.8331
45	6	136.64	.8289	136.67	.8288	137.27	.8271
46	8	142.99	.8122	142.96	.8123	143.50	.8110
47	3	—	—	—	—	150.64	.7962
48	9	150.91	.7958	150.90	.7958	152.06	.7937
49	8	152.13	.7936	152.10	.7937	153.26	.7917
50	3	162.24	.7796	162.19	.7796	164.68	.7772
51	8	165.53	.7764	165.54	.7764	166.22	.7759
52	5	167.98	.77450	167.98	.7745	168.85	.7739

All reflections with $2\theta > 90°$ are α_1 reflections.

by weight. Intermediate members of the scheelite-powellite series containing between 20 per cent and 80 per cent. $CaMoO_4$ are rare in nature, so that synthetic products had to be used in any case for those parts of the diagrams.

The *x*-ray diffraction angles for corresponding lines of natural scheelite and synthetic $CaWO_4$ are identical (see first two columns of Table 6), and it can, therefore, be inferred that the synthetic series will yield identical powder patterns to those of the minerals.

The diffraction angles for corresponding lines were found to increase in direct proportion to the $CaMoO_4$ content.

From Table 6 it is seen that the highest variations in 2θ are found in the high angle region, the higher the angle the larger the difference in 2θ. To establish the relationship between the variations of 2θ for corresponding lines in the spectra of different samples and the chemical composition, the lines marked 1, 2 and 3 in Fig. 3 were selected because they are:

(*a*) prominent and easily recognized,

(*b*) situated in the high angle region of the patterns where the accuracy of measurement is highest and the variation of 2θ is a maximum, and (*c*) the most intense and best defined back-reflection lines and unlikely to disappear when the sample is diluted with foreign material.

These three lines are identified as follows:

	Line No. 1	Line No. 2	Line No. 3
2θ (Cu)			
Scheelite	152.10°	150.90°	142.96°
Powellite	153.26°	152.06°	143.50°
d (Å)			
Scheelite	0.7937	0.7958	0.8123
Powellite	0.7917	0.7937	0.8111
Line No. in Table 6	49	48	46

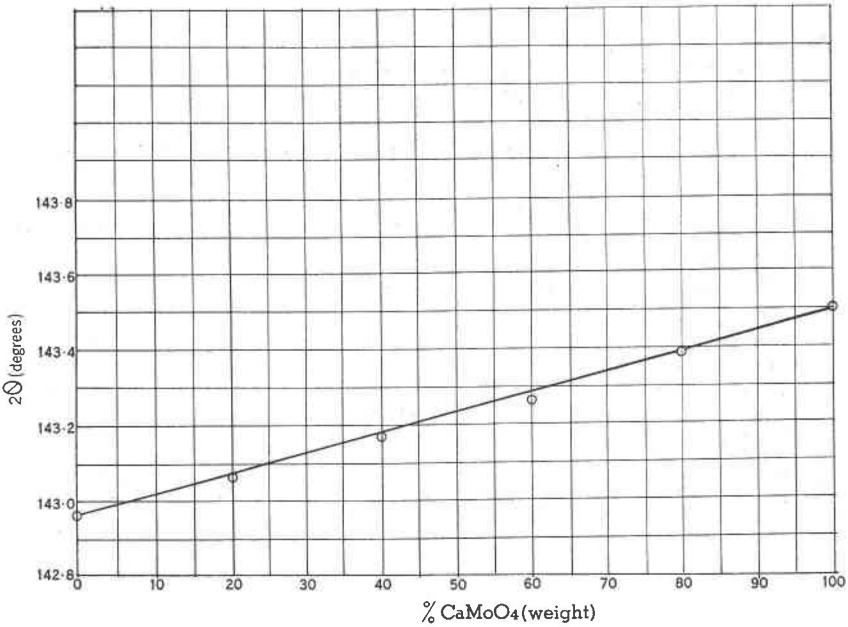

FIG. 6. Variation of 2θ for line No. 3 with the chemical composition in the scheelite-powellite series.

The three variation diagrams for different lines will suffice for practical purposes.

PRECISION

The values for 2θ are correct to 0.03 degrees, so that the diagrams represent the content of $CaMoO_4$ accurately to within 2 per cent. If all three lines used in the variation diagrams can be measured accurately, then the mean of these three values should give the MoO_3 content accurately to within 1 per cent.

ACKNOWLEDGMENTS

The author wishes to thank Dr. B. Wasserstein, Officer-in-Charge of the Mineralogical Laboratory of the Geological Survey, Pretoria, for his very helpful suggestions and keen interest and Dr. M. Fleischer of the Geochemistry and Petrology Branch of the United States Geological Survey, Washington, for his keen interest and assistance in finding references.

Special thanks are due to Professor Dr. B. V. Lombaard of the University of Pretoria for critically reviewing this paper and for his many valuable suggestions in this work.

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Manuscript received Feb. 1, 1952