SPIROFFITE,[1] A NEW TELLURITE MINERAL FROM MOCTEZUMA, SONORA, MEXICO

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ABSTRACT

Spiroffite, $(Mn,Zn,Ca)_2Te_3O_8$, occurs in small cleavable masses which range in color from red to purple. The luster is adamantine, hardness is $3\frac{1}{2}$, and specific gravity is 5.01. The mineral is biaxial positive, $2V=55°$, $\alpha=1.85$, $\beta=1.91$, $\gamma>2.10$. No euhedral crystals have been found. X-ray study shows that spiroffite is monoclinic with a space group of Cc or $C2/c$. Unit cell values are: $a=13.00$ Å, $b=5.38$ Å, $c=12.12$ Å, $a:b:c=2.416:1:2.253$, $\beta=98°$. Associated minerals are: tellurite paratellurite, native tellurium, and several other new tellurites. Spiroffite is named in honor of Kiril Spiroff, Professor of Mineralogy at the Michigan College of Mining and Technology, Houghton, Michigan.

INTRODUCTION AND OCCURRENCE

During the summer of 1960, one of the writers (S.J.W.) obtained a number of specimens from Mina Moctezuma (formerly known as La Bomboya), a gold-tellurium mine near the town of Moctezuma, Sonora, Mexico (Lat. 29° 47.5′N, Long. 109° 41′W). Recognizing that some of the minerals might be new, he sent them to the Royal Ontario Museum for further study. A preliminary investigation revealed five new species and a note on these was published by Mandarino and Williams (1961a). A progress report by the same writers (1961b) was presented at the 1961 Annual Meetings of the Geological Society of America in Cincinnati. In both papers, spiroffite was called "a manganese-zinc tellurite or tellurate."

Because the writers have been unable to visit the locality, this description must be restricted to laboratory findings. Spiroffite is associated with native tellurium, tellurite, paratellurite, a new calcium tellurite (or tellurate), and denningite. Denningite, $(Mn, Ca, Zn)Te_2O_5$, was described recently by the writers (1962). Spiroffite is apparently later than tellurite and native tellurium. The genetic relationships between spiroffite and the other tellurium minerals are not clearly shown in the specimens.

GENERAL FEATURES AND APPEARANCE

Spiroffite occurs as small cleavage masses ranging in size from $2\times2\times2$ mm to $5\times10\times20$ mm. The color varies from red to purple corresponding to RS-10-2° and RS-9-6° respectively, in the color classification of Villalobos (1947). The streak is colorless and the luster is adamantine. Spiroffite is translucent to transparent.

[1] Pronounced, SPĬR·AWFAIT according to the Royal Geographical Society (R.G.S.II) system as given in Hey (1955); or spĭr·off-īte according to the Oxford Dictionary System.

CRYSTALLOGRAPHIC CHARACTERISTICS

The entire crystallographic study had to be carried out by means of x-rays because no euhedral crystals were found.

X-ray data. As neither crystal faces nor good cleavage planes were present, a fragment was oriented by a series of transmission Laue photographs. Fortunately, one of the first films revealed a mirror plane. The crystal was then turned, a few degrees at a time, around the axis perpendicular to this plane. Laue films made at each position showed no additional symmetry. Rotation and Weissenberg (0−1, 1−1, and 2−1) films were made with unfiltered Cu radiation in a camera of 5.73 cm. diameter, using the axis perpendicular to the mirror plane. They confirmed the assumption that this was the monoclinic b-axis. Additional orientation work enabled a-axis rotation as well as 0−1, and 1−1 Weissenberg films to be made. A space group of either Cc or $C2/c$ is indicated by the characteristic missing reflections: hkl (missing with h+k odd); h0l (missing with l odd, and h odd); 0k0 (missing with k odd).

The measured x-ray powder data listed in Table 1 are the average values obtained from a total of five films made in two cameras with $CuK\alpha$ radiation. The two cameras had diameters of 11.46 cm. With some idea of the unit cell values determined from the Weissenberg films, it was possible to partially index the powder films. Procedures similar to those of the Hesse-Lipson method outlined by Azároff and Buerger (1958) were used. Unit cell values, determined from the partially indexed powder data, are: $a=13.00$ Å; $b=5.38$ Å; $c=12.12$ Å; $a:b:c=2.416:1:2.253$; $\beta=98°$.

Since no euhedral crystals were available, an accurate value of β could not be determined on the goniometer. Therefore, the reported value of β may be in

TABLE 1. *X*-RAY POWDER DATA FOR SPIROFFITE. CuK$_\alpha$ RADIATION, d VALUES ARE AVERAGES OBTAINED FROM MEASUREMENTS OF FIVE FILMS MADE IN TWO CAMERAS OF 11.46 CM DIAMETER

hkl	d (calc.) Å	d (meas.) Å	I (obs.)
200	6.44	6.44	vw
002	6.00		
110	4.96	4.98	s+
$\bar{2}$02	4.73		
$\bar{1}$11	4.68	4.68	mw
111	4.50	4.48	vw
202	4.11	4.06	s
$\bar{1}$12	3.93		
112	3.73	3.69	vvw
310	3.35		
$\bar{3}$11	3.33	3.31	s
400	3.22		
311	3.14		
$\bar{3}$12	3.07		
113	3.04		
$\bar{4}$02	3.02		
004	3.00	3.00	s+
$\bar{2}$04	2.88	2.84	mw
312	2.80	2.77	w
$\bar{3}$13	2.72		
020	2.69	2.69	w
402	2.68	2.65	vw
021, $\bar{1}$14	2.63		
204	2.58	2.60	w
114	2.51		
220	2.48		
$\bar{2}$21	2.46	2.46	mw
022	2.45		
313	2.44		
221	2.41		
$\bar{3}$14	2.37		
$\bar{4}$04	2.36		
$\bar{2}$22, $\bar{5}$11	2.34	2.33	w+
510	2.32		
$\bar{5}$12	2.26		
222	2.25	2.24	vw
		2.22	mw
		2.10	vw
		2.04	w
		2.00	vw
		1.95	w
		1.89	vw
		1.83	vw
		1.80	vw
		1.77	w
		1.72	vvw
		1.67	mw
		1.63	ms
		1.60	vvw
		1.57	mw

error. Also, the accuracy of the unit cell dimensions were necessarily affected. However, interplanar spacings calculated from these values reasonably match the observed data, and permit the observed d-spacings to be indexed. In Table 1, all calculated spacings allowed by space groups *Cc* and *C2/c* are listed for d$_{hkl} \geq 2.25$ Å. All spacings down to 1.57 Å were calculated, but so many different values match each of the measured reflections in this range that the inclusion of these data seems pointless. Using a molecular weight of 627.92 for $(Mn_{1.26}Zn_{0.72}Ca_{0.02})Te_3O_8$, and a measured specific gravity of 5.01, the value determined for Z is 4 (4.03 calculated).

PHYSICAL AND OPTICAL PROPERTIES

The specific gravity of several grains of spiroffite, weighing about 20 mg each, was measured with the Berman balance and found to be 5.01 ± 0.02 at 25° C. The calculated value is 4.97. The hardness is about $3\frac{1}{2}$. Spiroffite has a conchoidal fracture and at least two directions of cleavage. It has not been possible to determine the crystallographic orientation of the cleavages.

The optical properties of spiroffite are given in Table 2. The determination of the optical constants was complicated by the high refractive indices and the tendency of cleavage grains to assume a preferred orientation. Although most grains yielded obtuse bisectrix interference figures, a few grains showed centered or nearly-centered acute bisectrix interference figures. Since γ was higher than the highest index liquid available (2.10), it could not be measured. The value of γ calculated from α, β and 2V is also given in Table 2. The "average" index of refraction ($\sqrt[3]{\alpha\beta\gamma}$) is 1.98, which agrees with the average index calculated from the Gladstone-Dale relationship, 1.97. The axial angle was estimated at 60 degrees during the immersion work. Later, 2V was measured with a three-axis universal stage equipped with hemispheres of n = 1.699. The value of 2V, after the usual corrections for refraction differences, is 55 degrees. The universal stage work confirmed the fact that γ is the acute bisectrix. It was not possible to obtain good readings on the cleavages. Consequently, the orientation of the optical indicatrix in spiroffite is still unknown.

TABLE 2. OPTICAL PROPERTIES OF SPIROFFITE

$\alpha = 1.85 \pm 0.01$	
$\beta = 1.91 \pm 0.01$	Biaxial positive
$\gamma > 2.10$ (2.20 calculated)	2V = 55° ± 5°
$\gamma - \alpha$ (calculated) = 0.35	

CHEMICAL CHARACTERISTICS

Preliminary spectrographic analysis. A small sample of spiroffite from R.O.M. specimen No. M24880 was submitted to the Ontario Department of Mines for spectrographic analysis. The following results were obtained:

Major Constituents—Mn, Zn, Te
Minor Constituents—Pb, Bi, Al, Si
Trace Constituents—Sb, Cd, Mo, Fe, Cu, Co, Ca, Mg

Only the major constituents could be estimated with any certainty because of the sample's size.

Quantitative analysis. Several small masses of the mineral were removed from a specimen (R.O.M. No. M24879) and crushed. A clean concentrate of 500 mg was obtained by hand-picking under a binocular microscope. No other phases were observed in this concentrate under a magnification of $40\times$. *X*-ray powder patterns of several samples taken from the analysis lot showed no extraneous lines. Additional clean material from the same masses was used for *x*-ray, optical, and specific gravity determinations.

The 500 mg sample was submitted to Mr. C. O. Ingamells, Mineral Constitution Laboratories, Pennsylvania State University. In addition, a small impure sample was provided for exploratory analysis.

Preparatory to the wet chemical analysis, a quantitative spectrographic analysis was carried out by Mr. Norman H. Suhr of Pennsylvania State University. The results of this analysis are given in Table 3. Also included are flame photometer determinations of Na_2O and K_2O. No attempt was made to determine the precise amounts of TeO_2, ZnO, MnO, and CaO as this would be done later by wet chemical methods.

The results of Mr. Ingamells' quantitative analysis are shown in Table 4. The procedures used in the analysis are given in the appendix. The empirical formula derived from the data of Table 4 is:

$$(Mn_{1.26}Zn_{0.72}Ca_{0.02})Te_{3.01}O_{8.02}$$

or, simplified:

$$(Mn, Zn, Ca)_2Te_3O_8.$$
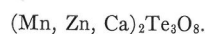
The natural hypothetical end-members have not yet been found. Attempts are being made to synthesize these compounds and the results will be reported later. Mellor (1931) lists no compounds of this type, although tritellurites of single divalent cations with the formulae of the type RTe_3O_7 have been synthesized.

(a) Degree of precision. According to Mr. Ingamells, the TeO_2 content is probably accurate to one

TABLE 3. EMISSION SPECTROGRAPHIC ANALYSIS OF SPIROFFITE. ROYAL ONTARIO MUSEUM NO. M24879, PENNSYLVANIA STATE NO. 61-1430. NORMAN H. SUHR, SPECTROGRAPHER. FLAME PHOTOMETER DETERMINATIONS OF Na_2O AND K_2O ARE INCLUDED

Constituent	Weight %
TeO_2	major[1]
ZnO	8.5[1]
CdO	0.07
PbO	0.05
MnO	18[1]
CaO	0.02?[1]
MgO	0.02
Bi_2O_3	0.08
Sb_2O_3	0.02
Al_2O_3	0.02
MoO_3	0.00
FeO	0.00
CoO	0.02
NiO	0.00
V_2O_5	0.00
TiO_2	0.00
Na_2O	0.0 (by flame photometer)
K_2O	0.0 (by flame photometer)

Total (less TeO_2, ZnO, MnO, and CaO) 0.28

[1] See Table 4 for chemical determinations of these constituents.

TABLE 4. QUANTITATIVE CHEMICAL ANALYSIS OF SPIROFFITE (ROM No. M24879, PENN. STATE No. 61-1430). C. O. INGAMELLS, ANALYST, MINERAL CONSTITUTION LABORATORIES, PENNSYLVANIA STATE UNIVERSITY. SEE APPENDIX FOR ANALYTICAL PROCEDURES

(1)	(2)	(3)	(4)	(5)
TeO_2	75.93	76.29	.478	3.01
ZnO	9.32	9.36	.115 ⎫	⎧ 0.72
MnO	14.13	14.20	.200 ⎬ .318	2.00 ⎨ 1.26
CaO	0.15[1]	0.15	.003 ⎭	⎩ 0.02
excess O_2	0.00			
H_2O	0.03			
insoluble	0.22[2]			
remainder	0.28[3]			
total	100.06	100.00		

[1] Includes SrO (less than 0.1%) if present.
[2] Material insoluble in 1:1 HCl—probably silica or silicate.
[3] Consists of minor constituents determined spectrographically (see Table 3).
(1) Constituent
(2) Weight %
(3) Major constituents recalculated to total 100.00%
(4) Molecular proportions
(5) Ratio of TeO_2 to divalent oxides

part in a thousand. The values for MnO, ZnO, and CaO (including SrO) are accurate to about $\pm 0.05\%$ absolute. The excess oxygen determination is true to $\pm 0.01\%$. Because of the small sample used, the H_2O determination may well be inaccurate. The value of 0.03% is only included to show that the mineral is not a hydrate. The emission spectrographic determinations are within 10% of the amounts present. The alkalies were run by flame photometry on extremely small samples and it is possible that as much as 0.1% of either Na_2O or K_2O may be present.

Chemical Tests. Spiroffite darkens and fuses easily in a gas flame. In both open and closed tubes it fuses quietly to a reddish-brown, glass-like substance. It is easily soluble in cold HCl and the resulting solution is yellow. No significant solution was noted in either hot HNO_3 or hot H_2SO_4.

NOMENCLATURE AND CLASSIFICATION

Spiroffite is an anhydrous tellurite of divalent manganese, zinc, and calcium. Of the known natural tellurites, only one other mineral has this same qualitative chemical composition. This mineral is denningite, $(Mn, Ca, Zn)Te_2O_5$. A comparison of the proper-

TABLE 5. COMPARISON OF SPIROFFITE AND DENNINGITE

	Spiroffite	Denningite
Chemical Formula	$(Mn, Zn, Ca)Te_3O_8$	$(Mn, Ca, Zn)Te_2O_5$
Crystallography Space group	Monoclinic Cc or $C2/c$	Tetragonal $P4_2/n\,b\,c$
Unit cell parameters	$a=13.00$ Å $b=\ 5.38$ Å $c=12.12$ Å $\beta=98°$	$a=\ 8.82$ Å $c=13.04$ Å
Z	4	8
H	$3\frac{1}{2}$	4
Sp. gr.	5.01	5.05
Optical properties	Biaxial $(+)$ $\alpha=1.85$ $\beta=1.91$ $\gamma=2.20$ (calc.) $2V=55°$	Uniaxial $(+)$ $\omega=1.89$ $\epsilon=2.00$
Strongest x-ray powder spacings	4.98 Å (S+) 3.00 Å (S+) 4.06 Å (S) 3.31 Å (S) 1.63 Å (MS)	4.42 Å (VS) 3.38 Å (S+) 3.12 Å (S) 2.62 Å (S) 2.03 Å (S)

ties of spiroffite and denningite is given in Table 5. There can be no doubt that these two species are distinct from each other. Spiroffite (as well as denningite) is a so-called "basic" tellurite. That is, the ratio of tellurium (IV) to oxygen is *not* one to three.

The name spiroffite should be restricted to the high manganese portion of the hypothetical system $Mn_2Te_3O_8-Zn_2Te_3O_8-Ca_2Te_3O_8$. Consequently, the material described here is properly termed a zincian spiroffite. The amount of CaO (0.15%) is not considered sufficiently high to warrant the use of the additional prefix, calcian.

Spiroffite is named in honor of Kiril Spiroff (1901–), Professor of Mineralogy and Geology, Department of Geology and Geological Engineering, Michigan College of Mining and Technology, Houghton, Michigan.

PRESERVATION OF SPECIMENS

The following specimens of spiroffite have been preserved in the mineral collections of the Royal Ontario Museum: M24879 (analyzed specimen), M24880, M24999, and M25001 (with denningite). Approximately six grams of spiroffite exist in these specimens.

Requests for loan of specimens should be addressed to:

> Curator of Mineralogy,
> Earth Sciences Division,
> Royal Ontario Museum,
> University of Toronto,
> 100 Queen's Park,
> Toronto 5, Ontario,
> Canada.

ACKNOWLEDGEMENTS

APPENDIX—METHOD OF ANALYSIS

The following procedures were used in the analysis of spiroffite. The writers are indebted to Mr. Ingamells for making this information available.

1. Grind all but a few mg. to pass 100 mesh. Pack powder in

glass and lucite holder and take *x*-ray fluorescence spectrum. Prepare synthetic mixtures of pure oxides to approximate composition of unknown, but with an excess of all the minor elements, and a deficiency of TeO_2. Make a preliminary estimate of sample composition.

2. Make several successive dilutions of the known mixtures with TeO_2, and prepare spectrograms of these as well as the unknown, using about 30 mg of sample. Obtain quantitative values for the trace elements and approximations for the majors, using emission spectrograph.

3. Determine total water on 100 mg in a closed tube.

4. Determine excess oxygen on 20 mg, running known salts of Te (IV) and Te (VI) as controls. Method: C. O. Ingamells (1960).

5. Using small impure sample provided, carry out exploratory analysis to determine behavior of material. Look for the alkali metals with the flame photometer.

6. Carry out main part of the analysis as follows, using 300 mg sample. Dry at 105°, weigh; dry at 160°, weigh. Dissolve in HCl, filter off insolubles, weigh. Precipitate Se with hydroxylamine, weigh; precipitate Te with SO_2, hydrazine, weigh. Examine precipitate for Bi, etc. Neither Se nor Bi were found in amounts sufficiently large to determine by these methods. Precipitate sulphide group, precipitate NH_3 group, examine precipitates. Triple oxalate precipitation, weigh CaO+Mn, Zn. Determine Mn, Zn contamination and correct. Double PO_4^{3-} precipitation, weigh $Mn_2P_2O_7$: determine Mg, Ca contamination and correct. Destroy NH_4^+ salts with HNO_3, determine Zn by weighing as pyrophosphate. Determine Mn contamination and correct.

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