DENNINGITE*, A NEW TELLURITE MINERAL FROM MOCTEZUMA, SONORA, MEXICO

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ABSTRACT

Denningite, $(Mn, Ca, Zn)Te_2O_5$, was found near Moctezuma, Sonora, Mexico. It occurs in small cleavable masses and occasionally in minute euhedral crystals. The colour ranges from pale green to colourless; the lustre is adamantine; hardness is 4; and specific gravity is 5.05. Denningite is optically uniaxial positive; $\omega = 1.89$ and $\epsilon = 2.00$. The mineral is tetragonal with a space group of $P4_2/nbc$; $a = 8.82$ Å; $c = 13.04$ Å; $a:c = 1:1.478$. The unit cell contains 8 $[(Mn, Ca, Zn)Te_2O_5]$. Strongest x-ray powder spacings are: 4.42 Å (VS), 3.38 Å $(S+)$, 3.12 Å (S), 2.62 Å (S), and 2.03 Å (S).

Denningite is associated with tellurite, paratellurite, native tellurium, spiroffite, and several other new tellurites. The name is given in honour of Reynolds M. Denning, Professor of Mineralogy at the University of Michigan.

INTRODUCTION AND OCCURRENCE

Preliminary data for denningite and several other new tellurite and/or tellurate minerals have been presented by Mandarino & Williams (1961a, 1961b). In both of these preliminary reports, denningite was called a "manganese tellurite or tellurate".

Denningite was found in specimens from Mina Moctezuma (formerly known as La Bomboya), near the town of Moctezuma, Sonora, Mexico (Lat. 29° 47.5′N, Long. 109° 41′W). Based on the suite of specimens at our disposal, denningite probably is the most abundant of the six new minerals being studied from this deposit. The writers have not been able to visit the deposit, so a definitive statement concerning the paragenesis cannot be made at this time.

Associated with denningite in our suite of specimens are: native tellurium, tellurite, paratellurite, and several new tellurites or tellurates. Among these new species is spiroffite. Other minerals identified from the deposit, but not present in the denningite specimens, are native selenium, chalcomenite, emmonsite, and mackayite.

Two types of denningite have been found: green cleavable masses and colourless euhedral crystals. Except where noted, the data given in the following pages are for the green cleavable material.

*Pronounced: DĔN·INGAIT using the Royal Geographical Society (R.G.S.II) system as given in Hey (1955); or dĕn·nĭng-ite using the Oxford Dictionary System.

GENERAL FEATURES AND APPEARANCE

Denningite usually occurs as platy, cleavable masses, but a few euhedral crystals have been found. The masses are a pale green similar to LG–14–4° in the colour classification of Villalobos (1947). They attain maximum dimensions of 10 × 20 × 3 mm., although their average size is 5 × 10 × 2 mm. The crystals are thin plates with maximum dimensions of 1 × 1 × 0.1 mm. On broken surfaces, the crystals are colourless to pale grey; however, they are usually covered with a thin brown coating. This coating is amorphous to x-rays, and therefore adds no extra lines to the x-ray powder pattern. It is probably the same iron tellurite or tellurate with which the crystals are usually associated.

Both types of denningite have a colourless streak and an adamantine lustre. They are translucent to transparent.

PHYSICAL AND OPTICAL PROPERTIES

The specific gravity was measured with the Berman balance, using five cleavage fragments, each weighing between 20 and 25 mg. The observed value at 25° C. is 5.05 ± 0.05. The calculated value is 5.07.

Denningite has a hardness of 4. It is fragile, with a perfect {001} cleavage and a conchoidal fracture. The mineral does not fluoresce under short- or long-wave ultra-violet light.

Denningite is uniaxial positive; $\omega = 1.89 \pm 0.01$, $\epsilon = 2.00 \pm 0.01$, and $\epsilon - \omega = 0.11$ (calculated). Some grains are slightly biaxial with a $2V$ up to 15 degrees. Crushed fragments are colourless. Most grains, because of the perfect {001} cleavage, yield centred or nearly-centred optic axis interference figures.

CRYSTALLOGRAPHY

Morphology

The few euhedral crystals found during this study are eight-sided plates, tabular parallel to {001}. Besides {001}, the only other forms observed are {110} and {100}.

X-ray Data

X-ray studies prove that denningite is tetragonal. Rotation patterns were made for crystals rotated about the a-axis, c-axis, and intermediate-axis. Several levels of Weissenberg patterns were also produced. All the single-crystal patterns were made with a camera of 5.73 cm. diameter using copper radiation. The space group $P4_2/nbc$ is indicated by the

characteristic extinct reflections: $hk0$ (missing with $h + k$ odd), $0kl$ (missing with k odd), hhl (missing with l odd). Furthermore, hkl reflections are usually very weak or absent when $h + k$ is even and l is odd. Naturally, this does not affect the choice of the space group. Single-crystal x-ray films were also used to determine the best choice for the a-axis and to obtain approximate unit cell values for indexing the powder patterns.

Five x-ray powder patterns of the euhedral material were made with CuK_α radiation in a camera of 11.46 cm. diameter. The measured interplanar spacings given in Table 1 represent average values obtained from these films. These data were partially indexed using a Hull-Davey chart (1921) and the approximate unit cell values previously determined by the single-crystal methods. Then the a and c constants were further refined from the powder data. These values are: $a = 8.78 \pm 0.05$ Å; $c = 12.99 \pm 0.05$ Å; $a:c = 1:1.479$. Using these constants, all possible interplanar spacings allowed by the $P4_2/nbc$ space group were calculated down to 1.36 Å. The excellent correlation with the observed data is evident from Table 1. In this table, all calculated values down to 1.82 Å are included; below 1.82 Å, only those data which closely match the observed data are listed. Five x-ray powder patterns of the green cleavable masses were also made. The interplanar spacings from these patterns are somewhat larger than those for the euhedral crystals. Indexed data for the green cleavable material are included in Table 1. The unit cell values calculated from these data are: $a = 8.82 \pm 0.05$ Å; $c = 13.04 \pm 0.05$ Å; $a:c = 1:1.478$. Using a molecular weight of 387.04 for $(Mn_{0.57}Ca_{0.30}Zn_{0.13})Te_2O_5$, and a measured specific gravity of 5.05, the value determined for Z is 8 (7.97 calculated).

TABLE 1. X-RAY POWDER DATA FOR DENNINGITE
CuK_α radiation, camera diameter 11.46 cm. Measured interplanar spacings
are averages of data obtained from five films.

	Euhedral crystals (ROM M25002)			Green cleavable material (ROM M25005)	
hkl	d (calc.) Å	d (meas.) Å	I (obs.)	d (meas.) Å	I (obs.)
002	6.50				
110	6.21	6.22	m	6.26	m
112	4.49				
020	4.39	4.40	S	4.42	VS
021	4.16			4.17	vw
121	3.76	3.75	vvw	3.78	vvw
022	3.64			3.63	vvw
122	3.36	3.36	S	3.38	$S+$
004	3.25	3.24	w	3.25	mw
220	3.10	3.11	MS	3.12	S
023	3.08				
123	2.91				

TABLE 1 (*Concluded*)

hkl	Euhedral crystals (ROM M25002)			Green cleavable material (ROM M25005)	
hkl	*d* (calc.) Å	*d* (meas.) Å	*I* (obs.)	*d* (meas.) Å	*I* (obs.)
114	2.88	2.89	*w*	2.90	*w*
222	2.80				
130	2.78	2.77	*w+*	2.78	*mw*
131	2.72				
024	2.61	2.61	*MS*	2.62	*S*
132	2.55				
124	2.50				
231	2.39				
133	2.34				
232	2.28	2.28	*vw*	2.29	*mw*
224, 025	2.24	2.24	*vw*	2.25	*w*
040	2.20				
125, 006	2.17				
041	2.16	2.16	*w*	2.18	*w*
233	2.12				
134	2.11				
141	2.10				
042	2.08				
330	2.07	2.07	*vvw*	2.08	*vw*
116	2.04				
142	2.02	2.02	*MS*	2.03	*S*
332	1.97				
240, 043	1.96				
234	1.95				
026, 241	1.94	1.94	*vw*	1.95	*vw*
143	1.91				
135, 126	1.90⎱	1.89	*mw*	1.90	*mw*
242	1.88⎰				
043	1.82				
334	1.75				
341	1.74	1.74	*mw*	1.75	*mw*
342	1.70	1.69	*w*	1.70	*mw*
244, 127, 045	1.68	1.68	*w*	1.69	*mw*
343	1.63				
008, 236, 251	1.62	1.62	*w*	1.63	*w+*
253	1.53				
028, 154, 146	1.52	1.52	*m*	1.53	*MS*
442, 350	1.51				
128, 336, 351	1.50	1.50	*mw*	1.51	*m*
228, 155	1.44				
161, 062	1.43	1.43	*vw*	1.44	*w*
353, 047	1.42				
162	1.41	1.41	*w*	1.41	*mw*
138, 444, 147	1.40				
029, 163, 354	1.37				
346, 451, 262	1.36	1.36	*vw*	1.37	*mw*
129, 238, 247, 156	1.35				

CHEMICAL COMPOSITION

Material for a qualitative spectrographic analysis was obtained from
R.O.M. Specimen No. M25003. Material for the quantitative analyses

(wet and spectrographic) was removed from a green cleavable mass on R.O.M. Specimen No. M25005. This green mass measured approximately $10 \times 20 \times 3$ mm. on the specimen. Additional grains from this mass were selected for optical, x-ray, and specific gravity determinations.

Qualitative Spectrographic Analysis

Early in the study, a very small sample of denningite was submitted to the Ontario Department of Mines for spectrographic analysis. The results were:

| Major Constituents	— Mn, Te, Zn
Appreciable Constituents	— Ca, Si
Minor Constituents	— Fe, Pb, Mg, Al

Because the sample was so small, the constituents were classified, "major, appreciable, or minor", on the basis of visual estimates alone.
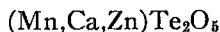
Quantitative Analysis

The material from R.O.M. Specimen No. M25005 was crushed and then examined with a binocular microscope. A concentrate of 500 mg. was hand-picked from the crushed sample. This concentrate was submitted for analysis to Mr. C. O. Ingamells, Mineral Constitution Laboratories, Pennsylvania State University. A small impure sample of denningite from the same specimen was also submitted for exploratory analysis. The procedures used by Mr. Ingamells are described in the appendix.

Before the wet chemical analysis was made, a quantitative spectrographic analysis was carried out by Mr. Norman H. Suhr of Pennsylvania State University. The results appear in Table 2. Precise measurements of the major constituents (TeO_2, ZnO, MnO, and CaO) were not attempted as they would be determined later by wet methods. Included in Table 2 are flame photometer determinations of Na_2O and K_2O.

The results of Mr. Ingamells' chemical analysis are shown in Table 3. The remainder (0.27%) includes all the minor and trace constituents reported in the quantitative spectrographic analysis. The empirical formula derived from the data in Table 3 is:

$$(Mn_{0.57}Ca_{0.30}Zn_{0.13})Te_{2.04}O_{5.08}$$

or, simplified:

$$(Mn,Ca,Zn)Te_2O_5$$
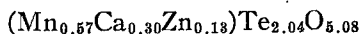
If the MgO determined spectrographically (0.20%) were added, the formula would read:
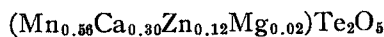
$$(Mn_{0.56}Ca_{0.30}Zn_{0.12}Mg_{0.02})Te_2O_5$$

TABLE 2. QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF DENNINGITE
(R.O.M. No. M25005). Emission spectrography by Norman H. Suhr,
Mineral Constitution Laboratories, Pennsylvania State University,
Flame photometer determinations of Na_2O and K_2O are included.

Constituent	Weight %	
TeO_2	major*	
ZnO	2.3*	
CdO	0.02	
PbO	0.01	
MnO	13*	
CaO	5.5*	
MgO	0.20	
Sb_2O_3	0.00	
MoO_3	0.00	
FeO	0.00	
CoO	0.04	
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)	0.27	

*See Table 3 for chemical determinations of these constituents.

TABLE 3. QUANTITATIVE CHEMICAL ANALYSIS OF DENNINGITE
(R.O.M. No. M25005, Penn. State No. 61–1431).
C. O. Ingamells, Analyst, Mineral Constitution Laboratories,
Pennsylvania State University. See Appendix for analytical procedures.

(1)	(2)	(3)	(4)	(5)	
TeO_2	82.34	82.77	.519	2.04	
ZnO	2.63	2.64	.032 ⎫		⎧0.13
MnO	10.28	10.34	.146 ⎬.254	1.00	⎨0.57
CaO	4.23*	4.25	.076 ⎭		⎩0.30
Excess O_2	0.09				
H_2O	0.03				
Insoluble	0.03†				
Remainder	0.27‡				
Total	99.90	100.00			

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

However, the accuracy of the spectrographic determination is considerably lower than that of the wet methods used for MnO, CaO, and ZnO. Therefore, the writers have excluded magnesium from the formula.

Natural $MnTe_2O_5$, $CaTe_2O_5$ and $ZnTe_2O_5$ have not yet been found. Attempts to synthesize these compounds are being made and the results will be published later. Mellor (1931) states that $CaTe_2O_5$ has been synthesized by Berzelius.

Degree of Precision

According to Mr. Ingamells, the TeO_2 content is probably accurate to one 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

Denningite darkens and fuses easily in a flame. It fuses quietly to a brown material in the closed tube and to a reddish-brown material in the open tube. It dissolves easily in cold HCl turning the solution yellow. It is insoluble in both hot and cold HNO_3, but is slightly soluble in H_2SO_4 with separation of a white milky material.

NOMENCLATURE AND CLASSIFICATION

Denningite is a tellurite of divalent manganese, calcium, zinc, and possibly magnesium. Its comparison with other minerals of related composition is simplified by the small number of known natural tellurites. Only one of these contains any of the cations present in denningite. This chemically similar mineral is spiroffite $(Mn,Zn,Ca)_2Te_3O_8$, which was described recently by Mandarino, Williams & Mitchell (1962). That denningite and spiroffite are distinct from one another can easily be seen by referring to Table 4, where their physical and chemical data are summarized.

The empirical formula of denningite (and of spiroffite) raises some interesting speculations about tellurites and related minerals. Before these species were discovered, all natural tellurites were considered normal tellurites and were formulated to contain TeO_3^{--} groups. Some of the poorly-defined tellurite species may really be basic tellurites with the ratio Te:O $\neq$ 1:3. The same possibility exists in the natural selenites and has been pointed out by Goni & Guillemin (1953).

There is no doubt that the ratio of divalent oxides to TeO_2 is 1:2 in denningite and that the ratio of Te:O is 2:5. The excess oxygen deter-

TABLE 4. COMPARISON OF DENNINGITE AND SPIROFFITE

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

mination by Ingamells clearly proves that the mineral is a tellurite and that the manganese is in the divalent state (a small amount of Mn^{+3} may be present). If, then, denningite were a normal tellurite with a formula of $(Mn_{0.57}Ca_{0.30}Zn_{0.13})TeO_3$, the amount of TeO_2 reported in the analysis would be 70.17% instead of 82.34%. The difference between these two figures is well beyond the analytical error. Contamination of the analysis sample by other tellurium minerals such as tellurite is always a possibility. However, the sample used for the analysis was very carefully examined for other phases under magnifications up to 40X. No foreign substances were seen, nor did the x-ray powder patterns of the analyzed sample contain any lines due to other phases.

Denningite should be classed as a pyrotellurite. Consequently, a new category must be provided in the existing mineralogical classifications: the anhydrous basic tellurites. No doubt, further work on poorly-defined selenites will reveal an analogous category. Numerous basic tellurites and selenites have been synthesized and are discussed by Mellor (1930, 1931).

It is suggested that the name denningite be restricted to the high manganese portion of the hypothetical system $MnTe_2O_5 - CaTe_2O_5 -$

$ZnTe_2O_5$. Consequently, the material described in this paper is properly termed a calcian zincian denningite.

Denningite is named in honour of Professor Reynolds M. Denning (1916—), Professor of Mineralogy, Department of Geology and Mineralogy, University of Michigan, Ann Arbor, Michigan.

Preservation of Specimens

The following specimens of denningite have been preserved in the mineral collections of the Royal Ontario Museum: M25000, M25001 (with spiroffite), M25002 (euhedral crystals present), M25003, M25004, and M25005 (analyzed specimen). Approximately five grams of denningite 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.

Acknowledgments

It is a pleasure to acknowledge the assistance of the following people. Messrs. D. A. Moddle and W. O. Taylor of the Ontario Department of Mines kindly ran the original spectrographic analysis of denningite. Messrs. L. I. Cowan and C. M. Spooner of the Royal Ontario Museum assisted in various phases of the laboratory work. Dr. V. B. Meen, Royal Ontario Museum, was a constant source of encouragement during this study and contributed several helpful suggestions.

Appendix

Method of Analysis

The following procedures were used in the analysis of denningite. 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 behaviour 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. 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^{---} 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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