

## THE CRYSTAL STRUCTURE OF MROSEITE, $\text{CaTeO}_2(\text{CO}_3)$

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### ABSTRACT

Mroseite crystallizes orthorhombic, space group *Pbca*, lattice constants  $a = 6.988(15)$ ,  $b = 11.201(10)$ ,  $c = 10.566(10)\text{\AA}$ , cell content  $8 \times \text{CaTeO}_2(\text{CO}_3)$ . The structure was determined from *x*-ray intensities collected on an automatic Weissenberg-type diffractometer. Full-matrix least-squares refinement for the 807 observed reflections, with anisotropic temperature factors for Te and Ca, and isotropic temperature factors for C and O resulted in  $R = 0.066$ .

The structure contains  $\text{CO}_3$  groups of the usual dimensions. Calcium is irregularly-coordinated by eight oxygens. Considering only Te-O bonds from 1.85 to 2.05  $\text{\AA}$ , tellurium forms  $\text{Te}_2\text{O}_4$  groups with the oxygens that are not bonded to carbon. These  $\text{Te}_2\text{O}_4$  groups consist of two  $\text{TeO}_3$  pyramids with a common O-O edge. Oxygen neighbours of the carbonate group with Te-O = 2.31 and 2.55  $\text{\AA}$  complete the coordination around tellurium.

### RÉSUMÉ

La mroséite se cristallise en orthorhombique avec un groupe spatial *Pbca*, des dimensions de maille  $a = 6.988(15)$ ,  $b = 11.201(10)$ ,  $c = 10.566(10)\text{\AA}$  et un contenu de  $8 \times \text{CaTeO}_2(\text{CO}_3)$ . La structure a été déterminée par les intensités des rayons-x amassées sur un diffractomètre automatique de type Weissenberg. Un résultat  $R = 0.066$  a été obtenu comme raffinement par la méthode des moindres carrés à matrice entière pour les 807 réflexions observées avec des facteurs de température anisotropiques pour Te et Ca et des facteurs de température isotropiques pour C et O.

La structure contient des groupes  $\text{CO}_3$  de dimensions habituelles. Le calcium est coordonné irrégulièrement par huit oxygènes. En considérant uniquement les liens Te-O de 1.85 à 2.05  $\text{\AA}$ , le tellurium forme des groupes  $\text{Te}_2\text{O}_4$  avec les oxygènes qui ne sont pas liés au carbone. Ces groupes  $\text{Te}_2\text{O}_4$  consistent de deux pyramides  $\text{TeO}_3$  avec une arête commune O-O. Les oxygènes voisins du groupe carbonate avec Te-O = 2.31 et 2.55  $\text{\AA}$  complètent la coordination autour du tellurium.

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### INTRODUCTION

Mroseite, a new orthorhombic tellurite mineral from Moctezuma, Sonora, Mexico, was

recently described by Mandarino *et al.* (1975). These authors analyzed the mineral and determined the *x*-ray crystallographic constants as follows: lattice constants  $a = 6.93$ ,  $b = 11.16$ ,  $c = 10.54\text{\AA}$ , space group *Pbca*; cell content  $8[\text{CaCO}_3\text{TeO}_2]$ .

As one would expect mroseite to contain the usual  $\text{CO}_3$  group, the mineral belongs to the class of inorganic compounds that consist of a salt-like part and an oxide part, *i.e.*, formal "double compounds". Therefore, it was of interest to determine the crystal structure to learn (1) if the oxygens of the  $\text{CO}_3$  group participate in the coordination around tellurium and (2) what kind of polymerization of tellurium-oxygen units occurs in this mineral.

### EXPERIMENTAL, AND STRUCTURE DETERMINATION

Mroseite from the type locality was used for the structure determination. *X*-ray intensities were measured from a tiny, irregular crystal fragment ( $\sim 100 \times 60 \times 60 \mu\text{m}$ ) on an automatic two-circle Weissenberg-type diffractometer with Mo radiation (Zr filter). The crystal was mounted with [100] parallel to the goniometer axis. The reflections of the zero through the 6th layer line with  $\sin \theta/\lambda \leq 0.70\text{\AA}^{-1}$  were taken into consideration, except for the *h*00 reflections which cannot be measured with this experimental procedure.

Lattice constants were determined to be  $a = 6.988(15)$ ,  $b = 11.201(10)$ ,  $c = 10.566(10)\text{\AA}$  (estimated errors in brackets), in good agreement with the values published by Mandarino *et al.* (1975). The space group *Pbca* given by the same authors was confirmed.

Of 936 crystallographically-independent reflections measured by the  $\omega$ -scan method, 807 with  $I(\text{obs}) \geq 2\sigma(I)$  were treated as observed for all further calculations. The data were corrected for the Lorentz and polarization factors. Because of the small crystal size and the use of Mo radiation, no absorption correction was necessary.

A three-dimensional Patterson function yielded the tellurium position and a subsequent

Fourier summation gave the calcium and some of the oxygen positions. After a preliminary least-squares refinement of the Ca and Te coordinates, a three-dimensional Fourier synthesis clearly showed all the atoms of the unit cell.

After several cycles of isotropic least-squares refinement,  $R = 0.08$  was reached. The comparison of  $F_o$  and  $F_c$  showed larger discrepancies for  $\sim 5\%$  of the reflections, possibly caused by uncontrolled errors in the electronics. These were carefully remeasured. The structure was refined with the final controlled set of data for several full-matrix least-squares cycles. The carbon and oxygen temperature factors were refined isotropically, the calcium and tellurium temperature factors anisotropically. The final conventional  $R$ -value for the 807 observed reflections was 0.066; if the 129 non-observed reflections are included with  $F_o = 0$ , one obtains  $R = 0.086$ .

Table 1 gives the atomic coordinates and the thermal parameters. The comparison of  $F_o$  and  $F_c$ , with  $F_o$  based on the scattering curves for neutral atoms as listed in the International Tables, Vol. III (1962) is given in Table 2\*.

\*Table 2 has been deposited with the Depository of Unpublished Data. Copies may be obtained on request to: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

TABLE 1. FRACTIONAL COORDINATES AND TEMPERATURE FACTORS

	$x$	$y$	$z$	$B$		
Ca	0.48009(49)	0.17222(25)	-0.00906(28)			
Te	0.09155(15)	0.01470(7)	0.13362(8)			
C	0.2632(32)	0.2619(15)	0.2573(17)	1.7(3)		
O(1)	0.3553(17)	0.3614(8)	0.2760(9)	0.6(2)		
O(2)	0.2283(19)	0.1962(9)	0.3503(10)	1.2(2)		
O(3)	0.2158(17)	0.2285(8)	0.1398(10)	0.7(2)		
O(4)	0.5226(19)	0.3919(10)	0.0270(10)	1.2(2)		
O(5)	0.1885(18)	0.4970(9)	0.0802(10)	1.0(2)		
	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Ca	0.417	0.366	0.675	-0.011	-0.037	0.039
Te	1.040	1.074	1.032	-0.049	0.084	-0.011

$$\text{ATF} = e^{-\frac{1}{2}(B_{11}a^2h^2 + \dots + 2B_{12}ab^*hk \dots)}$$

## DISCUSSION

The projection of the crystal structure of mroseite parallel to [100] is given in Figure 1. The important inter-atomic distances and bond angles are summarized in Table 3.

As expected, the structure contains a carbonate group with the usual dimensions. The Ca atoms are coordinated by eight oxygens with Ca-O = 2.38-2.73 Å; next-nearest neighbours are a carbon atom at 2.99 Å and an oxygen atom at 3.38 Å. The irregular CaO<sub>8</sub> polyhedra share three edges with each other and thereby form Ca<sup>8</sup>O<sub>8</sub> connections parallel to (001) (Fig 2). The shortest O-O distance in the CaO<sub>8</sub> polyhedron (2.20 Å) is a common edge with a carbonate group. The next nearest O-O distance (2.60 Å) is not, as one could expect, a common

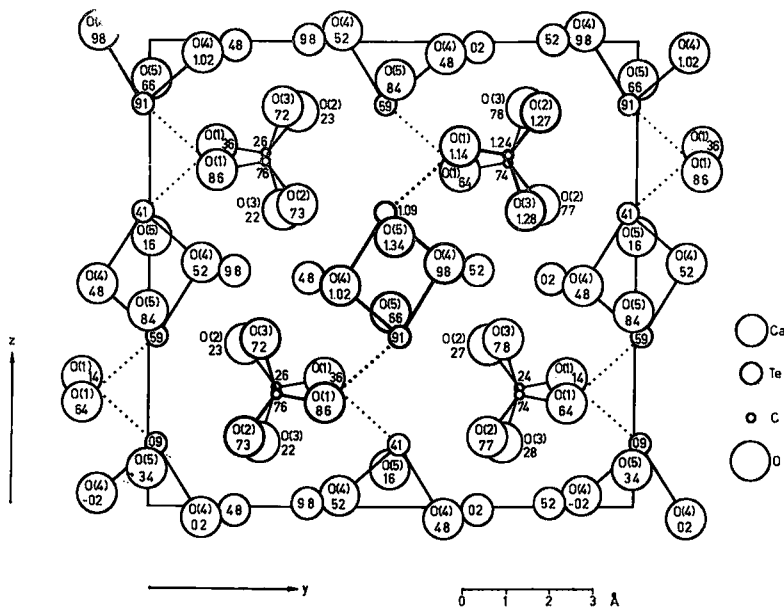


FIG. 1. Projection of the crystal structure of mroseite parallel [100]. Fractional coordinates are rounded to two decimals. To facilitate the recognition of important bonds, coordinates outside the unit cell are given for some atoms.

TABLE 3. SELECTED INTERATOMIC DISTANCES AND BOND ANGLES IN MROSEITE\*

$\text{CO}_3$ GROUP		
$\text{C}-\text{O}(1)_I = 1.30(3)\text{\AA}$	$\text{O}(1)_{II}-\text{O}(2)_I = 2.20(2)\text{\AA}$	$\text{O}(1)_{II}-\text{C}-\text{O}(2)_I = 118.7(1.2)^\circ$
$-\text{O}(2)_{II} = 1.25(3)$	$-\text{O}(3)_{II} = 2.29(2)$	$-\text{O}(3)_I = 120.2(1.1)$
$-\text{O}(3)_{II} = 1.34(3)$	$\text{O}(2)_{II}-\text{O}(3)_{II} = 2.26(2)$	$\text{O}(2)_{II}-\text{C}-\text{O}(3)_{II} = 121.1(1.2)$
$\text{CaO}_9$ POLYHEDRON		
$\text{Ca}-\text{O}(1)_{VII} = 2.46(1)\text{\AA}$	$\text{O}(1)_{VII}-\text{O}(2)_{VII} = 2.20(2)^a$	$\text{O}(2)_{VII}-\text{O}(3)_{II} = 3.60(2)$
$-\text{O}(2)_{VII} = 2.73(1)$	$-\text{O}(3)_{II} = 3.06(2)$	$-\text{O}(3)_{II} = 3.17(2)^c$
$-\text{O}(2)_{VII} = 2.43(1)$	$-\text{O}(5)_{II} = 3.02(2)$	$-\text{O}(4)_I = 2.92(2)$
$-\text{O}(3)_{II} = 2.51(1)$	$-\text{O}(5)_{VI} = 3.59(1)$	$-\text{O}(5)_{II} = 3.29(2)$
$-\text{O}(3)_{II} = 2.42(1)$	$\text{O}(2)_{VII}-\text{O}(3)_{II} = 3.17(2)^c$	$-\text{O}(5)_{VI} = 3.58(2)$
$-\text{O}(4)_I = 2.51(1)$	$-\text{O}(3)_{II} = 3.43(2)$	$\text{O}(3)_{II} - \text{O}(4)_I = 3.06(2)$
$-\text{O}(5)_{VI} = 2.39(1)$	$-\text{O}(4)_I = 2.95(2)$	$-\text{O}(5)_{VI} = 2.81(1)^b$
$-\text{O}(5)_{VI} = 2.38(1)$		$\text{O}(3)_{II} - \text{O}(4)_I = 2.60(2)^b$
		$-\text{O}(5)_{VI} = 3.10(1)$
		$\text{O}(5)_{II} - \text{O}(5)_{VI} = 2.79(1)^c$
$\text{TeO}_6$ POLYHEDRON		
$\text{Te}-\text{O}(1)_{VI} = 2.31(1)\text{\AA}$	$\text{O}(1)_{VI}-\text{O}(4)_{VI} = 4.05(1)\text{\AA}$	
$-\text{O}(3)_I = 2.56(1)$	$-\text{O}(5)_{VI} = 2.91(1)$	
$-\text{O}(4)_{II} = 2.05(1)$	$\text{O}(3)_I - \text{O}(4)_{II} = 2.60(2)^c$	
$-\text{O}(4)_{VI} = 1.95(1)$	$-\text{O}(4)_{VI} = 4.29(1)$	
$-\text{O}(5)_{VI} = 1.85(1)$	$-\text{O}(5)_{VI} = 2.81(1)^c$	
	$\text{O}(4)_{II}-\text{O}(4)_{VI} = 2.51(2)^{\dagger}$	
	$-\text{O}(5)_{VI} = 2.86(2)$	
$\text{O}(1)_{VI}-\text{O}(3)_I = 4.09(1)$	$\text{O}(4)_{VI}-\text{O}(5)_{VI} = 2.79(2)$	
$-\text{O}(4)_{II} = 2.90(1)$	$\text{O}(3)_I - \text{Te}-\text{O}(4)_{VI} = 144.9(7)^\circ$	
$\text{O}(1)_{VI}-\text{Te}-\text{O}(3)_I = 128.8(4)^\circ$	$-\text{O}(5)_{VI} = 77.7(4)$	
$-\text{O}(4)_{II} = 162.7(1.3)$	$\text{O}(4)_{II}-\text{Te}-\text{O}(4)_{VI} = 77.6(5)$	
$-\text{O}(4)_{VI} = 85.3(4)$	$-\text{O}(5)_{VI} = 91.4(5)$	
$-\text{O}(5)_{VI} = 88.1(4)$	$\text{O}(4)_{VI}-\text{Te}-\text{O}(5)_{VI} = 97.8(5)$	
$\text{O}(3)_I - \text{Te}-\text{O}(4)_{II} = 67.8(4)$		

\* Meaning of the Roman indices assigned to oxygen atoms, based on the coordinates given in Table 1.  
 A specific distance as tabulated may also refer to an oxygen in a neighbouring cell. The coordinates of Ca, Te and C are always those given in Table 1.  
 Standard deviations in brackets.

- a) common edge with  $\text{CO}_3$  group  
 b) common edge with  $\text{TeO}_6$  coordination  
 c) common edge with neighbouring  $\text{CaO}_9$  polyhedron  
 $\dagger$  common edge between two  $\text{TeO}_6$  pyramids

All O-O edges in the  $\text{CaO}_9$  polyhedron not listed in this table are longer than 4.0\AA.

edge between two  $\text{CaO}_9$  polyhedra, but rather a common edge between a  $\text{CaO}_9$  polyhedron and the "TeO<sub>6</sub>" coordination figure (including an oxygen with O-Te = 2.55\AA).

The distribution of the five nearest neighbours around tellurium corresponds to the known stereochemical behaviour of Te(IV) towards oxygen as summarized by Zemann (1971) and confirmed and extended by Pertlik & Zemann (1971), Lindqvist (1973), Meunier (1974) and Galy *et al.* (1975). The coordination around tellurium consists of three nearer oxygens that are non-bonded to carbon, and of two more-distant oxygens of the carbonate groups. The three nearer neighbours build a trigonal pyramid with the tellurium. Two such  $\text{TeO}_3$  pyramids have an edge in common. If the longer Te-O bonds are neglected, a finite  $\text{Te}_2\text{O}_4$  group results (Fig. 3). The Te-Te distance in this "Te<sub>2</sub>O<sub>4</sub> group" measures only 3.11\AA; this is, to the best of our knowledge, the shortest distance yet observed between two Te(IV). The

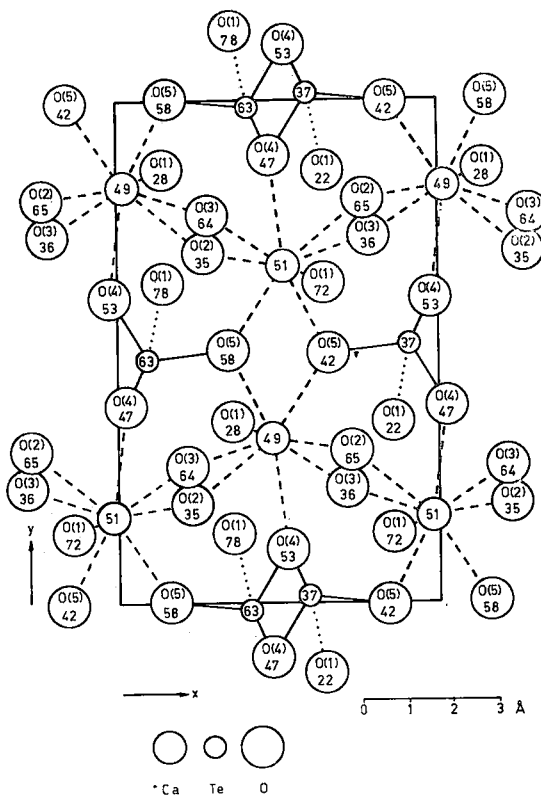


FIG. 2. Slice of the structure of mroseite projected parallel [001]. Fractional coordinates are rounded to two decimals. The slice comprises atoms between  $z \sim 1/4$  and  $z \sim 3/4$ .

Te-O distance of 2.31\AA undoubtedly represents a weak bond, and the Te-O distance of 2.55\AA indicates, in our opinion, more than a pure van der Waals interaction.

It is interesting to compare the tellurium-

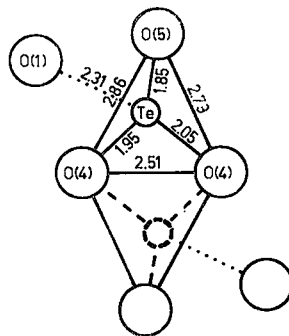


FIG. 3. "Te<sub>2</sub>O<sub>4</sub> group" of mroseite projected on the plane defined by the oxygen atoms O(4) and O(5). In addition, the carbonate-oxygen O(1) is drawn.

oxygen connection in mroseite with that in  $\text{TeO}_2$  modifications and with that in  $\text{Te}_2\text{O}_4 \cdot \text{HNO}_3$ . In orthorhombic  $\text{TeO}_2$  (tellurite; structure determination by Beyer *et al.* 1965, refinement by Beyer 1967), distorted  $\text{TeO}_4$  groups ( $\text{Te-O} = 1.88\text{-}2.20\text{\AA}$ ) are polymerized *via* corners and edges to form sheets. In tetragonal  $\text{TeO}_2$  (paratellurite; structure determination by Stehlik & Balak 1948, refinements by Leciejewicz 1961, and by Lindqvist 1968) less-distorted  $\text{TeO}_4$  groups ( $\text{Te-O} = 1.90\text{-}2.06\text{\AA}$ ) are connected only *via* corners to build a framework structure. In  $\text{Te}_2\text{O}_4 \cdot \text{HNO}_3$  the  $\text{TeO}_4$  units ( $\text{Te-O} = 1.88\text{-}2.16\text{\AA}$ ) are connected *via* corners and edges and form  $\text{TeO}_2$  sheets (Swink & Carpenter 1966).

The coordination around tellurium in mroseite is in some respects transitional between those in  $\text{Te}_2\text{O}_4 \cdot \text{HNO}_3$  and in  $\text{Te}_2\text{O}_3(\text{HPO}_4)$ . In the first compound, the oxygens of the  $\text{HNO}_3$  group do not participate in the coordination around tellurium (shortest distance of a nitrate-oxygen to Te:  $2.80\text{\AA}$ ); in mroseite, the shortest distance of a carbonate-oxygen to tellurium ( $2.31\text{\AA}$ ) indicates a weak bond; in  $\text{Te}_2\text{O}_3(\text{HPO}_4)$ , however, the shortest bond of a phosphate-oxygen to tellurium measures only  $2.12\text{\AA}$  (Mayer 1975) and represents, therefore, a rather strong bond.

The results of valence-bond summations after Donnay & Allmann (1970) and after Brown & Shannon (1973) and Brown (1975) are given in Table 4. The method of Donnay & Allmann gives somewhat less-satisfactory results, partly — in our opinion — the consequence of their somewhat arbitrary choice of  $L_{\text{max}}(\text{Te-O}) =$

$2.35\text{\AA}$ . But even a larger  $L_{\text{max}}$  for Te-O would, for example, not eliminate the difference in the valence-bond sums at O(4) and O(5); also, the summation after Brown & Shannon and Brown with no  $L_{\text{max}}$  gives different sums at O(4) and O(5).

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TABLE 4. VALENCE BOND SUMS IN MROSEITE\*

A. After Donnay & Allmann (1970):						
	Ca	Ca	Te	Te	C	$\Sigma O(x)$
0(1)	2.46		2.31		1.30	
$\sigma$	0.26(1)		0.13(4)		1.32(20)	1.71(20)
0(2)	2.73	2.43			1.25	
$\sigma$	0.17(1)	0.27(1)			1.46(20)	1.90(20)
0(3)	2.51	2.42			1.34	
$\sigma$	0.24(1)	0.27(1)			1.21(20)	1.72(20)
0(4)	2.51		2.05	1.95		
$\sigma$	0.24(1)		0.97(4)	1.29(4)		2.50(6)
0(5)	2.39	2.38		1.85		
$\sigma$	0.28(1)	0.28(1)	1.61(4)			2.17(5)
	$\Sigma\text{Ca} = 2.0$		$\Sigma\text{Te} = 4.0$		$\Sigma\text{C} = 4.0$	$\Sigma = 10.0$
B. After Brown & Shannon (1973) and Brown (1974):						
	Ca	Te	C	S	S	
$S_o$	0.250	1.333	1.333	Ca 2.01(2)	0(1) 2.00(15)	
$S_o^o$	2.468	1.813	1.290	Te 3.68(6)	0(2) 1.88(20)	
$S_o^o$	6.0	4.5	4.0	C 3.93(29)	0(3) 1.96(15)	
					0(4) 1.95(4)	
				$\Sigma=9.62$	0(5) 1.83(4)	
						$\Sigma=9.62$

\*Standard deviations as derived from the standard deviations of interatomic distances are given in brackets.

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