

THE CRYSTAL STRUCTURE OF SPIROFFITE

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ABSTRACT

The crystal structure of spiroffite, $\text{Mn}_2^{2+}\text{Te}_3\text{O}_8$, a 12.870(2), b 5.3813(5), c 11.888(2) Å, β 98.22(1)°, V 814.8(2) Å³, $C2/c$, Z 4, has been solved by direct methods and refined to an R index of 1.7% based on 1045 observed intensities measured with $\text{MoK}\alpha$ X-radiation on an automated four-circle diffractometer. Site-scattering refinement, stereochemical features and electron-microprobe analysis indicate that the composition of the crystal examined corresponds closely to the ideal end-member composition. Spiroffite is isostructural with synthetic $\text{Zn}_2\text{Te}_3\text{O}_8$. There are two distinct Te sites occupying the $4e$ and $8f$ positions, respectively: $\text{Te}(1)$ is coordinated by four oxygen atoms between 1.86 and 2.10 Å, all lying to one side of $\text{Te}(1)$; $\text{Te}(2)$ is coordinated by four oxygen atoms between 1.87 and 2.39 Å to one side, and two oxygen atoms between 2.83 and 3.13 Å to the other side of the central cation. This very asymmetric coordination is the result of stereoactive lone-pairs of electrons. The structure consists of open sheets of MnO_6 octahedra cross-linked into a framework by ladders of edge-sharing TeO_n polyhedra. Large open channels extend through the structure along [001], and accommodate the stereoactive lone-pairs of electrons of the peripheral Te atoms. The structure of denningite, $\text{CaMnTe}_4\text{O}_{10}$, shows a similar motif: chains of MnO_6 and CaO_8 polyhedra are linked into a framework by chains of TeO_n polyhedra, and open channels through the framework contain the stereoactive lone-pairs of electrons associated with Te^{4+} cations. The need to accommodate stereoactive lone-pairs of electrons has an important influence on structure topology in Te^{4+} -rich structures.

Keywords: spiroffite, crystal structure, tellurite, stereoactive lone-pair electrons.

SOMMAIRE

Nous avons affiné la structure cristalline de la spiroffite, $\text{Mn}_2^{2+}\text{Te}_3\text{O}_8$, a 12.870(2), b 5.3813(5), c 11.888(2) Å, β 98.22(1)°, V 814.8(2) Å³, $C2/c$, Z = 4, par méthodes directes, jusqu'à un résidu R de 1.7%, en utilisant 1045 intensités observées, et mesurées au moyen d'un rayonnement $\text{MoK}\alpha$ avec un diffractomètre automatisé à quatre cercles. Un affinement de la dispersion associée aux sites spécifiques montre que la composition du cristal étudié correspond bien à la composition idéale. La spiroffite est isostructurale avec le $\text{Zn}_2\text{Te}_3\text{O}_8$, synthétique. Il y a deux positions Te distinctes, $4e$ et $8f$, respectivement. $\text{Te}(1)$ est entouré de quatre atomes d'oxygène à une distance comprise entre 1.86 et 2.10 Å; tous les quatre sont du même côté de $\text{Te}(1)$. Par contre, $\text{Te}(2)$ est coordonné par quatre atomes d'oxygène situés entre 1.87 et 2.39 Å d'un côté, et deux autres entre 2.83 et 3.13 Å de l'autre du cation central. Cette coordination très asymétrique découle de la présence d'une paire isolée d'électrons stéréoactifs. La structure contient des feuillettes ouverts d'octaèdres MnO_6 inter-liés dans une trame d'échelles de polyèdres TeO_n à arêtes partagées. Des canaux ouverts et relativement volumineux traversent la structure le long de [001], et peuvent accommoder les paires isolées d'électrons stéréoactifs des atomes Te périphériques. La structure de la denningite, $\text{CaMnTe}_4\text{O}_{10}$, possède un motif semblable, avec des chaînes de polyèdres MnO_6 et CaO_8 liées dans une trame par des chaînes de polyèdres TeO_n , et des canaux ouverts traversant la trame, contenant ici aussi les paires isolées d'électrons stéréoactifs associés aux cations Te^{4+} . Cette exigence d'accommoder les paires isolées d'électrons stéréoactifs exerce une influence marquée sur la topologie de ces structures à Te^{4+} .

(Traduit par la Rédaction)

Mots-clés: spiroffite, structure cristalline, tellurite, paire isolée d'électrons stéréoactifs.

INTRODUCTION

Spiroffite, ideally $\text{Mn}_2\text{Te}_3\text{O}_8$, occurs as red to purple cleavable masses associated with tellurite, paratellurite, native tellurium and other tellurite minerals near

Moctezuma, Sonora, Mexico. It was described by Mandarino *et al.* (1963a), who reported significant Zn (9.32 wt% ZnO), to give a formula of $(\text{Mn}_{1.26}\text{Zn}_{0.72}\text{Ca}_{0.02})\text{Te}_{3.01}\text{O}_8$. The crystal structure of synthetic $\text{Zn}_2\text{Te}_3\text{O}_8$ was reported by Hanke (1966). The similarity of cell dimensions and space group between $\text{Zn}_2\text{Te}_3\text{O}_8$ and spiroffite indicates that the two materials are isostructural.

EXPERIMENTAL

The crystals used in this work are from Moctezuma, Sonora, Mexico and were purchased from a mineral dealer. A crystal was mounted on a Nicolet R3m automated four-circle diffractometer equipped with a Mo X-ray tube. Forty reflections were measured on a random-orientation photograph and aligned automatically on the diffractometer. From the resulting setting-angles, least-squares refinement gave the cell dimensions listed in Table 1, together with the orientation matrix. Intensity data were collected according to the procedure of Hawthorne & Groat (1985). A total of 1203 reflections was measured out to a maximum 2θ angle of 60° ($17 \leq h \leq 18$, $7 \leq k \leq 0$, $16 \leq l \leq 0$). A variable scan-speed from 1.72 to $14.65^\circ 2\theta \text{ min}^{-1}$ was used. Twelve strong reflections uniformly distributed with regard to 2θ were measured at 6° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector). These data were used to calculate an absorption correction, with the crystal modeled as an ellipsoid, which reduced the azimuthal R index from 3.6% to 1.4%; this correction was then applied to the normal intensity data. Data were corrected for Lorentz and polarization effects, averaged and reduced to structure factors. A reflection was considered as observed if its magnitude exceeded that of five standard deviations on the basis of counting statistics. Miscellaneous information pertaining to data collection and structure refinement is given in Table 1.

TABLE 1. MISCELLANEOUS INFORMATION FOR SPIROFFITE

| | | | |
|---|-----------|---------------------------------|--------------------|
| a (Å) | 12.870(2) | crystal size (mm) | 0.08 x 0.06 x 0.04 |
| b | 5.3813(5) | radiation | MoK α /Gr |
| c | 11.888(2) | No. of intensities | 1203 |
| β | 98.22(1) | No. of $ F_o > 5\sigma(F_o)$ | 1045 |
| V (Å ³) | 814.8(2) | R (azimuthal) % | 3.6 - 1.4 |
| Sp. Gr. | $C2/c$ | R (obs) % | 1.7 |
| D (calc) (g cm ⁻³) | 5.059 | wR (obs) % | 1.7 |
| μ (mm ⁻¹) | 13.64 | | |
| Cell content: 4[Mn ₂ Te ₃ O ₈] | | | |
| $R = \Sigma(F_o - F_c) / \Sigma F_o $ | | | |
| $wR = [\Sigma w(F_o - F_c)^2 / \Sigma F_o^2]^{1/2}$, $w = 1/\sigma^2[F]^{-1} \exp(-3.5[\sin\theta/\lambda]^2)$ | | | |

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from the *International Tables for X-ray Crystallography*, Vol. 4 (Ibers & Hamilton 1974). R and wR indices are of the conventional form and are given as percentages.

The structure was solved by direct methods. The E -statistics indicated that the structure is centrosymmetric, and we found a solution in the space group $C2/c$. The solution with the highest combined figure-of-merit refined to an R index of 1.7% for a model with anisotropic displacements. Final atomic positions and displacement parameters are given in Table 2, selected interatomic distances are given in Table 3, observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, and empirical bond-valence values are shown in Table 4.

DISCUSSION

Cation coordination

There is one crystallographically distinct Mn site occurring at the general position $8f$. It is surrounded by six anions in an octahedral arrangement, with Mn-O distances in the range 2.09–2.40 Å. The $\langle \text{Mn-O} \rangle$ distance of 2.198 Å is exactly equal to the sum of the constituent radii: 0.83 ($^{61}\text{Mn}^{2+}$) + 1.37 ($^{3.5}\text{O}^{2-}$) = 2.20 Å.

There are two crystallographically distinct Te sites: $Te(1)$ occurs at special position $4e$, and $Te(2)$ occurs at general position $8f$. $Te(1)$ is coordinated by four oxygen atoms between 1.86 and 2.10 Å, lying to one side of the cation (Fig. 1a), with a further two anions at 3.83 Å to the other side of the cation. $Te(2)$ is coordinated to four oxygen atoms between 1.87 and 2.39 Å, lying to one side of the cation (Fig. 1b), with a further two anions at 2.83 and 3.13 Å to the other side of the cation. This type of one-sided coordination is fairly characteristic for Te^{4+} with a stereoactive lone-pair of electrons (Andersson *et al.* 1973, Brown 1974).

Brown (1974) has discussed the details of the coordination of the isoelectronic series Sn^{2+} , Sb^{3+} , Te^{4+} , I^{5+} and Xe^{6+} by O^{2-} and F^- in terms of bond-

TABLE 2. FINAL PARAMETERS FOR SPIROFFITE

| Site | x | y | z | $^*U_{01}$ | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|---------|------------|------------|------------|------------|----------|----------|----------|----------|----------|----------|
| $Te(1)$ | 1/2 | 0.36091(7) | 1/4 | 101(1) | 92(2) | 106(2) | 105(2) | 0 | 14(1) | 0 |
| $Te(2)$ | 0.13776(2) | 0.18589(5) | 0.05780(2) | 97(1) | 96(1) | 111(1) | 82(1) | -6(1) | 8(1) | 17(1) |
| Mn | 0.22883(4) | 0.1987(1) | 0.35050(5) | 101(2) | 108(3) | 98(3) | 97(3) | -6(2) | 18(2) | -15(2) |
| O(1) | 0.0754(2) | 0.0761(6) | 0.3532(3) | 170(8) | 121(12) | 271(16) | 121(13) | -30(12) | 30(10) | -52(11) |
| O(2) | 0.3846(2) | 0.3853(5) | 0.3583(2) | 126(7) | 131(11) | 117(12) | 144(13) | -29(10) | 67(9) | -11(10) |
| O(3) | 0.2613(2) | 0.0158(5) | 0.0289(2) | 113(7) | 107(11) | 127(12) | 113(12) | 23(11) | 46(9) | 13(10) |
| O(4) | 0.1961(2) | 0.3612(5) | 0.1872(2) | 144(7) | 219(13) | 126(13) | 83(12) | -13(10) | 13(9) | -25(11) |

* $U = U \times 10^4$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN SPIROFFITE

| | | | |
|---------------|--------------------|----------|-----------------|
| Te(1)-O(1)e,b | 1.857(3) x2 | Mn-O(1) | 2.087(3) |
| Te(1)-O(2),d | <u>2.104(3)</u> x2 | Mn-O(2) | 2.233(3) |
| <Te(1)-O> | 1.981 | Mn-O(3)b | 2.220(3) |
| | | Mn-O(3)g | 2.398(3) |
| Te(2)-O(1)c | 2.826(3) | Mn-O(4) | 2.115(3) |
| Te(2)-O(1)h | 3.134(3) | Mn-O(4)e | <u>2.135(3)</u> |
| Te(2)-O(2)e | 1.943(3) | <Mn-O> | 2.198 |
| Te(2)-O(3) | 1.908(3) | | |
| Te(2)-O(3)f | 2.390(3) | | |
| Te(2)-O(4) | <u>1.868(3)</u> | | |
| <Te(2)-O> | 2.345 | | |

Te(1) trigonal bipyramid

| | | | |
|-------------|-----------------|-------------------|-----------------|
| O(2)-O(1)a | 2.669(4) x2 | O(2)-Te(1)-O(1)a | 84.5(1) |
| O(2)-O(1)b | 2.831(4) x2 | O(2)-Te(1)-O(1)b | 91.0(1) |
| O(1)a-O(1)b | <u>2.903(5)</u> | O(1)a-Te(1)-O(1)b | <u>102.8(2)</u> |
| <O-O> | 2.781 | <O-Te(1)-O> | 92.8 |

Te(2) trigonal bipyramid

| | | | |
|-------------|-----------------|-------------------|----------------|
| O(2)e-O(1)h | 2.669(4) | O(2)e-Te(2)-O(1)h | 57.9(1) |
| O(2)e-O(1)c | 3.400(4) | O(2)e-Te(2)-O(1)c | 88.9(1) |
| O(2)e-O(3) | 2.557(4) | O(2)e-Te(2)-O(3) | 83.2(1) |
| O(2)e-O(4) | 2.787(4) | O(2)e-Te(2)-O(4) | 94.0(1) |
| O(3)f-O(1)h | 5.286(5) | O(3)f-Te(2)-O(1)h | 145.9(1) |
| O(3)f-O(1)c | 3.826(4) | O(3)f-Te(2)-O(1)c | 94.0(1) |
| O(3)f-O(3) | 2.618(6) | O(3)f-Te(2)-O(3) | 74.1(1) |
| O(3)f-O(4) | 2.783(4) | O(3)f-Te(2)-O(4) | 80.6(1) |
| O(1)h-O(1)c | 4.307(5) | O(1)h-Te(2)-O(1)c | 92.4(1) |
| O(1)c-O(3) | 2.984(4) | O(1)c-Te(2)-O(3) | 75.4(1) |
| O(3)-O(4) | 2.856(4) | O(3)-Te(2)-O(4) | 98.3(1) |
| O(4)-O(1)h | <u>3.782(4)</u> | O(4)-Te(2)-O(1)h | <u>94.9(1)</u> |
| <O-O> | 3.321 | | 90.0 |

Mn octahedron

| | | | |
|-------------|-----------------|----------------|-----------------|
| O(1)-O(3)b | 3.338(4) | O(1)-Mn-O(3)b | 101.5(1) |
| O(1)-O(3)g | 2.984(4) | O(1)-Mn-O(3)g | 83.1(1) |
| O(1)-O(4)e | 3.260(4) | O(1)-Mn-O(4)e | 101.1(1) |
| O(1)-O(4) | 3.088(4) | O(1)-Mn-O(4) | 94.6(1) |
| O(2)-O(3)b | 2.557(4) | O(2)-Mn-O(3)b | 70.1(1) |
| O(2)-O(3)g | 3.494(4) | O(2)-Mn-O(3)g | 97.9(1) |
| O(2)-O(4)e | 3.027(4) | O(2)-Mn-O(4)e | 87.8(1) |
| O(2)-O(4) | 2.938(4) | O(2)-Mn-O(4) | 85.0(1) |
| O(3)b-O(3)g | 2.946(6) | O(3)b-Mn-O(3)g | 79.2(1) |
| O(3)g-O(4)e | 2.783(4) | O(3)g-Mn-O(4)e | 75.5(1) |
| O(4)e-O(4) | 3.287(3) | O(4)e-Mn-O(4) | 101.3(1) |
| O(4)-O(3)b | <u>3.443(4)</u> | O(4)-Mn-O(3)b | <u>105.1(1)</u> |
| <O-O> | 3.095 | <O-Mn-O> | 90.2 |

Symmetry operations: a: $x + \frac{1}{2}, y + \frac{1}{2}, z$; b: $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$; c: $x, \bar{y}, z - \frac{1}{2}$; d: $\bar{x} + 1, y, \bar{z} + \frac{1}{2}$; e: $\bar{x} + \frac{1}{2}, y - \frac{1}{2}, \bar{z} + \frac{1}{2}$; f: $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$; g: $x, \bar{y}, z + \frac{1}{2}$; h: $\bar{x}, y, \bar{z} + \frac{1}{2}$

valence theory, and showed that there are certain characteristic coordinations around these cations in crystals. In particular, Te⁴⁺ usually shows two end-member arrangements: (1) two strong *cis* bonds of approximately 1.12 valence units (*vu*), two intermediate-strength *trans* bonds of approximately 0.73 *vu*, and two weak *cis* bonds of approximately 0.15 *vu*; (2) two strong *cis* bonds of approximately 1.16 *vu*, two intermediate-strength *trans* bonds of approximately 0.98 and 0.40 *vu*, and two weak *cis* bonds of

TABLE 4. BOND-VALENCE (*vu*) ARRANGEMENT FOR SPIROFFITE*

| | Te(1) | Te(2) | Mn | Σ O |
|------|---------------------|-------|-------|-------|
| O(1) | 1.383 ^{x2} | 0.101 | 0.448 | 1.976 |
| | | 0.044 | | |
| O(2) | 0.709 ^{x2} | 1.096 | 0.302 | 2.107 |
| O(3) | | 1.205 | 0.313 | 2.039 |
| | | 0.328 | 0.193 | |
| O(4) | | 1.343 | 0.414 | 2.151 |
| | | | 0.394 | |
| | 4.184 | 4.117 | 2.064 | |

* calculated from the bond-valence curves of Brown & Altermatt (1985)

approximately 0.15 *vu*. From Table 4, it is apparent that Te(1) corresponds to type (1) [$2 \times 1.38, 2 \times 0.71, 2 \times 0.00$] and Te(2) corresponds to type (2) [$2 \times 1.27, 1 \times 1.10, 1 \pm 0.33, 2 \times 0.07$].

Chemical composition

The <Mn-O> distance of our crystal indicates that it is almost free of Zn [$r(^{65}\text{Zn}) = 0.74 \text{ \AA}$]. To test this further, we did a site-scattering refinement with the Mn site occupied by (Mn,Zn). The composition refined to complete Mn occupancy, in accord with the <Mn-O> distance. Mandarino *et al.* (1963a) reported the chemical composition of the spiroffite that they characterized as $(\text{Mn}_{1.26}\text{Zn}_{0.72}\text{Ca}_{0.02})\text{Te}_{3.01}\text{O}_8$. We mounted the crystal from our structure determination in epoxy and analyzed it with a Cameca SX-50 electron microprobe (15 kV, 20 μA , $\phi\rho z$ correction) using the

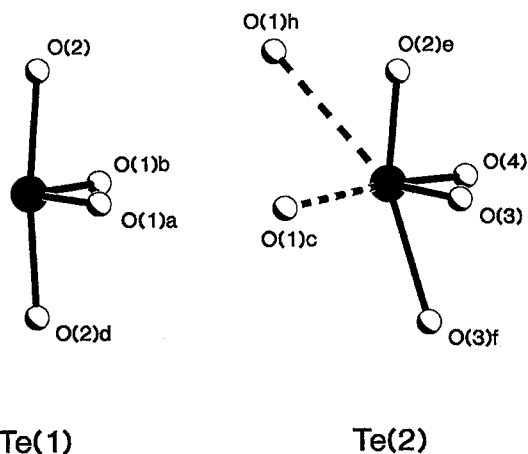


Fig. 1. The coordination of the Te atoms in spiroffite; black spheres: Te atoms; highlighted spheres: O atoms; long Te(2)-O bonds are shown by the broken lines.

TABLE 5. CHEMICAL COMPOSITION AND UNIT FORMULA OF SPIROFFITE

| | EMPA * | | σ | EMPA | |
|------------------|--------|-----|----------|----------|-------|
| TeO ₂ | 75.62 | wt% | 0.32 | Te | 2.992 |
| MnO | 20.67 | | 0.27 | | |
| ZnO | 1.18 | | 0.16 | Mn | 1.840 |
| MgO | 0.38 | | 0.02 | Zn | 0.091 |
| FeO | 0.03 | | 0.03 | Mg | 0.059 |
| CaO | 0.18 | | 0.08 | Fe | 0.003 |
| PbO | 0.14 | | 0.21 | Ca | 0.020 |
| Total | 98.20 | | | Pb | 0.004 |
| | | | | Σ | 2.017 |

Note: Al, Cd, Co, Cu, Bi, S, Cl not detected
* mean of 10 analyses

following standards: Te, FeTe₂O₅(OH); Zn(K α): gahnite; Mg: olivine; Mn: spessartine; Ca: diopside; Pb: PbTe. The results are given in Table 5, together with the unit formula based on 8 O atoms. The crystal is not significantly zoned, and is close to the ideal end-member composition, as also indicated by the structure-refinement results.

Structure topology

Two MnO₆ octahedra share an edge to form [Mn₂O₁₀] dimers (Fig. 2) that share corners to form a sheet of [Mn₂O₈] octahedra parallel to (100). This [Mn₂²⁺O₈] sheet is also found in the structure of nissonite, [CuMg(PO₄)(OH)(H₂O)₂]₂(H₂O); Groat & Hawthorne 1990], and shows exactly the same type of kinking of alternate columns of dimers in alternate directions. These sheets are cross-linked into a framework by the Te cations. The Te(1) cations lie on the (100) plane at $x = 0$, an equal distance from each adjacent sheet of octahedra (Fig. 3). The strong Te(1)–O bonds bridge adjacent [Mn₂O₈] sheets, and the

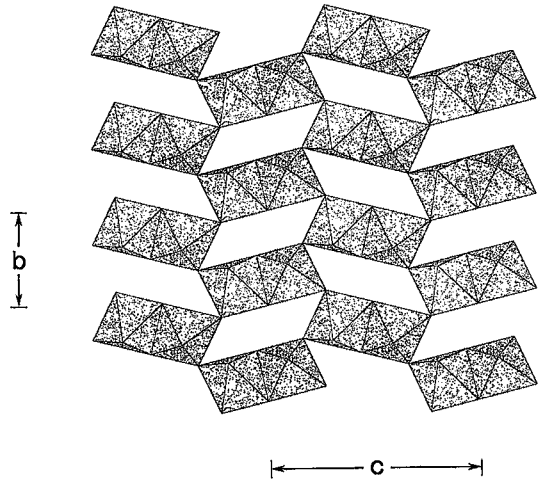


FIG. 2. The linkage of the [Mn₂O₁₀] dimers to form a sheet of the form [Mn₂O₈] in the (100) plane in spiroffite; MnO₆ octahedra are random-dot shaded.

one-sided nature of the Te(1) coordination occurs in the [010] direction. The Te(2) cations lie at the margins of the sheets of octahedra (Fig. 3). All of the four strong Te(2)–O bonds are to one sheet, and a single weak Te(2)–O bond bridges adjacent sheets. Thus the primary intersheet linkage is *via* the Te(1) cations. The Te cations and the associated Te–O bonds form strongly bonded [Te₃O₁₂] trimers that are weakly linked *via* long Te–O bonds to form a ladder-like chain along [001] (Fig. 3). These ladders are shown very well “end-on” in Figure 4. Between the sheets and the ladders are large tunnels approximately 3.2 × 5.5 Å across. Spiroffite can thus be considered as a heteropolyhedral framework structure with tunnels lined with TeO_n polyhedra. The lone pair of electrons of the Te(1) cation presumably projects into this tunnel, effectively

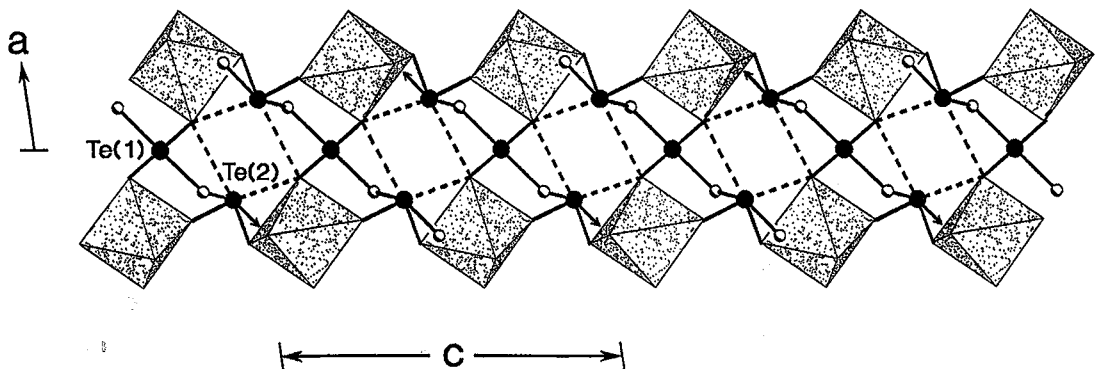


FIG. 3. The polymerization of the TeO₄ and TeO₆ groups along [001]; legend as in Figures 1 and 2.

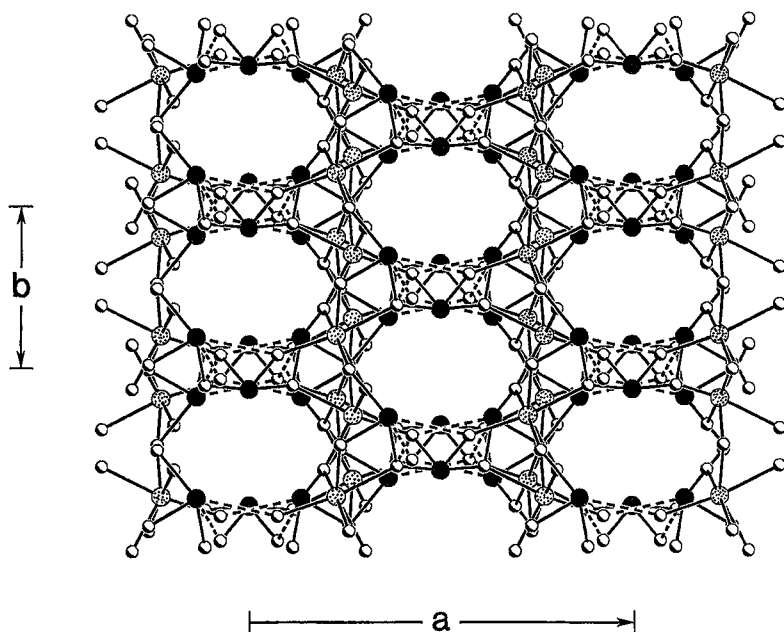


FIG. 4. The structure of spiroffite projected down [001]; legend as in Figure 1, with Mn atoms shown as dotted spheres.

reducing the smaller dimensions (3.2 Å) of the tunnel in the [010] direction, and explaining for why these channels do not contain "zeolitic" H_2O groups.

Related structures

At Moctezuma, spiroffite is associated with denningite (Mandarino *et al.* 1963b). The structure of denningite (Walitzi 1965) is shown in Figures 5 and 6. Denningite is tetragonal and consists of columns of edge-sharing MnO_6 and CaO_8 polyhedra extending along [001] and cross-linked by Te atoms to form an open checkerboard pattern. It is apparent from the structure of denningite that the formula unit should be written as $(\text{Ca},\text{Mn})(\text{Mn},\text{Zn})\text{Te}_4\text{O}_{10}$ rather than $(\text{Mn},\text{Ca},\text{Zn})\text{Te}_2\text{O}_5$, with the ideal end-member $\text{CaMn}^{2+}\text{Te}_4\text{O}_{10}$. The cross-linkage of adjacent $[\text{CaMnO}_{10}]$ chains is shown in Figure 5. The linking

Te^{4+} cation has three short bonds (1.84–2.04 Å) and two longer bonds or contacts (2.36 and 2.90 Å), and two TeO_5 polyhedra share a vertex to form a strongly bonded $[\text{Te}_2\text{O}_5]$ dimer. These dimers link along [001] via long bonds (Fig. 5) to form chains that cross-link the $[\text{CaMnO}_{10}]$ columns. The resulting structure (Fig. 6) is a very open framework that appears to have zeolitic affinities. However, the stereoactive lone-pairs of electrons of the Te^{4+} cations project into the channel from each of the four corners, and hence the interstitial pore-space in the structure is far less than Figure 6 suggests.

Although the details of the polymerization within the structural units of spiroffite (Fig. 4) and denningite (Fig. 6) are quite different, the overall appearance of the two structures has one striking similarity: they both can be envisioned as a packing of one-dimensional channels. The underlying reason for this type of

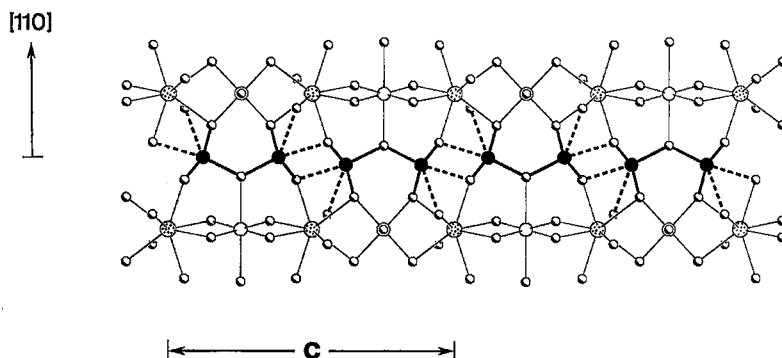


FIG. 5. The structure of denningite projected onto the (110) plane; black spheres: Te atoms; dotted spheres: Ca atoms; high-lighted spheres: O atoms; unshaded spheres: Mn atoms.

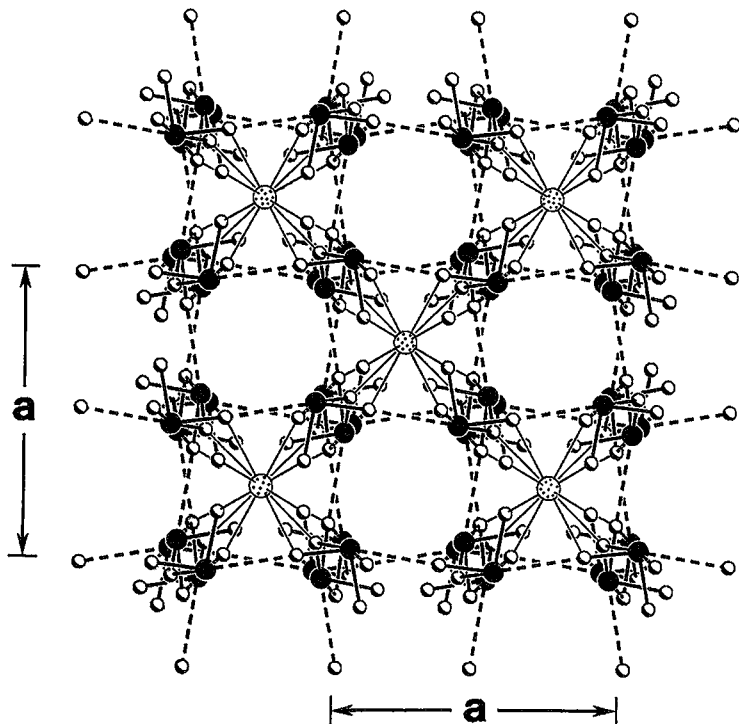


FIG. 6. The structure of denningite projected down [001]; legend as in Figure 5, with long Te-O bonds shown by broken lines.

packing is the need to have sufficient interstitial space within the structure to accommodate the stereoactive lone-pairs of electrons. In Te^{4+} -rich structures, this requirement will be a very important factor in determining the overall atomic arrangement.

ACKNOWLEDGEMENTS

We thank Andy MacDonald, Scott Ercit and Bob Martin for their comments on this manuscript. This work was supported by the Natural Sciences and Engineering Research Council of Canada *via* Operating, Major Equipment and Infrastructure Grants to FCH.

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Received August 30, 1995, revised manuscript accepted March 6, 1996.