

Carlfriesite: crystal structure, revision of chemical formula, and synthesis

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Abstract

The structure of natural carlfriesite, given by Williams and Gaines (1975) as $H_4Ca(TeO_3)_8$, was determined by single-crystal standard X-ray procedures. The least-squares refinement for 595 observed reflections resulted in a conventional reliability index $R = 0.027$ (with anisotropic temperature factors for Ca and Te and isotropic for O). The cell content obtained is $Ca_4Te_{12}O_{32}$, with one third of the Te atoms in octahedral coordination, as characteristic for Te(VI), and the rest in the usual one-sided coordination of Te(IV). Carlfriesite was synthesized by the hydrothermal treatment of a stoichiometric mixture of TeO_2 , $Te(OH)_6$, and CaO at 150–230°C.

Introduction

Carlfriesite is a rare tellurium mineral from Moctezuma, Sonora, Mexico. Williams and Gaines (1975) gave a mineralogical and crystallographic description of this new species. From electron microprobe analyses and a water determination by the Penfield method on 1.879 mg they derived the formula $H_4Ca(TeO_3)_8$.

In connection with the continued interest of the senior author (J.Z.) in the stereochemistry of tellurium minerals, we decided to determine the atomic arrangement of carlfriesite. A preliminary note has been published by Effenberger and Mayer (1977).

Determination of the structure

After many trials a tiny crystal (approximate average dimensions: $29 \times 15 \times 25 \mu m$, irregularly broken on one side) suitable for single-crystal work was isolated from material from the type locality. A least-squares refinement of Philips PW-1100 four-circle diffractometer data yielded for the unit cell $a = 12.576(2)$, $b = 5.662(3)$, $c = 9.994(2) \text{ \AA}$ and $\beta = 115.56(3)^\circ$, in excellent agreement with the values published by Williams and Gaines (1975). In full agreement with the previous authors, the systematic

extinctions corresponded to space groups $C2/c-C_{2h}^6$ and $Cc-C_4^2$. Since the structure was determined to be centrosymmetric, $C2/c$ is considered to be the correct space group.

Diffraction intensities were collected on the same diffractometer with $MoK\alpha$ radiation, graphite monochromator, θ - 2θ scan, scanning rate $0.25^\circ/\text{min}$, scanning range 0.87 – 1.00° and background measurements 0.62 – 4.02 min. Integrated intensities were collected up to $\sin\theta/\lambda = 0.66 \text{ \AA}^{-1}$. Of the 774 possible independent reflections in this region, 535 with $I \geq 3\sigma(I)$ were considered to be observed.

The tellurium and calcium positions were found by direct methods (MULTAN) in connection with the interpretation of a 3-dimensional Patterson function. Subsequent 3-dimensional Fourier maps revealed the positions of the oxygen atoms and led to a cell content of $Ca_4Te_{12}O_{32}$ ($CaTe_3O_8$ with $Z = 4$).

The full-matrix least-squares refinement with the 535 observed reflections, with anisotropic temperature factors for Ca and Te, isotropic for O, and scattering curves for neutral atoms after Cromer and Mann (1968), resulted in a conventional reliability index $R = 0.027$. The atomic coordinates and temperature factors are given in Table 1, a list of observed

Table 1. Atomic coordinates and temperature factors with standard deviations in parentheses, A.T.F. = $\exp[-1/4(B_{11}a^2h^2 + \dots + 2 \cdot B_{12}a \cdot b \cdot hk + \dots)]$, $B_{iso} = (B_{11} + B_{22} + B_{33})/3$

| Atom | x | y | z | B_{iso} | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} | |
|--------|------|------------|-------------|------------|----------|-----------|-----------|-----------|------------|-----------|------------|
| Te(IV) | 8(f) | 0.71563(5) | 0.58751(12) | 0.85825(7) | 0.793 | 0.850(22) | 0.858(24) | 0.673(21) | -0.006(19) | 0.358(16) | -0.086(18) |
| Te(VI) | 4(a) | 0.0 | 0.0 | 0.0 | 0.496 | 0.531(29) | 0.665(30) | 0.291(27) | -0.062(25) | 0.110(21) | -0.002(23) |
| Ca | 4(e) | 0.0 | 0.4404(5) | 0.25 | 0.41 | 0.34(9) | 0.45(10) | 0.44(8) | 0.0 | 0.03(7) | 0.0 |
| O(1) | 8(f) | 0.0804(6) | 0.2183(12) | 0.6616(7) | 0.76(10) | | | | | | |
| O(2) | 8(f) | 0.0980(6) | 0.2441(12) | 0.1171(7) | 0.83(11) | | | | | | |
| O(3) | 8(f) | 0.1043(5) | 0.0928(12) | 0.4068(6) | 0.56(10) | | | | | | |
| O(4) | 8(f) | 0.6839(5) | 0.1042(12) | 0.4098(7) | 0.67(10) | | | | | | |

and calculated structure factors in Table 2¹. Due to the neglect of absorption (maximum and minimum transmissions ~ 0.80 and ~ 0.65 , respectively) the "temperature factors" are in part corrections for absorption; therefore no physical interpretation is attempted.

Table 3 compares the theoretical X-ray powder diffractogram based on our structure determination with the observed powder data of Williams and Gaines (1975); the agreement is quite satisfactory.

Revision of the chemical formula of carlfriesite and discussion of the atomic arrangement

Table 4 gives important interatomic distances and bond angles in carlfriesite and Figure 1 is an oblique projection of the atomic arrangement.

The result of our structure determination fails to agree with the original formula $H_4Ca(TeO_3)_3$ (Williams and Gaines, 1975), in that the ratio Te:O found by us is 3:8 and the octahedral coordination of one third of the tellurium atoms indicates a hexavalent state.

In this connection it seems worth mentioning that (1) a final 3-dimensional difference Fourier synthesis did not reveal any further atoms, (2) the structure does not contain O-O distances which would be characteristic for hydrogen bridges, (3) an analytical water determination on synthetic (impure) carlfriesite gave approximately 1/10 of the H content given by Williams and Gaines, (4) the theoretical Ca and Te contents for the formula $CaTe_3O_8$ (7.28 and 69.49 weight percent, respectively) are in excellent agreement with the microprobe analyses given by Williams and Gaines: 7.3, 7.2 and 7.5 weight percent for Ca, 69.3, 69.3 and 70.0 weight percent for Te, and (5) the

stereochemistry of the determined structure is in agreement with the hexavalent state for one third of the tellurium atoms.

The coordination figures and interatomic distances in carlfriesite correspond to the expectations from crystal chemistry. For surveys of the stereochemistry of tellurium (IV) and (VI) the reader is referred to Bayer (1969), Galy *et al.* (1975), Lindqvist (1973), and Zemann (1968, 1971, 1974), for the stereochemistry of calcium to Hahn and Eysel (1970).

The tellurium atoms in position 4a show the usual octahedral coordination of Te(VI) with Te-O distances as observed in other comparable compounds (Table 5). The tellurium atoms on the general position 8f have the one-sided coordination geometry

Table 3. Powder diffractogram of carlfriesite as calculated from determined structure. Estimated intensities of natural carlfriesite according to Williams and Gaines (1975) are given in brackets

| h | k | l | d_{cal} | I_{cal} | | h | k | l | d_{cal} | I_{cal} |
|---|---|----|-----------|-----------|--------|---|---|----|-----------|-----------|
| 1 | 1 | 0 | 5.066 | 61 | (6) | 4 | 2 | -3 | 1.967 | 10 |
| 1 | 1 | -1 | 4.832 | 26 | (3) | 6 | 0 | -4 | 1.910 | 13 |
| 1 | 1 | 1 | 4.093 | 12 | (2) | 2 | 2 | -4 | 1.873 | 15 |
| 3 | 1 | -1 | 3.369 | 25 | (4) | 1 | 3 | -1 | 1.849 | 4 |
| 3 | 1 | -2 | 3.167 | 100 | (10) | 4 | 2 | 1 | 1.841 | 10 |
| 1 | 1 | 2 | 3.085 | 99 | } (9B) | 2 | 0 | 4 | 1.840 | 11 |
| 4 | 0 | -2 | 3.071 | 33 | | 1 | 3 | 1 | 1.798 | 4 |
| 2 | 0 | 2 | 2.961 | 16 | (1) | 3 | 3 | -1 | 1.721 | 14 |
| 4 | 0 | 0 | 2.836 | 21 | } (6) | 7 | 1 | -2 | 1.708 | 9 |
| 1 | 1 | -3 | 2.835 | 7 | | 5 | 1 | 2 | 1.669 | 5 |
| 0 | 2 | 0 | 2.831 | 16 | } (3) | 6 | 2 | -3 | 1.659 | 7 |
| 3 | 1 | -3 | 2.713 | 4 | | 7 | 1 | -4 | 1.638 | 11 |
| 0 | 2 | 1 | 2.701 | 17 | (3) | 2 | 2 | -5 | 1.624 | 6 |
| 2 | 2 | -1 | 2.571 | 5 | (1) | 6 | 2 | -4 | 1.583 | 4 |
| 2 | 0 | -4 | 2.497 | 27 | (2) | 3 | 1 | 4 | 1.583 | 8 |
| 1 | 1 | 3 | 2.390 | 5 | } (6) | 8 | 0 | -2 | 1.559 | 4 |
| 2 | 2 | 1 | 2.325 | 5 | | 5 | 1 | -6 | 1.552 | 14 |
| 5 | 1 | -1 | 2.261 | 4 | } (6) | 2 | 2 | 4 | 1.543 | 6 |
| 0 | 0 | 4 | 2.254 | 4 | | 1 | 3 | 3 | 1.535 | 7 |
| 1 | 1 | -4 | 2.225 | 4 | } (6) | 6 | 0 | 2 | 1.525 | 5 |
| 2 | 2 | -3 | 2.152 | 8 | | 1 | 1 | -6 | 1.523 | 11 |
| 5 | 1 | 0 | 2.106 | 12 | } (6) | 0 | 2 | 5 | 1.521 | 4 |
| 2 | 2 | 2 | 2.046 | 13 | | 5 | 3 | -1 | 1.499 | 4 |
| 4 | 0 | 2 | 2.037 | 5 | } (6) | 2 | 4 | 0 | 1.373 | 5 |
| 4 | 2 | 0 | 2.004 | 14 | | 9 | 1 | 0 | 1.230 | 4 |

¹ To obtain a copy of Table 2, order Document AM-78-082 from the Business Office, Mineralogical Society of America, 1909 K Street, NW, Washington, DC 20006. Please remit \$1.00 in advance for the microfiche.

Table 4. Interatomic distances and angles with standard deviations given in parentheses

| Bond Distance (Å) | Bond Angle (°) | Edge Length (Å) |
|-------------------------------|--------------------------------------|-------------------------------|
| Te(IV) - O(4) = 1.910(7) | O(1) - Te(IV) - O(3) = 92.2(2) | O(1) - O(3) = 2.926(10) |
| Te(IV) - O(3) = 1.956(8) | O(1) - Te(IV) - O(4) = 75.6(3) | O(1) - O(4) = 2.464(10) |
| Te(IV) - O(1) = 2.102(6) | O(1) - Te(IV) - O(4') = 150.6(3) | O(3) - O(4) = 2.938(10) |
| Te(IV) - O(4') = 2.110(6) | O(3) - Te(IV) - O(4) = 98.9(3) | O(3) - O(4') = 2.938(10) |
| Te(IV) - O(2) = 2.442(8) | O(3) - Te(IV) - O(4') = 84.5(3) | O(4) - O(4') = 2.480(10) |
| Te(IV) - O(2') = 2.906(7) | O(4) - Te(IV) - O(4') = 76.0(3) | |
| | O(2) - Te(IV) - O(1) = 108.1(3) | |
| | O(2) - Te(IV) - O(3) = 159.6(2) | |
| | O(2) - Te(IV) - O(4) = 85.4(3) | |
| | O(2) - Te(IV) - O(4') = 77.2(3) | |
| Te(VI) - O(2) = 1.885(6) (2x) | O(1) - Te(VI) - O(2) = 89.1(3) (2x) | O(1) - O(2) = 2.681(10) (2x) |
| Te(VI) - O(1) = 1.936(6) (2x) | O(1) - Te(VI) - O(2') = 90.9(3) (2x) | O(1) - O(2') = 2.723(10) (2x) |
| Te(VI) - O(3) = 1.979(8) (2x) | O(1) - Te(VI) - O(3) = 89.5(3) (2x) | O(1) - O(3) = 2.756(12) (2x) |
| | O(1) - Te(VI) - O(3') = 90.5(3) (2x) | O(1) - O(3') = 2.782(10) (2x) |
| | O(2) - Te(VI) - O(3) = 84.4(4) (2x) | O(2) - O(3) = 2.596(14) (2x) |
| | O(2) - Te(VI) - O(3') = 95.6(4) (2x) | O(2) - O(3') = 2.864(10) (2x) |
| Ca - O(4) = 2.360(6) (2x) | | |
| Ca - O(2) = 2.436(9) (2x) | | |
| Ca - O(3) = 2.505(7) (2x) | | |
| Ca - O(1) = 2.512(8) (2x) | | |
| | Te(IV) - Te(IV) = 3.169(1) Å | |
| | Te(IV) - Te(VI) = 3.469(1) Å | |

typical for Te(IV), with four shortest Te-O bonds in the range of 1.91–2.11 Å. A fifth neighbor with Te-O = 2.44 Å is nearer than in the average Te(IV) coordination, and a clear tendency towards a one-sided five-coordination is observed. Similar cases have, however, already been reported in the literature (Table 6).

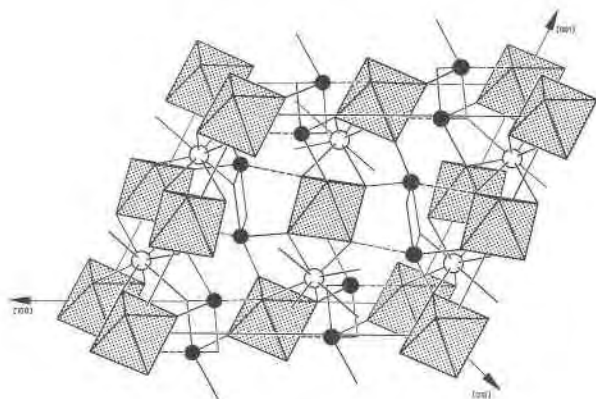


Fig. 1. Oblique projection of the crystal structure of carlfriesite. Coordination octahedra around Te(VI) are dotted. The eight Ca-O bonds and the four shortest Te(IV)-O bonds are drawn in full lines, the fifth shortest Te(IV)-O bond (2.44 Å) in broken lines.

The bond directions around Te(IV) are given in Figure 2 in stereographic projection as proposed by Zemann (1971); it is seen that their mutual orientation corresponds to common experience. Each two coordination figures around Te(IV) share an edge with O-O = 2.48 Å (Fig. 3). A similar edge-sharing of tellurium(IV)-oxygen coordination figures is also observed in the minerals denningite (Walitzi, 1965), tellurite (Beyer *et al.*, 1965; Beyer, 1967), and mroseite (Fischer *et al.*, 1975). $Zn_2Te_3O_8$, a synthetic compound closely related to spioffite (Hanke, 1966, *cf.* also Zemann, 1968) also seems worth mentioning in this connection.

Table 5. Some Te(VI)-O bond lengths in compounds containing both Te(VI) and Te(IV)

| Substance | Bond - length Te(VI) ^[6] - O | Mean | Literature |
|-----------------------------|--|-------|--------------------------------|
| Carlfriesite $CaTe_3O_8$ | 1.885 - 1.979 | 1.933 | |
| Te_2O_5 | 1.848 - 1.972 | 1.919 | LINDQVIST and MORET, 1973a |
| $H_2Te_2O_5$ | 1.864 - 1.952 | 1.918 | LINDQVIST and MORET, 1973b |
| Te_4O_9 | 1.903 - 1.948 | 1.926 | LINDQVIST <i>et al.</i> , 1975 |

Table 6. Te-O bond lengths in compounds showing a tendency towards a five-coordination around Te(IV), and bond lengths in 5-coordinated Te(IV) halogenides

| Substance | | Bond Length (in Å) | | | | | Literature |
|---|---|--------------------|------|------|------|------|---------------------------|
| Carlfriesite, CaTe_3O_8 | Te - O | 1.91 | 1.96 | 2.10 | 2.11 | 2.44 | |
| | $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ | Te(1) - O | 1.89 | 1.94 | 1.99 | 2.28 | 2.55 |
| | Te(2) - O | 1.90 | 1.92 | 2.03 | 2.20 | 2.39 | |
| Mroseite, $\text{CaTeO}_2(\text{CO}_3)$ | Te - O | 1.85 | 1.95 | 2.05 | 2.31 | 2.55 | FISCHER et al., 1975 |
| $\text{UO}_2[\text{Te}_3\text{O}_7]$ | Te - O | 1.78 | 2.02 | 2.15 | 2.16 | 2.55 | GALY and MEUNIER, 1971 |
| $\text{Te}_2\text{O}_3(\text{SO}_4)$ | Te - O | 1.91 | 1.95 | 2.01 | 2.27 | 2.60 | MAYER and PUPP, 1975 |
| Tellurite, TeO_2 , rh. | Te - O | 1.88 | 1.93 | 2.07 | 2.20 | 2.64 | BEYER, 1967 |
| Te - Catecholate | Te - O | 1.98 | 1.98 | 2.01 | 2.11 | 2.64 | LINDQVIST, 1967 |
| KTeF_5 | Te - F | 1.86 | 1.95 | 1.95 | 1.95 | 1.95 | MASTIN et al., 1970 |
| TeF_4 | Te - F | 1.80 | 1.87 | 1.92 | 2.08 | 2.26 | EDWARDS and HEWAIDY, 1968 |
| PTeCl_9 | Te - Cl | 2.35 | 2.36 | 2.38 | 2.49 | 2.50 | KREBS et al., 1973 |

The calcium ion shows, somewhat distorted, the well-known tetragonal antiprismatic oxygen coordination with an average Ca-O distance of 2.45(7)Å. This value compares well with the average Ca-O distance of 2.48(11)Å in mroseite ($\text{CaTeO}_2\text{CO}_3$; Fischer *et al.*, 1975) where calcium is also eight-coordinated.

Bond-valence sums were computed using the empirical parameters of Brown and Wu (1976). For

Te(IV)-O, bond distances up to 2.91Å were taken into consideration. The results are given in Table 7. The bond-valence sums show only the usual deviations from the ideal values.

Synthesis

Carlfriesite was synthesized by hydrothermal treatment of stoichiometric mixtures of CaO, $\text{Te}(\text{OH})_6$, and TeO_2 at 150–240°C with water at the vapor pres-

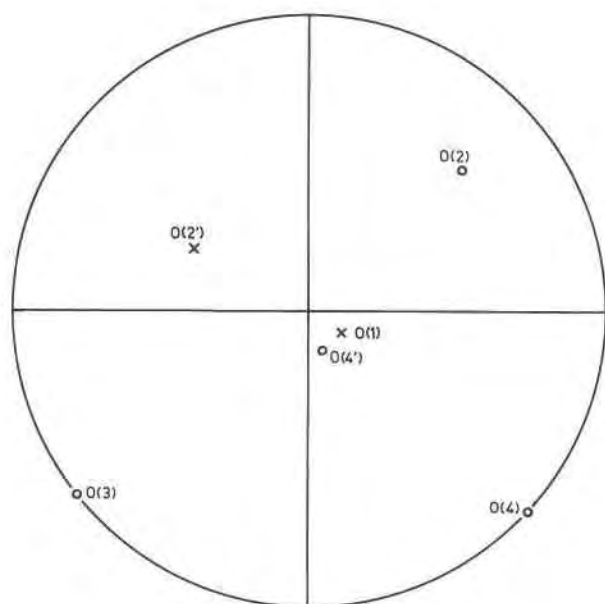


Fig. 2. Stereographic projection of the Te(IV)-O bond directions in carlfriesite, following the orientation convention of Zemann (1971).

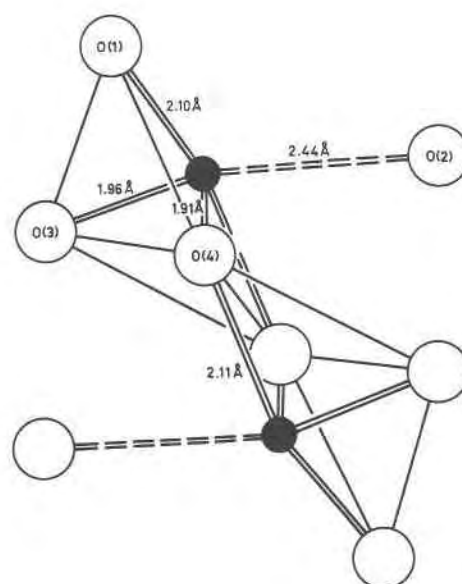


Fig. 3. Oblique projection of two neighboring Te(IV) coordinations in carlfriesite, showing edge-sharing.

Table 7. Bond valence sums after Brown and Wu (1976)

| Oxygen | Central Atom | Bond Length in Å | Bond Strength | |
|--------|--------------|------------------|---------------|----------|
| | | | single | together |
| O(1) | Ca | 2.512 | 0.23 | 1.83 |
| | Te(IV) | 2.102 | 0.69 | |
| | Te(VI) | 1.936 | 0.91 | |
| O(2) | Ca | 2.436 | 0.27 | 1.88 |
| | Te(IV) | 2.442 | 0.35 | |
| | Te(IV) | 2.906 | 0.16 | |
| | Te(VI) | 1.885 | 1.10 | |
| O(3) | Ca | 2.505 | 0.23 | 1.96 |
| | Te(IV) | 1.956 | 0.95 | |
| | Te(VI) | 1.979 | 0.78 | |
| O(4) | Ca | 2.360 | 0.32 | 2.07 |
| | Te(IV) | 1.910 | 1.08 | |
| | Te(IV) | 2.110 | 0.67 | |

Bond strength for the central atoms:

| | |
|--------|------|
| Ca | 2.10 |
| Te(IV) | 3.90 |
| Te(VI) | 5.58 |

sure of the system. The reaction products were always very fine-grained; they consisted essentially of globular aggregates of tiny, platy, colorless carlfriesite crystals (average size $\sim 10 \mu\text{m}$). As shown by X-ray diffractometry, the products contained predominantly carlfriesite, with at least some paratellurite (~ 10 –15 percent).

Due to the small grain size it was not possible to isolate a few tenths of a gram of pure carlfriesite. The chemical analysis was, therefore, limited to water determinations of impure material. A Penfield determination on about 1 g material containing at least 80 percent carlfriesite (estimated from X-ray diffractometry) gave 0.64 weight percent H_2O , *i.e.*, approximately one-tenth of the H_2O content given by Williams and Gaines for the natural mineral. Repeated checks with less material confirmed this order of magnitude. We consider it very probable that this small water content is caused by minor impurities [possibly $\text{Ca}(\text{OH})_2$], and that carlfriesite is indeed CaTe_3O_8 with at most trace amounts of hydroxyl groups. In any case the water content of synthetic carlfriesite is not higher than approximately one tenth of the value given by Williams and Gaines (1975) for the mineral.

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