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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 $H_4Ca(TeO_3)_3$, 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 $H_4Ca(TeO_3)_3$.

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 × 15 × 25 μm, 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)A and β = 115.56(3)°, 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_s^4. 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 Mo$K\alpha$ radiation, graphite monochromator, θ-2θ scan, scanning rate 0.25°/min, scanning range 0.87–1.00° and background measurements 0.62–4.02 min. Integrated intensities were collected up to $\sin\theta/\lambda = 0.66A^{-1}$. 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

0003-004X/78/0910-0847$02.00

H,0,0

2	485	-456
4	3234	3188
6	561	534
8	1016	1010
10	2854	2889
12	175*	-0
14	2058	2054

H,1,0

1	2089	2157
3	367	-361
5	2437	2414
7	1177	-1213
9	2607	2619
11	379	-371
13	976	972

H,2,0

0	2797	2853
2	299	320
4	2896	2885
6	1728	1742
8	1301	1272
10	1517	1490
12	244*	269
14	1341	1349

H,3,0

1	911	917
3	1152	1136
5	1149	1138
7	1183	1175
9	597	621
11	790	751
13	509	502

H,4,0

0	111*	-105
2	2547	2610
4	242*	237
6	1069	1013
8	1094	1109
10	264*	330
12	1416	1417

H,5,0

1	813	786
3	1985	1955
5	100*	-254
7	2224	2192
9	485	-533
11	1615	1596

H,6,0

0	1279	-1286
2	1959	1998
4	150*	-102
6	1107	1091
8	803	753

H,7,0

1	550	517
3	1503	1450
5	213*	188

H,1,-1

-15	354*	409
-13	0*	-196
-11	0*	-102
-9	0*	122
-7	1241	-1242
-5	1328	1347
-3	2069	-2076
-1	1371	1441
1	1239	-1212
3	171*	38
5	724	726
7	1302	-1285
9	704	688
11	967	-956
13	562	544

H,2,1

-14	1317	1256
-12	1357	-1369
-10	1723	1754
-8	1045	-1036
-6	1051	1068
-4	683	666
-2	1272	-1307
0	2130	2179
2	1365	-1386
4	2710	2674
6	1506	-1487
8	963	1000
10	0*	-134
12	0*	-55

H,3,1

-13	891	-827
-11	511	-511
-9	506	529
-7	1526	-1504
-5	2109	2146
-3	3317	-3428
-1	1468	1519
1	1661	-1676
3	60*	-67
5	740	750
7	2035	-2048
9	1365	1358
11	1440	-1459
13	861	826

H,4,1

-12	1034	-1018
-10	1335	1306
-8	615	-653
-6	1091	1093
-4	573	593
-2	656	-634
0	1494	1500
2	1225	-1214
4	1957	1991
6	832	-841
8	921	960
10	134*	93
12	22*	-34

H,5,1

-11	320*	-263
-9	266*	-56
-7	801	-832
-5	407	406
-3	842	-881
-1	196*	228
1	670	-672
3	290*	-237
5	177*	36
7	655	-639
9	131*	209

H,6,1

-8	59*	232
-6	256*	41
-4	139*	25
-2	454	394
2	266*	397
4	55*	23
6	256*	304
8	0*	12

H,7,1

-5	1076	-990
-3	802	732
-1	792	-783
1	402*	381
3	0*	-141

H,0,2

-14	0*	111
-12	1636	1584
-10	1155	-1141
-8	3037	2973
-6	1530	-1510
-4	3805	3790
-2	226	211
0	679	663
2	2747	2696
4	2357	-2296
6	3446	3402
8	918	-929
10	1916	1950
12	196*	174

H,1,2

-15	364*	-233
-13	2144	2171
-11	288*	237
-9	1756	1780
-7	2763	2764
-5	144*	108
-3	4349	4447
-1	357	-371
1	4635	4600
3	772	752
5	2272	2193
7	1524	1477
9	555	585
11	2116	2229
13	0*	-135

H,2,2

-14	259*	246
-12	999	1030
-10	0*	187
-8	2193	2243
-6	108*	28
-4	1221	1250
-2	0*	-49
0	1087	1093
2	2681	2680
4	377	305
6	1698	1666
8	3[illegible]6	-497
10	1015	1072
12	573	539

H,3,2

-13	733	729
-11	1132	1123
-9	1171	1199
-7	1105	1106
-5	1423	1486
-3	1104	1166
-1	1564	1632
1	1540	1546
3	1558	1569
5	1247	1266
7	1033	1080
9	914	922
11	769	751

H,4,2

-12	340*	350
-10	1432	1433
-8	331*	-351
-6	1887	1946
-4	551	543
-2	1950	2003
0	1209	1192
2	53*	-234
4	1932	1937
6	0*	-30
8	1944	1933
10	387	254

H,5,2

-11	1315	1288
-9	278*	367
-7	0*	95
-5	2121	2129
-3	398	-367
-1	2499	2540
1	801	-768
3	1495	1501
5	459	407
7	835	789
9	1226	1261

H,6,2

-8	453	-398
-6	2145	2140
-4	224*	-43
-2	1270	1348
0	1151	1204
2	172*	64
4	2259	2275
6	398*	-455

H,7,2

-5	1097	999
-3	486*	-429
-1	1490	1443
1	347*	-342
3	1147	1131

H,1,3

-13	911	884
-11	992	-1034
-9	498	522
-7	331	-325
-5	1106	1080
-3	1095	1102
-1	1381	-1374
1	1331	1325
3	1449	-1414
5	1455	1468
7	346	-362
9	286*	55

H,2,3

-14	391*	482
-12	236*	-81
-10	1363	-1405
-8	1345	1354
-6	2512	-2517
-4	2400	2456
-2	1934	-1964
0	99*	59
2	430	-436
4	898	-907
6	1075	1083
8	1508	-1546
10	990	1007
12	1132	-1121

H,3,3

-13	1556	1589
-11	1077	-1063
-9	1589	1600
-7	678	-723
-5	493	472
-3	1178	1233
-1	1452	-1491
1	2710	2742
3	1962	-1978
5	2196	2205
7	566	-567
9	145*	222
11	677	628

H,4,3

-12	81*	-133
-10	967	-921
-8	946	935
-6	1883	-1891
-4	1242	1290
-2	1719	-1760
0	214*	176
2	352	-309
4	708	-661
6	768	741
8	1328	-1365
10	700	642

H,5,3

-11	348*	-430
-9	570	534
-7	0*	60
-5	437	432
-3	655	630
-1	429	-375
1	804	799
3	238*	-297
5	779	810
7	41*	-36

H,6,3

-8	414*	-484
-6	69*	83
-4	376*	-356
-2	191*	-16
0	0*	-162
2	104*	-308
4	0*	-188
6	0*	-293

H,7,3

-5	137*	-110
-3	148*	-210
-1	870	851
1	598	-610

H,0,4

-16	2211	2204
-14	0*	-81
-12	1836	1854
-10	846	861
-8	1387	1389
-6	4156	4049
-4	90*	20
-2	4246	4195
0	1864	-1810
2	4229	4070
4	1528	1484
6	1454	1445
8	2126	2110
10	589	-547
12	2104	2127

H,1,4

-15	833	881
-13	372	-365
-11	2133	2142
-9	1286	-1295
-7	3185	3166
-5	109*	-165
-3	1061	1099
-1	1432	1388
1	591	-594
3	2969	2905
5	722	-693
7	1911	1980
9	484	-407
11	985	941

H,2,4

-14	386*	435
-12	1467	1515
-10	1110	1114
-8	1080	1094
-6	1970	1970
-4	559	565
-2	3139	3174
0	963	954
2	2525	2482
4	835	836
6	882	867
8	1528	1491
10	565	571

H,3,4

-15	594	572
-13	723	787
-11	533	614
-9	1002	1003
-7	585	615
-5	1002	1013
-3	1229	1242
-1	1091	1093
1	1228	1225
3	745	698
5	819	818
7	642	686
9	760	790

H,4,4

-12	297*	390
-10	975	955
-8	1169	1174
-6	490	498
-4	2034	2085
-2	0*	-129
0	2028	2079
2	176*	50
4	1366	1402
6	1202	1193
8	399	305

H,5,4

-11	376*	-340
-9	2383	2401
-7	488	-470
-5	1800	1793
-3	674	743
-1	519	529
1	1936	1933
3	372	-344
5	2078	2097
7	112*	-137

H,6,4

-8	853	820
-6	356*	-412
-4	1717	1720
-2	650	-650
0	2197	2175
2	504	-398
4	803	782

H,7,4

-3	765	705
-1	829	811

H,1,5

-15	451	-406
-13	385	-419
-11	374	373
-9	717	-717
-7	1203	1201
-5	1359	-1339
-3	648	652
-1	1298	-1216
1	131*	21
3	326*	349
5	799	-767
7	844	856
9	869	-931
11	509	426

H,2,5

-14	1121	-1117
-12	1759	1777
-10	1183	-1215
-8	997	989
-6	358	345
-4	715	-768
-2	2391	2406
0	2043	-2007
2	1909	1868
4	1062	-1035
6	1082	1026
8	0*	160
10	319*	-212

H,3,5

-15	406*	-458
-13	0*	-119
-11	739	701
-9	1925	-1987
-7	1039	1028
-5	2211	-2256
-3	1901	1955
-1	1201	-1195
1	270*	-265
3	66*	31
5	1522	-1519
7	1455	1444
9	1510	-1503

H,4,5

-14	708	-680
-12	1457	1485
-10	739	-786
-8	641	660
-6	0*	148
-4	327	-333
-2	1806	1839
0	1097	-1111
2	1552	1549
4	868	-839
6	833	819
8	274*	168

H,5,5

-11	0*	-13
-9	512	-558
-7	440	449
-5	852	-920
-3	229*	126
-1	687	-635
1	0*	-166
3	0*	35
5	595	-548

H,6,5

-9	343*	199
-6	349*	213
-4	469	334
-2	139*	-218
0	475	349
2	285*	61
4	157*	320

H,0,6

-14	1771	1793
-12	971	-915
-10	2514	2482
-8	1099	-1060
-6	2279	2227
-4	249*	263
-2	525	479
0	1998	1938
2	811	-810
4	2963	2946
6	1080	-1092
8	1470	1475
10	0*	-70

H,1,6

-15	2000	2025
-13	379	318
-11	1569	1613
-9	1636	1616
-7	184*	121
-5	3869	3891
-3	502	-466
-1	3579	3479
1	171*	247
3	1781	1777
5	1715	1670
7	386*	431
9	1801	1779

H,2,6

-14	1108	1068
-12	0*	12
-10	1465	1460
-8	0*	-114
-6	1570	1565
-4	979	977
-2	994	966
0	1243	1191
2	180*	-248
4	1562	1546
6	291*	170
8	1236	1238

H,3,6

-15	621	640
-13	861	871
-11	851	861
-9	1045	1039
-7	1299	1381
-5	982	1052
-3	1418	1486
-1	1002	1032
1	1138	1132
3	1029	1088
5	968	925
7	1040	1012

H,4,6

-12	1362	1401
-10	0*	62
-8	1698	1746
-6	370	33[illegible]
-4	882	94[illegible]
-2	933	937
0	559	576
2	1891	1896
4	264*	-88
6	1334	1377

H,5,6

-11	365*	415
-9	542	489
-7	1647	1639
-5	920	-898
-3	2234	2207
-1	461	-441
1	1773	1762
3	591	484

H,6,6

-8	1876	1840
-6	167*	3
-4	1145	1138
-2	1201	1125
0	197*	246
2	1803	1802

H,1,7

-15	519	626
-13	641	-594
-11	1094	1100
-9	112*	36
-7	349	-287
-5	0*	51
-3	762	-734
-1	1553	1519
1	614	-576
3	911	877
5	565	-604
7	152*	152

H,2,7

-14	349*	-243
-12	663	-640
-10	1257	1265
-8	2066	-2055
-6	1499	1509
-4	2039	-2063
-2	819	767
0	0*	47
2	1015	-977
4	802	845
6	1422	-1412
8	917	926

H,3,7

-13	1225	-1204
-11	1239	1188
-9	324*	-379
-7	261*	226
-5	1123	1177
-3	925	-947
-1	1895	1904
1	1584	-1572
3	1491	1515
5	492	-575
7	557	532

H,4,7

-12	745	-721
-10	645	685
-8	1566	-1584
-6	1110	1125
-4	1372	-1393
-2	420	466
0	329*	-306
2	856	-862
4	486	511
6	1107	-1094

H,5,7

-11	743	733
-9	130*	23
-7	164*	129
-5	191*	247
-3	256*	-217
-1	894	922
1	168*	-193
3	572	591

H,6,7

-6	512	-484
-4	180*	-69
-2	245*	-253
0	0*	-195

H,0,8

-16	274*	-314
-14	1748	1765
-12	1055	1030
-10	737	664
-8	2549	2507
-6	539	-543
-4	3506	3498
-2	0*	23
0	2688	2742
2	421	463
4	877	855
6	1675	1696

H,1,8

-15	265*	-194
-13	1783	1776
-11	744	-728
-9	2157	2162
-7	593	-625
-5	1356	1315
-3	1350	1336
-1	0*	-231
1	2126	2105
3	948	-919
5	1682	1743
7	330*	-70

H,2,8

-14	1322	1292
-12	954	971
-10	872	893
-8	1649	1651
-6	513	475
-4	2121	2165
-2	475	457
0	1666	1653
2	863	834
4	1055	1093
6	1288	1320

H,3,8

-13	567	534
-11	876	837
-9	687	679
-7	929	955
-5	765	747
-3	674	666
-1	983	923
1	667	646
3	856	932
5	694	603

H,4,8

-12	635	637
-10	1101	1104
-8	201*	289
-6	1637	1690
-4	0*	-34
-2	1587	1574
0	425	382
2	1071	1132
4	710	722

H,5,8

-9	464	-401
-7	1819	1771
-5	442*	526
-3	407*	511
-1	1561	1612
1	350*	-331

H,1,9

-15	0*	-49
-13	419	457
-11	937	-876
-9	665	633
-7	1221	-1175
-5	612	608
-3	249*	-242
-1	184*	108
1	0*	115
3	762	-772
5	434*	431

H,2,9

-14	1150	1145
-12	930	-908
-10	925	894
-8	224*	116
-6	451	-472
-4	1366	1371
-2	1379	1420
0	1832	1857
2	976	-926
4	668	637

H,3,9

-13	247*	278
-11	1367	-1424
-9	1595	1637
-7	1506	1529
-5	726	758
-3	1205	-1252
-1	0*	-208
1	495	464
3	770	-804

H,4,9

-12	645	-657
-10	853	840

H,4,9

-8	0*	30
-6	249*	-23
-4	1004	98
-2	1139	-1057
0	1412	1428
2	580	-552

H,5,9

-9	213*	147
-7	800	-803
-5	396*	261
-3	501	-370
-1	189*	-65

H,0,10

-14	970	-985
-12	2245	2224
-10	623	-615
-8	1629	1667
-6	108*	229
-4	201*	151
-2	1646	1707
0	560	-550
2	1823	1828

H,1,10

-15	0*	167
-13	1164	1146
-11	1336	1346
-9	409*	427
-7	2417	2378
-5	461	-455
-3	2568	2591
-1	0*	210
1	1450	1503
3	1190	1122

H,2,10

-14	43*	11
-12	1223	1219
-10	0*	-27
-8	1067	1108
-6	520	509
-2	1127	1103
0	0*	176
2	1214	1238

H,3,10

-13	975	797
-11	775	778
-9	792	875
-7	744	771
-5	997	1084
-3	1000	825
-1	992	1011
1	796	858

H,4,10

-10	1339	1331
-8	192*	297
-6	874	833
-4	1004	1025
-2	239*	233
0	1183	1223

H,1,11

-13	509	492
-11	464	-441
-9	0*	-2
-7	801	763
-5	317*	-367
-3	802	760
-1	783	-836
1	526	487

H,2,11

-12	647	578
-10	1384	-1357
-8	1230	1216
-6	1177	-1148
-4	539	540
-2	394	-434
0	677	-647

H,3,11

-11	403*	-315
-9	42*	158
-7	831	832
-5	1077	-1039
-3	1396	1397
-1	952	-920

H,4,11

-8	755	789
-6	1052	-1096
-4	400*	293

H,0,12

-12	628	600
-10	1936	1959
-8	388*	-382
-6	2428	2447
-4	289*	-329
-2	1757	1802

H,1,12

-11	1537	1501
-9	0*	-103
-7	998	985
-5	612	639
-3	0*	-124
-1	1536	1539

H,2,12

-10	1260	1281
-8	530	465
-6	1581	1597
-4	382*	287
-2	1224	1222

H,3,12

-7	559	639
-5	713	660

H,1,13

-7	564	551