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Refinement of the Crystal Structure of Stilbite

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Stilbite, $Na_{1\cdot28}Ca_{4\cdot18}Mg_{0\cdot18}[Al_{10\cdot30}Si_{25\cdot71}O_{72}].34\cdot07\ H_2O$, a zeolite belonging to the heulandite group, crystallizes in the monoclinic, pseudo-orthorhombic, system, space group $C2/m$ with $a=13\cdot64$, $b=18\cdot24$, $c=11\cdot27$ Å and $\beta=128°$; $Z=1$. The structure was refined by three-dimensional electron density syntheses and least-squares to a final reliability index R of 12·3% for observed reflexions. The silicate framework can be described as consisting of a fundamental polyhedral configuration containing four- and five-membered rings of tetrahedra. In the stilbite framework there are two sets of channels, the biggest running parallel to the a axis, the smallest to the c^* axis. Several attempts to identify the ordering of Si and Al atoms in the framework were made and the results discussed. As in related zeolites the exchangeable cations and water molecules occur within the cavities formed by the intersecting channels. Calcium atoms have been found to be completely insulated from framework atoms by a sphere of hydration of their own. Sodium atoms lie in interstices between these spheres and the framework wall. The (010) cleavage and habit of stilbite are well explained by the small number of oxygen bridges linking the tetrahedral sheets. Explanations of the twinning are suggested.

Introduction

Stilbite is a common natural zeolite formed as a result of late-stage hydrothermal activity and it occurs mainly in cavities of basalts and in crevices of metamorphic rocks.

Gabuda, Lundin & Mikhailov (1963) investigated the position of the water molecules in stilbite by the nuclear magnetic resonance method.

The description of the unrefined framework of tetrahedra of stilbite has been given by Galli & Gottardi (1966).

The purpose of this work was to refine the structure, locate the exchangeable-cation and water-molecule positions and investigate the Si/Al distribution within the framework. The results of this research, along with derived data, are given in this report.

Experimental

The stilbite studied was from a basalt from Iceland (specimen No. 3157 of the Museo di Mineralogia dell' Università di Pisa). The crystal data used in this investigation, the same as used by Galli & Gottardi (1966) are:

$$\begin{aligned} a &= 13\cdot64 \pm 0\cdot03 \text{ Å},\\ b &= 18\cdot24 \pm 0\cdot04\\ c &= 11\cdot27 \pm 0\cdot02\\ \beta &= 128°0' \pm 15'\\ U &= 2209 \text{ Å}^3 \end{aligned}$$

Space group $C2/m$

In the unit cell there is one stoichiometric unit $Na_{1\cdot28}Ca_{4\cdot18}Mg_{0\cdot18}[Al_{10\cdot30}Si_{25\cdot71}O_{72}].34\cdot07H_2O$

$D_{\text{calc}} = 2\cdot23$ g.cm^{-3}
$D_{\text{exp}}\ 2\cdot19 \pm 0\cdot01$ g.cm^{-3}.

The experimental density was obtained with a torsion microbalance, on small splinters weighing a few milligrams.

As direction [102] is almost normal to **a**, stilbite is pseudo-orthorhombic with unit-cell dimensions

$$a=13\cdot64,\ b=18\cdot24,\ c=8\cdot88 \text{ Å};\ \beta=89°5'.$$

Photographic data were collected on a Weissenberg camera with equi-inclination geometry and on a Buerger retigraph modified after Corni & Gottardi (1964). On the whole intensities of 1360 independent reflexions were obtained and measured by visual estimation using the multiple film technique. The measured reflexions comprise approximately 55% of the total number of reflexions in the Cu *Kα* limiting sphere.

Refinement

The refinement was carried out by a combination of three-dimensional electron density syntheses and least-squares techniques. The starting coordinates of Si, O and Ca atoms were those of Galli & Gottardi (1966) which gave a discrepancy index value of 19%. First Na atom and water molecule positions were found by means of two successive three-dimensional electron density syntheses and electron density difference syntheses.

The refinement was then continued on an IMB 7094 computer employing the *ORFLS* program by Busing, Martin & Levy (1962). In the initial stage of the refinement, the atomic scattering factors used in the calculations of structure factors were those for neutral atoms taken from *International Tables for X-ray Crystallography* (1962).

As the temperature factors of some Si atoms using the atomic scattering factors for neutral atoms persisted in being negative during the first cycles of least-squares, in further calculations it was advisable to use the atomic scattering factors for half-ionized atoms.

After the introduction of water molecules and Na atoms the reliability index reduced to 14%. Further refinement cycles reduced the *R* value for observed reflexions to a final value of 12·3%.

The final positional and thermal parameters with their standard deviations are given in Table 1. The observed and calculated structure factors are listed in Table 2.

By the atomic coordinates obtained from the last cycle of the least squares, a three-dimensional electron density difference synthesis was computed in order to locate further sites containing exchangeable cations or water molecules.

Two sites were located, both only statistically occupied probably by water molecules: the first with an occupancy of 13% the second with an occupancy of 6%. However all attempts to refine these positions by the least-squares method failed. Although the assignment of electron density to these two positions led to a reduction of the *R* value, and the interatomic distances with neighbours were rather regular, both the sites were neglected since the temperature factors were noticeably higher than the others ($B=20$ Å^2 or more).

The crystallochemical results obtained at the end of the refinement are in good agreement with the data of the chemical analysis.

Refinement revealed 29·40 water molecules as against the 34·07 water molecules revealed by chemical analysis; this agreement is quite satisfactory owing to the difficulty in locating the water molecules in the crystal structure of the zeolites. The refinement gave a total of 5·76 exchangeable cations; this value agrees satisfactorily with that of 5·64 indicated by the chemical analysis.

The silicate framework

A general description of the framework of stilbite has been given by Galli & Gottardi (1966). The fundamental unit of this framework can be considered the characteristic polyhedral configuration of tetrahedra which occurs also in related zeolites of the heulandite

Table 1. *Final atomic parameters with their standard deviations*

	Number of atoms in unit cell	x/a	y/b	z/c	B(Å^2)	Occupancy observed
Si(1)	8	0·4830 ± 0·0003	0·3042 ± 0·0002	0·2420 ± 0·0004	0·46 ± 0·06	1·00
Si(2)	8	0·2653 ± 0·0003	0·3097 ± 0·0002	0·2619 ± 0·0004	0·33 ± 0·06	1·00
Si(3)	8	0·1892 ± 0·0004	0·0893 ± 0·0002	0·4846 ± 0·0004	0·40 ± 0·06	1·00
Si(4)	8	0·1124 ± 0·0003	0·3166 ± 0·0002	0·5013 ± 0·0004	0·43 ± 0·06	1·00
Si(5)	4	0·0000 ± 0·0000	0·2610 ± 0·0003	0·0000 ± 0·0000	0·42 ± 0·08	1·00
O(1)	8	0·4645 ± 0·0010	0·2911 ± 0·0006	0·0842 ± 0·0011	1·40 ± 0·17	1·00
O(2)	8	0·1164 ± 0·0010	0·3162 ± 0·0006	0·1189 ± 0·0011	1·38 ± 0·17	1·00
O(3)	8	0·0512 ± 0·0011	0·2661 ± 0·0006	0·3516 ± 0·0012	2·03 ± 0·20	1·00
O(4)	8	0·0638 ± 0·0010	0·1199 ± 0·0006	0·3226 ± 0·0011	1·41 ± 0·18	1·00
O(5)	8	0·2935 ± 0·0011	0·2308 ± 0·0006	0·3453 ± 0·0012	2·01 ± 0·20	1·00
O(6)	8	0·3001 ± 0·0011	0·3796 ± 0·0006	0·3714 ± 0·0012	1·76 ± 0·19	1·00
O(7)	8	0·3406 ± 0·0010	0·3162 ± 0·0006	0·1914 ± 0·0011	1·40 ± 0·18	1·00
O(8)	8	0·3157 ± 0·0011	0·1119 ± 0·0006	0·5024 ± 0·0012	1·78 ± 0·19	1·00
O(9)	4	0·1863 ± 0·0016	0·0000 ± 0·0000	0·4876 ± 0·0017	1·75 ± 0·27	1·00
O(10)	4	0·0000 ± 0·0000	0·3509 ± 0·0008	0·5000 ± 0·0000	1·15 ± 0·23	1·00
Ca	4	0·2805 ± 0·0005	0·0000 ± 0·0000	0·0949 ± 0·0006	2·15 ± 0·09	1·00
Na	8	0·5055 ± 0·0043	0·0659 ± 0·0021	0·0392 ± 0·0042	4·28 ± 1·29	0·22 ± 0·03
H_2O(1)	8	0·1347 ± 0·0025	0·0776 ± 0·0015	0·1067 ± 0·0030	7·45 ± 0·98	0·84 ± 0·06
H_2O(2)	8	0·3306 ± 0·0018	0·1258 ± 0·0018	0·1013 ± 0·0020	4·71 ± 0·58	0·91 ± 0·05
H_2O(3)	4	0·3691 ± 0·0024	0·0000 ± 0·0000	0·3549 ± 0·0027	3·58 ± 0·71	0·85 ± 0·06
H_2O(4)	4	0·5124 ± 0·0038	0·0000 ± 0·0000	0·2416 ± 0·0045	9·98 ± 1·06	1·00
H_2O(5)	4	0·4028 ± 0·0023	0·5000 ± 0·0000	0·1632 ± 0·0026	4·72 ± 0·51	1·00
H_2O(6)	4	0·1712 ± 0·0039	0·5000 ± 0·0000	0·1040 ± 0·0046	10·16 ± 1·07	1·00

Table 2. *Observed and calculated structure factors* (× 10)

K	L	FO	FC
H = 0			
2	0	2091	-2181
4	0	601	584
6	0	1325	1354
8	0	282	33
10	0	2902	3317
12	0	571	584
14	0	586	-725
16	0	1847	1896
18	0	668	-843
20	0	379	355
22	0	935	912
0	1	916	-1126
2	1	405	292
4	1	1652	1985
6	1	852	771
8	1	315	-174
10	1	477	-486
12	1	274	-202
14	1	852	751
16	1	349	305
18	1	405	251
20	1	229	261
22	1	578	-534
0	2	954	986
2	2	1149	1313
4	2	1021	-901
6	2	1220	-1225
8	2	1231	1015
10	2	466	-347
12	2	1614	1344
16	2	721	-729
18	2	248	425
20	2	214	-251
22	2	522	527
0	3	1547	-1475
2	3	1032	-1050
4	3	1322	1209
6	3	1506	-1022
8	3	1641	1076
10	3	1052	-1586
12	3	833	-800
14	3	304	309
18	3	436	445
22	3	574	-703
0	4	1093	1282
2	4	1145	-1071
4	4	698	-614
6	4	379	305
8	4	2208	-1997
10	4	1089	1128
12	4	338	349
14	4	957	-961
16	4	398	475
18	4	1509	-1322
20	4	454	533
0	5	2467	-2630
2	5	552	-450
4	5	788	744
6	5	702	-607
8	5	312	311
10	5	1408	-1425
12	5	405	-425
14	5	180	30
16	5	206	-209
0	6	781	808
4	6	642	-581
6	6	1231	-1135
8	6	920	946
10	6	777	-685
12	6	939	950
14	6	586	-636
16	6	526	-406
18	6	443	314
0	7	1753	-1832
4	7	312	363
10	7	942	-879
0	8	2253	2277
2	8	1044	-941
6	8	308	301
8	8	833	-756
10	8	924	949
12	8	379	298
14	8	627	-622
16	8	680	681
0	9	394	-371
2	9	255	-126
4	9	593	686
6	9	372	-325
8	9	747	712
10	9	405	-505
12	9	259	-164
14	9	319	304
0	10	458	513
2	10	334	287
4	10	210	-225
8	10	248	313
4	11	541	590
H = 1			
3	0	409	-443
5	0	563	-577
7	0	781	-835
9	0	379	335
11	0	604	508
13	0	871	-918
15	0	882	919
17	0	999	-1051
19	0	428	534
3	1	2519	-2004
5	1	2410	2304
7	1	826	-805
9	1	1051	-1036
11	1	972	943
13	1	1483	-1549
15	1	462	516
19	1	390	-427
21	1	252	251
23	1	289	-370
3	-1	616	694
5	-1	146	-127
7	-1	240	94
9	-1	503	391
11	-1	619	-609
13	-1	875	836
19	-1	514	559
21	-1	263	-417
23	-1	259	339
1	2	1066	-1203
3	2	1491	1089
5	2	169	-49
7	2	578	-483
11	2	315	-205
13	2	1100	1106
15	2	788	-785
17	2	751	-699
19	2	447	392
21	2	353	-484
1	-2	413	-452
3	-2	2009	2034
5	-2	1813	-2184
7	-2	890	875
9	-2	807	742
11	-2	695	-619
13	-2	1134	1019
17	-2	368	-401
19	-2	770	812
21	-2	522	-597
23	-2	507	637
1	3	890	-892
3	3	935	-932
5	3	1318	-1212
7	3	848	967
9	3	939	-734
11	3	762	-663
13	3	1078	-957
1	-3	1352	1334
21	3	758	-941
3	-3	1408	-1413
5	-3	278	377
7	-3	826	820
9	-3	436	-383
11	-3	1307	1292
13	-3	1295	-1168
15	-3	882	867
17	-3	375	228
21	-3	289	331
1	4	387	-410
7	4	1040	-894
11	4	548	546
13	4	447	-353
17	4	976	-918
21	4	252	302
1	-4	529	405
3	-4	214	86
5	-4	1032	992
9	-4	638	542
11	-4	405	363
15	-4	687	503
3	5	1231	-1170
5	5	1483	1483
9	5	777	-775
11	5	544	617
13	5	1194	-1070
15	5	608	540
17	5	308	332
19	5	372	-358
1	-5	417	448
3	-5	278	-310
7	-5	935	966
9	-5	511	-589
11	-5	740	749
1	6	481	408
3	6	1246	1266
5	6	1708	-1872
7	6	965	997
9	6	503	404
13	6	593	590
19	6	368	428
1	-6	785	-698
3	-6	1265	1264
5	-6	736	-699
7	-6	905	839
19	-6	315	315
1	7	195	-240
3	7	683	668
7	7	969	969
13	7	345	330
17	7	413	456
1	-7	364	362
3	-7	792	-835
5	-7	353	179
11	-7	616	519
13	-7	571	-524
19	-7	345	-448
1	8	589	513
3	8	233	337
9	8	469	367
11	8	574	665
15	8	383	480
1	-8	935	-946
3	-8	327	372
5	-8	330	-425
7	-8	237	-194
9	-8	447	-344
11	-8	424	-433
13	-8	390	-335
17	-8	526	-662
1	9	191	130
3	9	623	-613
5	9	604	636
11	9	349	243
5	-9	278	-337
9	-9	379	-361
11	-9	252	282
1	10	146	-65
3	10	766	859
5	10	657	-849
1	-10	304	-359
3	-10	259	265
5	-10	248	-296
11	-10	420	-546
1	11	285	-295
1	-11	338	354
3	-11	345	-334
H = 2			
0	0	702	-709
2	0	1840	-1856
4	0	1021	939
6	0	368	-255
8	0	680	-537
10	0	1156	-1084
12	0	732	-691
22	0	661	-684
0	1	1877	1882
2	1	740	-794
4	1	357	276
6	1	833	-803
8	1	229	-148
10	1	845	830
18	1	345	-354
0	-1	879	636
2	-1	390	-359
4	-1	511	-540
6	-1	2140	-2518
8	-1	308	-174
14	-1	409	-351
16	-1	680	-619
18	-1	315	-220
0	2	263	-219
2	2	1686	-1653
4	2	567	460
6	2	270	265
10	2	916	-915
16	2	413	336
0	-2	909	-775
2	-2	1389	-1779
4	-2	713	545
6	-2	263	163
8	-2	1494	-1372
10	-2	1288	-1309
14	-2	462	-502
16	-2	304	370
20	-2	424	-358
0	3	638	571
2	3	811	752
4	3	206	-52
6	3	1002	-1030
8	3	1517	1542
10	3	244	-22
12	3	364	303
14	3	345	153
18	3	473	353
0	-3	1716	1794
2	-3	146	137
4	-3	135	76
6	-3	976	-1155
8	-3	417	-503
10	-3	526	-84
12	-3	501	1102
14	-3	567	-521
18	-3	466	-381
22	-3	357	319
0	4	274	231
6	4	725	734
8	4	987	778
10	4	330	-364
14	4	518	491
20	4	285	287
0	-4	950	930
2	-4	432	-312
4	-4	319	482
6	-4	773	867
8	-4	466	498
10	-4	668	-606
12	-4	360	-218
16	-4	807	750
22	-4	338	-361
0	5	1126	1027
2	5	282	-171
4	5	668	582
6	5	319	-151
10	5	676	509
12	5	466	415
16	5	424	409
18	5	334	-313
0	-5	1261	1224
2	-5	1415	1446
4	-5	728	808
6	-5	541	-525
8	-5	999	1007
10	-5	548	666
12	-5	1070	1164
20	-5	387	363
0	6	758	714
6	6	563	426
8	6	364	298
12	6	462	422
14	6	387	-362
16	6	537	609
0	-6	976	-948
4	-6	717	687
6	-6	507	507
8	-6	864	917
10	-6	1070	-1096
16	-6	631	586
18	-6	398	274
2	7	451	325
4	7	375	206
6	7	496	-402
8	7	578	530
10	7	319	-376
12	7	668	573
0	-7	867	752
2	-7	980	904
4	-7	466	-407
6	-7	1246	-1102
8	-7	1445	1454
10	-7	252	237
12	-7	372	437
18	-7	252	193
2	8	439	-401
4	8	402	317
10	8	274	-308
12	8	210	202
0	-8	458	-388
2	-8	875	-811
4	-8	1051	931
6	-8	563	529
10	-8	492	-596
16	-8	267	241
0	9	484	499
2	9	571	-499
0	-9	1231	1197
2	-9	507	-442
6	-9	563	-518
8	-9	319	-275
10	-9	668	592
12	-9	274	270
14	-9	312	-365
0	10	255	-160
2	10	334	-214
2	-10	792	-794
6	-10	312	339
10	-10	402	-506
12	-10	285	-301
14	-10	312	-375
2	-11	158	115
6	-11	721	-903
2	-12	589	-608
4	-12	206	257
H = 3			
1	0	184	-147
3	0	826	-840
5	0	1389	1543
7	0	345	305
9	0	481	497
13	0	1231	-1236
15	0	875	861
17	0	360	247
19	0	173	344
23	0	214	-249
1	1	717	767
3	1	758	777
5	1	826	771
7	1	323	279
9	1	788	866
11	1	315	258
13	1	1145	1230
17	1	867	-847
19	1	743	620
1	-1	1010	1088
3	-1	428	-475
5	-1	1126	-1204
7	-1	826	765
9	-1	184	237
11	-1	683	588
13	-1	443	-433
15	-1	574	593
17	-1	751	-852
23	-1	259	354
1	2	815	694
3	2	278	-339
5	2	1111	1058
7	2	1352	1479
11	2	503	678
13	2	1078	-1167
15	2	646	650
17	2	879	918
19	2	199	217
21	2	458	-477
1	-2	1400	-1656
3	-2	116	13
5	-2	180	-167
7	-2	293	-243
9	-2	743	-725
11	-2	661	-665
13	-2	360	-287
15	-2	634	-619
17	-2	402	-443
21	-2	477	-503
1	3	886	843
3	3	229	134
5	3	586	629
7	3	158	-153
9	3	222	172
11	3	950	1036
13	3	601	433
17	3	537	-562
1	-3	199	-295
3	-3	1216	1308
5	-3	1352	-1670
7	-3	176	207
9	-3	409	-396
11	-3	158	-119
13	-3	811	891
15	-3	349	-333
17	-3	1168	-1060
19	-3	477	437
21	-3	308	-381
23	-3	357	500
1	4	747	-703
3	4	420	-385
5	4	526	552
7	4	173	-189
9	4	285	-234
11	4	244	-247
13	4	845	-761
15	4	308	343
1	-4	420	-521
3	-4	980	-1226
5	-4	1021	-1014
7	-4	135	-155
9	-4	574	-681
13	-4	2027	-1930
15	-4	548	545
21	-4	409	-362
1	5	188	-87
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10	-6	833	-798
14	-6	282	349
16	-6	274	-273
18	-6	484	492
0	-7	1108	1047
2	-7	646	-503
4	-7	360	361
6	-7	762	-695
10	-7	364	311
0	-8	139	33
2	-8	1002	-1035
0	-9	327	266
2	-9	127	-2
0	-10	860	-959
0	-11	830	876
2	-11	484	-413
0	-12	394	415
2	-12	586	-625
4	-12	248	168
6	-12	548	639
12	-12	357	-441
0	-13	469	588
2	-13	143	59
0	-14	1085	-1122
2	-14	526	462
H = 13			
1	0	158	-89
1	1	455	338
1	-1	285	-207
1	-2	589	-622
1	-3	319	279
1	-6	169	-94
7	-6	522	532
11	-6	255	-224
13	-6	330	-237
1	-7	571	546
7	-7	267	-342
11	-7	740	758
15	-7	522	664
1	-10	353	-414
1	-11	169	187
1	-13	477	-486
3	-13	1239	1072
5	-13	1224	-1273
7	-13	398	402
1	-14	191	-198
H = 14			
0	0	368	-309
2	-1	586	546
0	-2	518	-599
0	-3	1577	1592
2	-3	1070	-946
0	-4	417	-464
2	-4	267	-248
2	-5	150	-202
2	-6	297	-310
6	-6	488	-432
8	-6	488	400
10	-6	417	-318
0	-7	1213	1155
2	-7	1100	-1014
4	-7	383	346
6	-7	383	349
8	-7	916	-901
10	-7	728	655
14	-7	529	-449
2	-8	184	131
4	-8	364	358
6	-8	563	-581
8	-8	556	639
10	-8	417	-408
12	-8	327	96
14	-8	327	483
0	-9	300	304
2	-9	150	222
2	-10	150	245
0	-11	758	828
2	-11	751	-611
0	-12	297	-172
2	-12	443	345
0	-13	229	-294
2	-13	308	-214
0	-14	282	196
H = 15			
1	2	571	446
1	-4	169	191
1	-5	496	-497
1	-6	319	282
1	-7	488	-600
5	-7	255	203
11	-7	717	-659
1	-8	312	201
5	-8	312	-525
11	-8	608	536
1	-9	319	-385
1	-10	544	-71
1	-11	364	-353
1	-12	364	440
1	-13	274	-168
H = 16			
0	3	345	-253
0	-4	770	771
2	-5	349	-249
0	-6	563	616
2	-6	143	171
2	-7	514	-356
4	-7	481	443
0	-8	1269	1228
2	-8	743	-596
8	-8	237	-272
10	-8	334	347
0	-9	511	-568
2	-10	436	281
0	-11	784	-439
2	-11	436	-346
0	-12	668	586
2	-12	436	-358
H = 17			
1	6	353	-302
1	-7	646	655
1	-8	338	-235
3	-8	338	361
5	-8	297	359
3	-9	270	414
5	-9	695	585
1	-10	544	-444
1	-11	533	405
H = 18			
0	9	417	-322
2	-9	800	711
0	-10	451	405

group and consists of four- and five-membered rings of tetrahedra (Meier, 1968). The units are connected with each other giving rise to elongated chains in the same direction as **c*** and to sheets parallel to (010). The sheets are linked together by relatively few oxygen-bridges which occur at $y/b=0$ and $y/b=\frac{1}{2}$.

Two dimensional systems of channels are therefore formed. The intersecting channels are relatively large; ten-membered rings surround those channels running parallel to the *a* axis and eight-membered rings surround those running parallel to the *c* axis. All the channels are bisected by the mirror plane at heights of 0 and $\frac{1}{2}$ on the crystallographic *b* axis and are limited by a complex layer arrangement of six-, five- and four-membered ring groups. The stereographic views of Fig. 1 (*a*) and (*b*) show the silicate framework as seen along the *a* axis and [102] axis. The (Si,Al)–O bond length and bond angles are presented in Tables 3 and 4, as well as

Table 3. *Interatomic distances with their standard errors within the framework*

Interatomic distances symmetrically equivalent are bracketed.

Distances		Distances	
Si(1) tetrahedron		Si(3) tetrahedron	
Si(1) —O(1)	1·65±0·01 Å	Si(3)—O(4)	1·65±0·01 Å
Si(1) —O(3^{iii})	1·62±0·01	Si(3)—O(6^{vi})	1·64±0·01
Si(1) —O(4^{iii})	1·65±0·01	Si(3)—O(8)	1·66±0·01
Si(1) —O(7)	1·67±0·01	Si(3)—O(9)	1·63±0·01
Average	1·64	Average	1·64
O(1)—O(3^{iii})	2·68±0·02	O(4)—O(6^{vi})	2·73±0·02
O(1)—O(4^{iii})	2·68±0·02	O(4)—O(8)	2·71±0·02
O(1)—O(7)	2·65±0·02	O(4)—O(9)	2·69±0·01
O(3)—O(4)	2·70±0·02	O(6^{vi}) -O(8)	2·70±0·02
O(3^{iii})-O(7)	2·72±0·02	O(6^{vi}) -O(9)	2·65±0·01
O(4^{iii})-O(7)	2·70±0·02	O(8)—O(9)	2·64±0·02
Si(2) tetrahedron		Si(4) tetrahedron	
Si(2) —O(2)	1·65±0·01	Si(4)—O(3)	1·63±0·01
Si(2) —O(5)	1·63±0·01	Si(4)—O(5^{vi})	1·63±0·01
Si(2) —O(6)	1·63±0·01	Si(4)—O(8^{vi})	1·65±0·01
Si(2) —O(7)	1·64±0·01	Si(4)—O(10)	1·65±0·01
Average	1·63	Average	1·64
O(2)—O(5)	2·68±0·02	O(3)—O(5^{vi})	2·69±0·02
O(2)—O(6)	2·63±0·02	O(3)—O(8^{vi})	2·70±0·02
O(2)—O(7)	2·64±0·02	O(3)—O(10)	2·67±0·01
O(5)—O(6)	2·73±0·02	O(5)—O(8)	2·70±0·02
O(5)—O(7)	2·69±0·02	O(5^{vi}) -O(10)	2·67±0·02
O(6)—O(7)	2·67±0·02	O(8^{vi}) -O(10)	2·62±0·01

Si(5) tetrahedron	
Si(5)—O(1^{iv})	1·61±0·01 Å
Si(5)—O(1^{v})	
Si(5)—O(2)	1·65±0·01
Si(5)—O(2^{i})	
Average	1·63
O(1^{iv})-O(1^{v})	2·61±0·02
O(1^{iv})-O(2)	2·70±0·02
O(1^{v}) -O(2^{i})	
O(1^{iv})-O(2^{i})	2·68±0·02
O(1^{v}) -O(2)	
O(2) —O(2^{i})	2·60±0·02

The atoms of the different asymmetric units are related to the atoms of the fundamental unit as follows:

Superscript	Coordinates		
none	x	y	z
i	$-x$	y	$-z$
ii	$1-x$	$-y$	$-z$
iii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
iv	$x-\frac{1}{2}$	$\frac{1}{2}-y$	z
v	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
vi	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
vii	x	$-y$	z
viii	$1-x$	y	$1-z$
ix	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-z$

This also applies in Tables 4 and 5 and Fig. 2.

their standard errors. The whole structural model of stilbite projected on (010) plane is shown in Fig. 2. The average value of 1·64 Å for all (Si, Al)–O distances is the same as that expected for Si, Al ratio of 25·7/10·3.

Discussion of the structure

1. *Order–disorder of* Al, Si *atoms*

Single-crystal Weissenberg and precession photographs of stilbite show monoclinic symmetry with extinctions hkl, $h+k=2n+1$ which is consistent with the space groups $C2/m$, Cm or $C2$.

Although stilbite was refined with the centrosymmetric space group the Si/Al arrangement in the framework may have lower symmetry. In fact only if the Si and Al atoms are completely disordered will the symmetry be centrosymmetric, but only on a statistical basis. However, the problem of the Si/Al distribution in zeolites is far too involved to be easily resolved.

The only reliable method of determining the occupancy of the tetrahedral sites by Si or Al is based on the length of the interatomic distances which differ by no more than about 0·13 Å.

The stilbite refinement in space group $C2/m$ gave distances equal within experimental error in all framework tetrahedra.

The calcium site, which should be closely associated with aluminum-substituted tetrahedra to minimize the Coulomb energy, did not help solve the problem, since this atom is near the middle of the channels and completely surrounded by eight water molecules and not by framework oxygen atoms. After the last centrosymmetric refinement, a careful inspection of the three-dimensional electron density map did not reveal any evidence of departure from mirror symmetry, as the peaks of the atoms at $y/b=\frac{1}{2}$ did not exhibit significant deviations from sphericity.

However, several attempts to refine the crystal structure of stilbite were made using both the non-centrosymmetric space groups $C2$ and Cm. Twelve different models have been tested, each obtained by placing aluminum into two or three sites according to the rule 'two aluminum tetrahedra cannot be directly linked'.

The passage from $C2/m$ to Cm or $C2$ was obtained by splitting up the atoms, which in the centrosymmetric space group are single, into double in the non-centrosymmetric space group, excluding, of course, the atoms not splitting for reasons of symmetry.

The data obtained from the different trials in non-centrosymmetric space groups show that:

(*a*) It is impossible to draw conclusions on the reliability of the different models because the R values for all postulated models reached equal values, which in turn were just a little smaller than the value obtained for space group $C2/m$;

(*b*) The (Si, Al)–O distances within each tetrahedron show a range of values too large to be reliable;

(*c*) If the average distances within each tetrahedron of the two structural models proposed for space group Cm give insufficient evidence, the average values (Si, Al)–O for all ten suggested models for space group $C2$ show similarities in preferential occupation by aluminum.

Those similarities can be summarized as follows:

(*d*) Any presence of aluminum in the Si(4) tetrahedron seems to be rejected; this agrees with the

Table 4. *Bond angles with their standard errors within the framework*

Bond angles symmetrically equivalent are bracketed.

Si(1) tetrahedron	Bond angle	Si(4) tetrahedron	Bond angle
O(1)—Si(1)–O(3$^{\text{iii}}$)	109·96 ± 0·59°	O(3)—Si(4)—O(5$^{\text{vi}}$)	111·44 ± 0·62°
O(1)—Si(1)–O(4$^{\text{iii}}$)	108·73 ± 0·56	O(3)—Si(4)—O(8$^{\text{vi}}$)	110·72 ± 0·60
O(1)—Si(1)–O(7)	106·09 ± 0·58	O(3)—Si(4)—O(10)	108·95 ± 0·56
O(3$^{\text{iii}}$)–Si(1)–O(4$^{\text{iii}}$)	111·66 ± 0·60	O(5$^{\text{vi}}$)–Si(4)—O(8$^{\text{vi}}$)	110·75 ± 0·63
O(3$^{\text{iii}}$)–Si(1)–O(7)	111·50 ± 0·60	O(5$^{\text{vi}}$)–Si(4)—O(10)	109·44 ± 0·54
O(4$^{\text{iii}}$)–Si(1)–O(7)	108·72 ± 0·58	O(8$^{\text{vi}}$)–Si(4)—O(10)	105·35 ± 0·66
Average	109·44	Average	109·44
Si(2) tetrahedron		Si(5) tetrahedron	
O(2)—Si(2)–O(5)	109·83 ± 0·58	O(1$^{\text{iv}}$)–Si(5)—O(1$^{\text{v}}$)	107·80 ± 0·79
O(2)—Si(2)–O(6)	107·04 ± 0·59	O(1$^{\text{iv}}$)–Si(5)—O(2)	111·69 ± 0·52
O(2)—Si(2)–O(7)	106·47 ± 0·59	O(1$^{\text{v}}$)–Si(5)—O(2$^{\text{i}}$)	
O(5)—Si(2)–O(6)	113·51 ± 0·60	O(1$^{\text{iv}}$)–Si(5)—O(2$^{\text{i}}$)	110·60 ± 0·57
O(5)—Si(2)–O(7)	110·35 ± 0·59	O(1$^{\text{v}}$)–Si(5)—O(2)	
O(6)—Si(2)–O(7)	109·35 ± 0·60	O(2)—Si(5)—O(2$^{\text{i}}$)	104·55 ± 0·80
Average	109·42	Average	109·48
Si(3) tetrahedron			
O(4)—Si(3)–O(6$^{\text{vi}}$)	112·24 ± 0·60	Si(1)—O(7)—Si(2)	140·11 ± 0·69
O(4)—Si(3)–O(8)	109·97 ± 0·59	Si(1$^{\text{iv}}$)–O(4)—Si(3)	141·12 ± 0·67
O(4)—Si(3)–O(9)	109·79 ± 0·74	Si(1$^{\text{iv}}$)–O(3)—Si(4)	157·59 ± 0·80
O(6$^{\text{vi}}$)–Si(3)–O(8)	110·01 ± 0·60	Si(1$^{\text{iv}}$)–O(1$^{\text{iv}}$)–Si(5)	144·66 ± 0·70
O(6$^{\text{vi}}$)–Si(3)–O(9)	108·25 ± 0·74	Si(2)—O(6)—Si(3$^{\text{vi}}$)	145·86 ± 0·77
O(8)—Si(3)–O(9)	106·39 ± 0·80	Si(2)—O(5)—Si(4$^{\text{vi}}$)	146·38 ± 0·77
Average	109·44	Si(2)—O(2)—Si(5)	137·98 ± 0·70
		Si(3)—O(8)—Si(4$^{\text{vi}}$)	147·51 ± 0·75
		Average	144·40

Al–O–Al avoidance rule since each Si(4) tetrahedron is connected to an equivalent one across the twofold axis at $z/c=\frac{1}{2}$.

(*e*) There is a large amount of evidence to show that the two independent positions obtained by splitting the Si(5) position are preferentially occupied one by aluminum, and the second by silicon respectively.

(*f*) Also the two positions obtained by splitting the Si(1) eightfold position of the centrosymmetric space group, although less clear than the preceding one, seems preferentially occupied, one by Al and the second by Si. The same also holds for the Si(2) and Si(3) positions but here the evidence is more uncertain.

Therefore, if the ordering really occurs in the non-centrosymmetric *C*2 space group, bearing in mind the possible Al arrangements which can be postulated in this space group according to the earlier mentioned rule, when three positions contemporaneously are occupied by aluminum atoms, in the author's opinion the pattern of Al distribution follows the scheme *T*(1*D*), *T*(3*D*), *T*(5*D*), or its opposite *T*(1*U*), *T*(3*U*), *T*(5*U*), where, in the *C*2 space group, *T*(*nD*) and *T*(*nU*) are the two groups having independent positions which correspond to one group only having equivalent positions *T*(*n*) in the centrosymmetric *C*2/*m* space group; *T*(*nD*) are the positions with $y/b<\frac{1}{2}$ and *T*(*nU*) those with $y/b>\frac{1}{2}$.

2. *The water molecules and exchangeable cations*

In the structural model of stilbite the exchangeable cations and water molecules have been found to occur completely inside the cavities formed at the intersection of the larger channels, which are parallel to **a**, with the smaller channels which are parallel to the [102] direction.

The calcium atom lies nearly on the screw axis at $z/c=0$. It is wholly surrounded by and bonded to eight water molecules.

Of these eight water molecules, four lie on the mirror (010) plane; the other four lie on a plane which is normal to the mirror plane and parallel to the larger channel axis, obviously two above and two under the mirror.

Table 5. *Bond lengths from exchangeable cations to water molecules and oxygens ions of the framework*

Interatomic distances symmetrically equivalent are bracketed.

Ca polyhedron	
Ca–H_2O(1) Ca–H_2O(1^{vii})	2·51 ± 0·03 Å
Ca–H_2O(2) Ca–H_2O(2^{vii})	2·38 ± 0·02
Ca–H_2O(3)	2·38 ± 0·03
Ca–H_2O(4)	2·51 ± 0·04
Ca–H_2O(5^{v})	2·40 ± 0·03
Ca–H_2O(6^{v})	2·70 ± 0·04

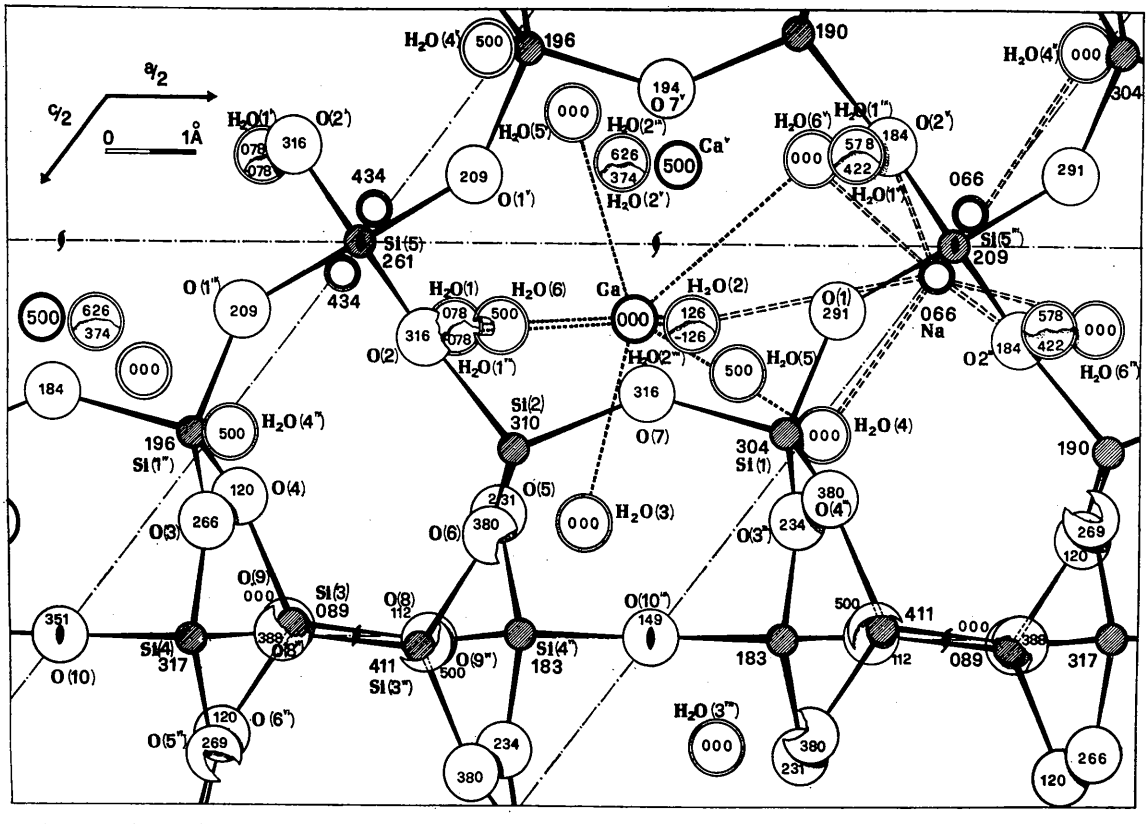
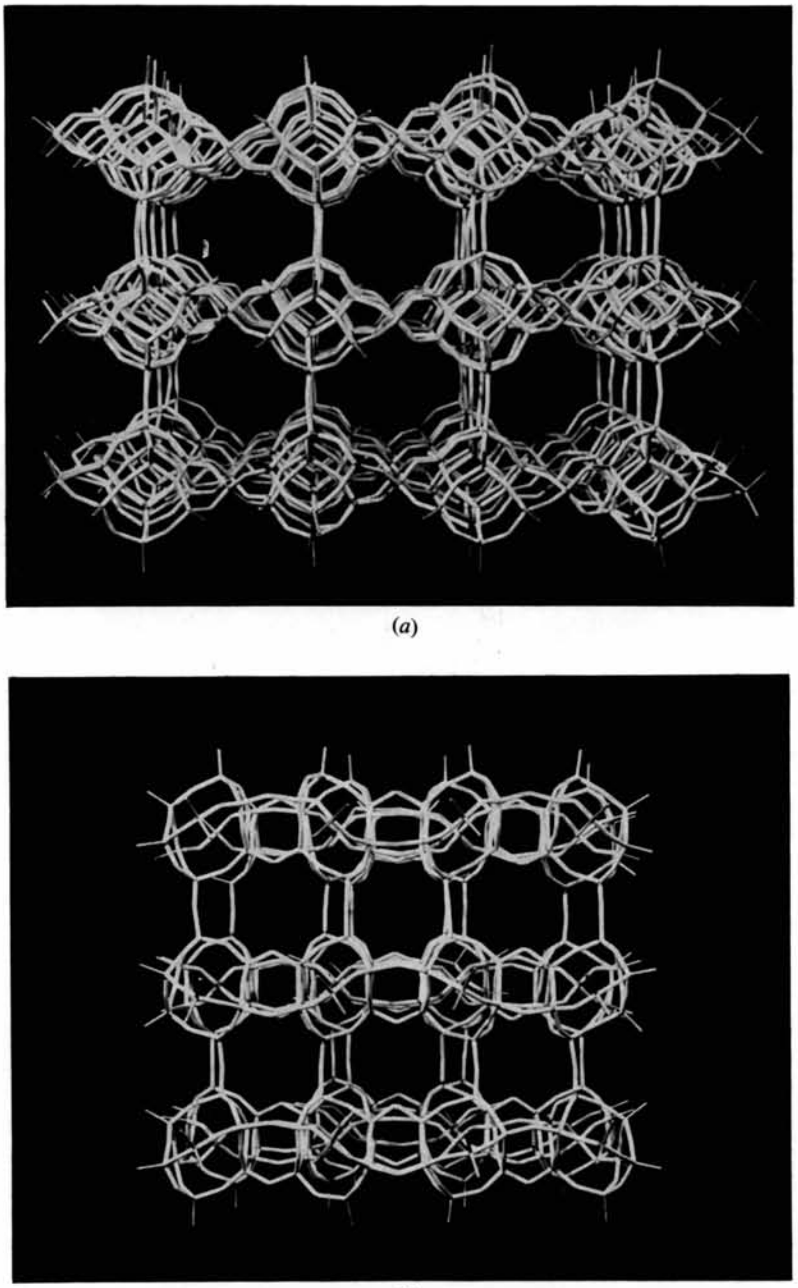


Fig. 2. Projection of the stilbite structure on the (010) plane. Numbers give the heights of the atoms in thousandths of the cell edge. Continous lines are Si–O bonds; dashed lines are cation–water (or oxygen) bonds.



(a)

(b)

Fig. 1. Stereographic view of the stilbite framework viewed (*a*) along **a** and (*b*) along the [102] axis.

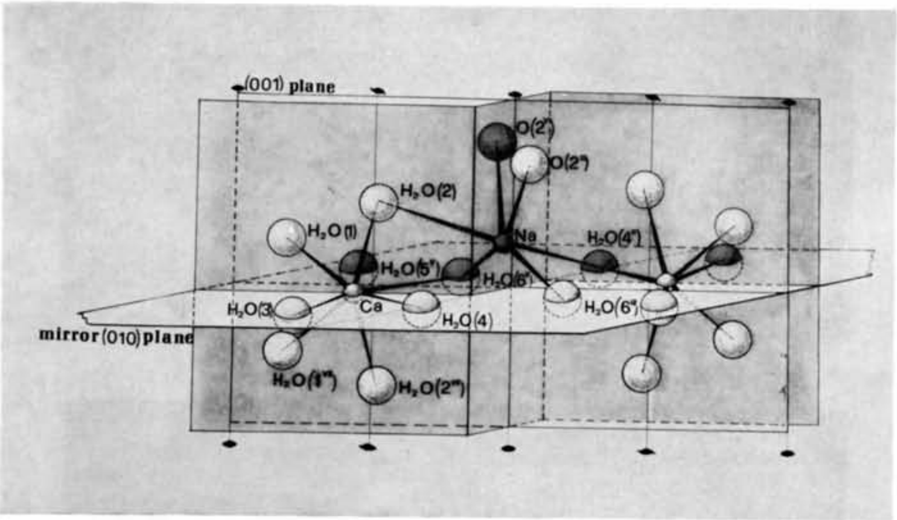


Fig. 3. Assonometric view of the Ca–$8H_2O$ spheroids lying on the mirror (010) plane. A sodium atom is also shown; it coordinates four water molecules and two framework oxygen atoms which are the two highest anions in the Figure. Although the sodium is near the twofold axis, only one atom is shown because of its low (22 %) statistical occupancy.

Table 5 (*cont.*)

Ca–All oxygens ≥ 4·22	
Na polyhedron	
$Na-O(2^{iii})$	2·46 ± 0·04
$Na-O(2^{v})$	2·63 ± 0·04
$Na-H_2O(2)$	3·07 ± 0·05
$Na-H_2O(4)$	2·53 ± 0·05
$Na-H_2O(4^{ii})$	3·25 ± 0·05
$Na-H_2O(6^{iii})$	2·25 ± 0·06
$Na-H_2O(6^{v})$	2·25 ± 0·06

Essentially there is a spheroidal hydrated Ca-8H_2O group as shown in Fig. 3. The Ca–H_2O distances are listed in Table 5. Seven distances fall in a narrow range (from 2·38 Å to 2·51 Å), the eight Ca–H_2O distance is a little larger than the preceding ones (2·70 Å). The biggest channels surrounded by ten-tetrahedra rings are filled by Ca–8H_2O spheroids. Between these spheroids and channel walls there are cavities; sodium atoms occupy these sites statistically; in reality these positions are occupied by a lesser amount of other exchangeable cations such as Ca and Mg, which, of course, are statistically distributed over these sites too. These positions are surrounded by three water molecules and two framework oxygen atoms, if atoms at a distance of more than 3 Å are neglected. The five Na–O, H_2O distances vary from 2·25 to 2·63 Å, in close agreement with the lengths given in the literature; two more distances of 3·07 and 3·25 Å respectively seem too large to be considered here. Therefore the coordination number of sodium atoms, excluding the two largest distances, can be taken as five and the coordination polyhedron can be described as a tetragonal pyramid parallel to the [101] direction, sharply skewed to one side.

Not all water molecules sites are completely filled; occupancy factors from 80 to 90% may occur. Table 6 lists all distances less than 3·65 Å between water molecules, and between water molecules and framework oxygen atoms. The coordination of the water molecules in stilbite are complex and varied, which is not surprising in view of the patterns found in other zeolites.

It is not really possible to draw a line between bonded and non-bonded neighbours for distances larger than 3 Å. As the value of 3·01 Å is taken as the largest distance from close neighbours it may be seen that the coordination around water molecules varies from triangular to octahedral as shown in Table 6.

The $H_2O(1)$ and $H_2O(3)$ molecules are surrounded by four neighbouring water molecules, the $H_2O(4)$ and $H_2O(2)$ by three and two water molecules respectively, while $H_2O(5)$ and $H_2O(6)$ are linked only to one water molecule. All water molecules are bonded to one framework oxygen atom, except $H_2O(4)$ and $H_2O(6)$ which

Table 6. *Distances less than* 3·65 Å *related to water molecules*

Interatomic distances symmetrically equivalent are bracketed.

$H_2O(1)$ polyhedron	Distances
$H_2O(1)-H_2O(1^{i})$	2·90 ± 0·06 Å
$H_2O(1)-H_2O(1^{vii})$	2·83 ± 0·05
$H_2O(1)-H_2O(2)$	2·85 ± 0·03
$H_2O(1)-H_2O(3)$	3·01 ± 0·04
$H_2O(1)-H_2O(5^{v})$	3·10 ± 0·04
$H_2O(1)-O(1^{iv})$	3·23 ± 0·03
$H_2O(1)-O(1^{v})$	2·93 ± 0·03
$H_2O(1)-O(4)$	3·22 ± 0·03
$H_2O(1)-O(5)$	3·54 ± 0·03
$H_2O(1)-O(8)$	3·58 ± 0·03
$H_2O(2)$ polyhedron	
$H_2O(2)-H_2O(1)$	2·85 ± 0·03
$H_2O(2)-H_2O(3)$	3·44 ± 0·03
$H_2O(2)-H_2O(4)$	3·01 ± 0·03
$H_2O(2)-H_2O(5)$	3·55 ± 0·03
$H_2O(2)-H_2O(6^{v})$	3·25 ± 0·04
$H_2O(2)-O(1)$	3·59 ± 0·02
$H_2O(2)-O(1^{v})$	3·54 ± 0·03
$H_2O(2)-O(2^{v})$	3·16 ± 0·02
$H_2O(2)-O(5)$	3·63 ± 0·02
$H_2O(2)-O(7)$	3·60 ± 0·02
$H_2O(2)-O(7^{v})$	2·82 ± 0·02
$H_2O(2)-O(10)$	3·60 ± 0·02
$H_2O(3)$ polyhedron	
$H_2O(3)-H_2O(1)$	3·01 ± 0·04
$H_2O(3)-H_2O(1^{vii})$	
$H_2O(3)-H_2O(2)$	3·44 ± 0·03
$H_2O(3)-H_2O(2^{vii})$	
$H_2O(3)-H_2O(3^{viii})$	3·01 ± 0·05 Å
$H_2O(3)-H_2O(4)$	2·92 ± 0·05
$H_2O(3)-O(8)$	2·99 ± 0·02
$H_2O(3)-O(9)$	3·61 ± 0·03
$H_2O(3)-O(10^{iii})$	3·11 ± 0·02
$H_2O(4)$ polyhedron	
$H_2O(4)-H_2O(2)$	3·01 ± 0·03
$H_2O(4)-H_2O(2^{vii})$	
$H_2O(4)-H_2O(3)$	2·92 ± 0·05
$H_2O(4)-H_2O(6^{v})$	3·07 ± 0·06
$H_2O(4)-H_2O(6^{vi})$	3·35 ± 0·06
$H_2O(5)$ polyhedron	
$H_2O(5)-H_2O(1^{v})$	3·10 ± 0·04
$H_2O(5)-H_2O(1^{ix})$	
$H_2O(5)-H_2O(2)$	3·55 ± 0·03
$H_2O(5)-H_2O(2^{ix})$	
$H_2O(5)-H_2O(6)$	2·80 ± 0·05
$H_2O(5)-O(4^{iii})$	2·82 ± 0·02
$H_2O(5)-O(7)$	3·52 ± 0·01
$H_2O(6)$ polyhedron	
$H_2O(6)-H_2O(2^{v})$	3·25 ± 0·04
$H_2O(6)-H_2O(2^{ix})$	
$H_2O(6)-H_2O(4^{v})$	3·07 ± 0·06
$H_2O(6)-H_2O(4^{iv})$	3·35 ± 0·06
$H_2O(6)-H_2O(5)$	2·80 ± 0·05
$H_2O(6)-O(2)$	3·46 ± 0·02
$H_2O(6)-O(6)$	3·24 ± 0·03

have bond lengths not less than 3·24 Å with the framework oxygen atoms. Only these two water molecules are contemporaneously bonded either to Ca or Na atoms.

Increasing the limit suggested above to 3·65 Å, the coordinations obviously become larger and more complex. The arrangement of water molecules in the specimen of stilbite used for this investigation does not confirm the Gabuda *et al.* (1963) hypothesis. In their specimen the above workers found that in the temperature range −60 to +150 °C the water molecules are grouped in pairs with a distance of 2·74 ± 0·15 Å and that the distances between different pairs of molecules are considerably larger than the distances between the grouped molecules. As can be seen from Table 6 this hypothesis has not been confirmed with the specimen used for this investigation, the range of the water–water distances within each possible pair and between the different pairs being too close to satisfy it.

Cleavage

The (010) cleavage of stilbite is very good and can readily be explained on consideration of Fig. 1(*a*) and (*b*). The planes $y/b=0,\frac{1}{2}$ cut a minimum number of Si–O–Si bonds. The values of 1·7 bonds per 100 Å^2 is the lowest found in zeolite structures (Meier, 1968). Moreover, the perfect cleavage must be related also to the very small number of bonds between the exchangeable cations and framework oxygen atoms.

The lamellar habit of stilbite can, of course, also be explained in a similar way.

Twinning

Stilbite crystals exhibit complex twins which show components with four different orientations, and also zones with fine sheaf-like intergrowth of uncertain significance [see Fig. 4(*a*)]. Bearing in mind that:

(*a*) stilbite is pseudo-orthorhombic,

(*b*) the morphology of the twins is the same as the untwinned crystals,

(*c*) the orientation of the optical indicatrix is almost the same in all components of the twins,

one can conclude for a pseudosymmetry twinning: the tetrahedral framework continues throughout the twins with only a slight distortion, so that in the different part the **a** direction is the same, and the [101] and **c** direction are interchanged, as shown in Fig. 4(*b*). As the sum of the different angles around the centre is no longer 180° [see Fig. 4(*c*)], a sheaf-like aggregate is necessary to 'close' the angle to 180°.

Relationship with other zeolites

It is not difficult to place stilbite in the heulandite group, because of the presence in its framework of rings of 4, 5, 6 and 8 tetrahedra and of the common presence of the characteristic polyhedral configuration quoted above. The exchangeable cations environment, however, is partially different.

If in all zeolites of this group the cations are situated within the cavities formed by intersecting channels, stilbite is the first zeolite in which a type of cation site is completely insulated from direct contact with the framework by a sphere of hydration. An example of this type has been said to occur only in levinite where a cation position has been found to be coordinated by 9 water atoms (Kerr & Williams, 1969). A similar coordination also occurs in chabazite where the calcium is surrounded by six water molecules and by one framework oxygen atom (Smith, Rinaldi & Dent Glasser, 1963). In stilbite a second type of cation position is

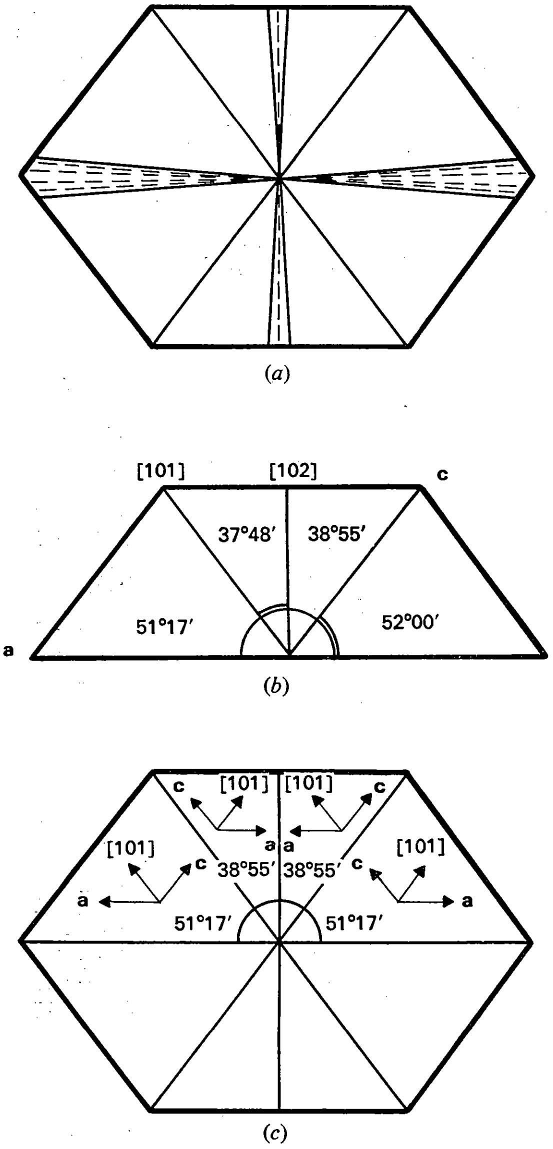


Fig. 4. (*a*) Schematic drawing of a stilbite twin; (*b*) angular values emphasizing the pseudo ortho-rhombicity of stilbite; (*c*) proposed interpretation of the twins shown in (*a*).

present; it is occupied only on a statistical basis (occupancy of 22 %) by sodium atoms. This cation could be said to be attached to the cavity wall, while the surface still exposed is coordinated by water molecules. This type of coordination is usual in zeolites and has been found, for instance in harmotome (Sadanaga, Marumo & Takéuchi, 1961), jugawaralite, and has also been noted in gismondite and levinite (Kerr & Williams, 1969).

Note added in proof: Since the acceptance of this paper another study on the refinement of stilbite has been published (Slaughter, 1970). Differences between the two papers are slight: Slaughter examines cation positions < 5 % occupancy; he suggests a different interpretation of the distribution of Si/Al atoms; temperature factors are slightly different.

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The Crystal Structure of L-Dopa Hydrochloride, 3-(3,4-Dihydroxyphenyl)-L-Alanine Hydrochloride, $C_9H_{12}O_4NCl$*

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The crystal structure of L-dopa hydrochloride. 3-(3,4-dihydroxyphenyl)-L-alanine hydrochloride, was determined from three-dimensional data collected manually with a General Electric XRD6 diffractometer using Cu $K\alpha$ radiation. The crystals are monoclinic, $P2_1$, with $a = 6{\cdot}261 \pm 0{\cdot}007$, $b = 5{\cdot}821 \pm 0{\cdot}001$, $c = 15{\cdot}646 \pm 0{\cdot}003$ Å, and $\beta = 112{\cdot}66 \pm 0{\cdot}02°$. The structure was refined to a conventional R value of 7·9%. Extensive intermolecular hydrogen bonding is present. The aromatic ring forms an angle of of 39·1° with the plane of the carboxyl group.

The compound 3-(3,4-dihydroxyphenyl)-L-alanine (L-dopa) (Fig. 1) has been used for the treatment of Parkinson's disease. Slowly increasing oral doses of L-dopa have been reported to induce at least partial improvement of some of the manifestations of Parkinson's disease, and in some cases the improvement has been dramatic (Cotzias, Papvasiliou & Gellene, 1969). Because of the interest in this compound as a promising therapeutic agent, the study of the crystal structure of the hydrochloride of this amino acid was undertaken.

Experimental

Crystals of the hydrochloride of L-dopa were obtained by the evaporation of a solution of L-dopa in concentrated hydrochloric acid. The L-dopa was obtained from Nutritional Biochemicals Corporation. The crystal was aligned with the unique b axis parallel to the φ axis of a General Electric XRD6 diffractometer single-crystal orienter. The space group was determined to be $P2_1$ by searching for reflections with the diffracto-

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*The opinions or assertions contained herein are the private views of the authors and are not to be construed as official or as reflecting the views of the Department of the Army or the Department of Defense.

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