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CRYSTAL STRUCTURE OF STILBITE

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ABSTRACT

Stilbite is monoclinic, $C2/m$ with unit cell $a=13.69$; $b=18.25$; $c=11.31$ Å, $\beta=128.2°$; $8Z=Na_{2.7}$, $Ca_{3.4}Mg_{0.2}(Al_{9.9}Si_{26.1}O_{72.0})\cdot 24.5H_2O$. The structure refined by the least squares and differential Fourier synthesis to $R=0.11$.

The framework of stilbite is pseudo-orthorhombic with 10-member rings and 8-member rings forming approximately normal channels parallel to a and pseudo-orthorhombic c respectively. Eight-member rings are parallel to the ab plane and of two types: equant and narrow elongate. The equant rings form a channel parallel to c at 128° to the 10-member ring channel. Elongate and equant rings alternate to form a restricted channel parallel to pseudo-orthorhombic c.

Unlike most related zeolites the Ca ions are near the middle of the channel surrounded by and bonded to eight water molecules but no framework oxygens.

There are five Na ion or Mg ion sites including the Ca ion site. Na ions are attached to one or two water molecules as well as framework oxygens. Aluminum substituted for silica is not well ordered and Na sites are nearly evenly occupied on several of the sites.

INTRODUCTION

The structure of the calcium-sodium zeolite stilbite was partially determined by Galli and Gottardi (1967). They determined the structure of the silica-alumina framework and the position of the calcium ions. Presented here is a refined structure of the framework with the determination of the calcium, sodium and water positions of stilbite.

Galli and Gottardi using film data, determined the structure of the framework of a stilbite of approximate composition $Na_2Ca_4[Al_{10}Si_{26}O_{72}]\cdot 28H_2O$. They did not determine the position of the sodium ions, water molecules and final temperature factors. At the time their paper was published we were collecting data on a stilbite. Subsequent analysis of our data confirmed Galli and Gottardi's framework and calcium position. Galli and Gottardi also suggested disordered substitution of aluminum in the silica tetrahedra. This analysis confirms their suggestion.

EXPERIMENTAL

The specimen used in this investigation was from a basalt from Nova Scotia. Stilbite crystals formed aggregated groups. The chemical analysis by Booth, Garret, and Blair Inc., Philadelphia, Pennsylvania, of crystals from which the structure was determined is given in Table 1. The chemical formula of the stilbite based on 72 oxygens in the anhydrous cell according to the chemical analysis is

$$Na_{6.08}K_{.02}Ca_{2.02}Mg_{.01}(Al_{10.38}Si_{25.62}O_{72})\cdot 20.38H_2O.$$

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TABLE 1. CHEMICAL ANALYSIS OF STILBITE

Oxide	Percent
SiO_2	56.44
Al_2O_3	19.40
CaO	4.15
K_2O	0.04
Na_2O	6.91
MgO	0.01
SrO	0.00
$H_2O(+)$	12.48
$H_2O(-)$	0.97

The approximate formula

$$Na_6Ca_2(Al_{10}Si_{26}O_{72})\cdot 20H_2O$$

was used in the initial structural solution. However as the refinement progressed the formula of the individual crystal used in the analysis approximated

$$Na_{2.7}Ca_{3.4}Mg_{0.2}(Al_{9.9}Si_{26.1}O_{72.0})\cdot 24.5H_2O.$$

The "ideal" formula for stilbite is

$$Na_2Ca_4(Al_{10}Si_{26}O_{72})\cdot 32H_2O.$$

Cell constants obtained from least-squares refinement employing the separation of $K_{\alpha 1}$, $K_{\alpha 2}$ reflections are as follows: monoclinic, $a=13.69\pm.01$, $b=18.25\pm.01$, $c=11.31\pm.02$ Å, and $\beta=128.2°\pm.2$. The space group determined from Weissenberg photographs and confirmed by refinement is $C2/m$.

The intensity data were collected on a Buerger-Supper diffractometer from a rectangular crystal measuring 0.04×0.07×0.12 mm. Lorentz-polarization factors were applied to the data but no absorption corrections were made. There were 1251 reflections measured and 1240 reflections used for refinement[1].

DETERMINATION OF THE STRUCTURE

The Framework. The atomic positions of the framework of the stilbite structure of Galli and Gottardi (1967) provided the initial coordinates. Refinement proceeded to a discrepancy index, R of 0.26. Addition of Ca and Na on the calcium site of Galli and Gottardi reduced R to 0.19. Refinement was done using differential Fourier synthesis programs written by Slaughter (1964) and the Busing, Martin, and Levy (1962) least squares refinement program. The final atomic coordinates were nearly identical using the two methods.

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[1] To obtain a copy of structure factor tables, order NAPS Document #00843 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for microfiche or $3.00 for photocopies, payable in advance to ASIS-NAPS.

TABLE 2. FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS[a]

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	Occupancy
Si, Al (1)	0.9828	0.1960	0.2421	0.003 Å	0.003 Å	0.003 Å	.88 Å^2	.66, .34
Si, Al (2)	.2646	.3093	.2610	.003	.004	.003	.77	.76, .24
Si, Al (3)	.1892	.0889	.4841	.003	.003	.003	.90	.73, .28
Si, Al (4)	.1110	.3168	.5004	.003	.003	.003	.75	.78, .23
Si, Al (5)	.0000	.2623	.0000	—	.005	—	1.27	.78, .24
O (1)	.9635	.2078	.0843	.009	.009	.008	1.48	1.0
O (2)	.1158	.3154	.1190	.007	.011	.010	1.33	1.0
O (3)	.0499	.2673	.3508	.011	.010	.010	2.05	1.0
O (4)	.0614	.1191	.3223	.012	.090	.007	1.80	1.0
O (5)	.2938	.2307	.3456	.012	.009	.008	1.66	1.0
O (6)	.3036	.3787	.3755	.011	.011	.012	1.78	1.0
O (7)	.3410	.3165	.1934	.011	.010	.009	1.55	1.0
O (8)	.3153	.1126	.5012	.013	.012	.009	1.88	1.0
O (9)	.1863	.0000	.4872	.012	—	.011	1.96	1.0
O (10)	.0000	.3509	.5000	—	.010	—	1.50	1.0
Ca, Na	.2806	.0000	.0959	.006	—	.004	2.3, 3.3	.84, .16
Na (1)	.4861	.0721	.9535	.040	.039	.057	3.3	.195
Na (2)	.126	.055	.725	.041	.028	.031	3.3	.03
Na (3)	.035	.035	.542	.044	.053	.060	3.3	.04
X[b]	.475	.056	.579	.045	.029	.072	3.3	.03
HOH (1)	.3337	.1241	.1038	.029	.013	.023	4.0	.82
HOH (2)	.1479	.0793	.1168	.016	.024	.028	4.3	.65
HOH (3)	.1007	.0000	.8385	.038	—	.029	3.9	.88
HOH (4)	.3668	.0000	.3554	.046	—	.024	4.1	.84
HOH (5)	.5130	.0000	.2472	.025	—	.046	4.1	.64
HOH (6)	.3281	.0209	.8960	.037	.056	.028	4.1	.41

[a] Coordinates from differential synthesis and least squares refinement, temperature factors and occupancy factors from differential synthesis refinement.

[b] See discussion for explanation.

Framework, Cations and Water Molecules. Cation and Water positions were found by successive Fourier, difference Fourier, and differential Fourier synthesis. Several water and sodium positions failed to refine by least squares because of low occupancy at some sites and occupancy of multiple overlapping sites. Therefore, all final automatic refinement was done by differential synthesis. The final atomic parameters and standard deviations are given in Table 2. Interatomic distances are listed in Table 3. The final value of R was 0.11. Observed and calculated structure factors are available from the author on request.

DISCUSSION OF THE STRUCTURE

The Tetrahedral Framework. The crystal structure of stilbite is characterized by large intersecting, relatively open channels of 10- and 8-member tetrahedral rings. The axis of the 10-member ring channels is parallel to *a*. Eight-member rings are of two types: open equant and narrow elongate. Both types of 8-member rings are parallel to the *ab*-plane, have mirror symmetry across the planes at $b=0$, 1/2, and alter-

TABLE 3. INTERATOMIC DISTANCES

Atom Pair	Distance in Å		Distance in Å
Si, Al(1)–O(1)	1.649	Si, Al(3)O(4)–O(8)	2.739
O(3)	1.629	O(4)–O(9)	2.681
O(4)	1.657	O(8)–O(9)	2.650
O(7)	1.674		
		Si, Al(4)O(3)–O(5)	2.701
Mean	1.652	O(3)–O(8)	2.683
		O(3)–O(10)	2.658
Si, Al(2)–O(2)	1.644	O(5)–O(8)	2.681
O(5)	1.631	O(5)–O(10)	2.674
O(6)	1.647	O(8)–O(10)	2.623
O(7)	1.638		
		Si, Al(5)O(1)–O(1)	2.710
Mean	1.640	O(1)–O(2)	2.691
		O(2)–O(2)	2.600
Si, Al(3)–O(4)	1.661		
O(8)	1.671	Ca, Na–HOH(1)	2.363
O(9)	1.627	HOH(2)	2.45±.10
O(9)	1.624	HOH(3)	2.385
		HOH(4)	2.394
Mean	1.645	HOH(5)	2.515
		HOH(6)	2.738
Si, Al(4)–O(3)	1.622	All Oxygens	≥4.23
O(5)	1.637		
O(8)	1.644	Na(1)– O(2)	2.601
O(10)	1.640	O(2)	2.328
		HOH(5)	2.630
Mean	1.636	HOH(6)	2.500
Si, Al(5)–O(1)	1.654	Na(2)– O(4)	2.56
O(1)	1.654	O(6)	2.25
O(2)	1.621	O(7)	2.46
O(2)	1.621	HOH(6)	2.59
Mean	1.638	Na(3)– O(6)	2.38
		O(9)	2.58
Si, Al(1)O(1)–O(3)	2.695	HOH(3)	2.95
O(1)–O(4)	2.685		
O(1)–O(7)	2.662	X– O(8)	2.06
O(3)–O(4)	2.739	O(10)	2.04
O(3)–O(7)	2.720	HOH(4)	2.24
O(4)–O(7)	2.679	HOH(5)	2.13
Si, Al(2)O(2)–O(5)	2.680	Ca, Na–Na(1)	4.223
O(2)–O(6)	2.674	Na(1)	3.801
O(2)–O(7)	2.648	Na(2)	3.481
O(5)–O(6)	2.715	Na(3)	4.995
O(5)–O(7)	2.684	X	3.250
O(6)–O(7)	2.663	X	4.470

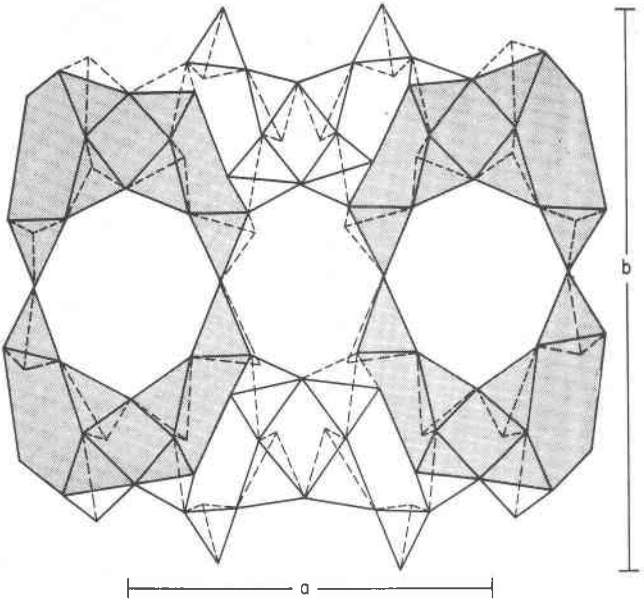

FIG. 1. Schematic representation of part of the silica-alumina framework of stilbite viewed parallel to $c \sin \beta$ of the monoclinic cell. Stippled area outlines the largest portion of the framework cage.

nate in the *a* direction. The 8-member ring tetrahedra are illustrated in Figure 1. The equant 8-member rings form a continuous channel whose axis is the *z*-axis and therefore make an angle of 128° with the axis of the 10-member ring channels. The planes of the 10-member rings of silica-alumina tetrahedra are approximately normal to *a*. Ten-member rings form an open channel parallel to *a*. The center of the channel is a zigzag line in the *ac* plane along the *x*-axis. The 10-member tetrahedra rings are illustrated in Figure 2. Figure 3 is a projection on the *ac* plane of the framework atoms of one half of the cell.

Aluminum Substitution. Galli and Gottardi (1967) found no evidence that there is aluminum substituting at silicon sites preferentially. We found some preferential substitution of aluminum for silicon but much less than in related zeolites.

The proportion of aluminum at each site is given in Table 2. The proportion of aluminum substituted for silicon was found by linear interpolation with the mean Si, Al-O distances of Table 3. Interpolation was was between bond distances 1.607 Å for an Si-O bond and 1.746 Å for an Al-O bond. Total aluminum atoms per cell computed from bond

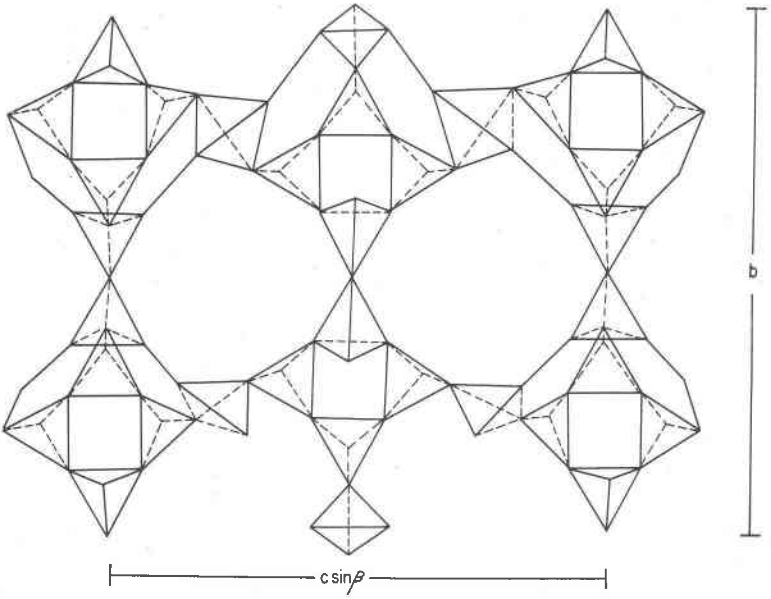

FIG. 2. Schematic representation of part of the silica-alumina framework viewed parallel to *a*.

distances was 9.8±0.3 (vs. 10.4 atoms by chemical analysis). The positive charges on all charge balancing cations totaled 9.6 to 9.9.

The tetrahedra nearest the mirror planes contain slightly more aluminum than those nearest the plane 1/4*y*.

The X Site. The *X* site (Table 2) is a possible cation site and is probably real. Fourier maps showed a spherical volume of positive electron density at the *X* site. The spherical volume of electron density was similar to each of the other low occupancy sites containing cations. Fourier maps and computed curvatures from differential synthesis showed displacement toward this site of part of the water molecules lying within bonding distances to ions at the site. The site also lies in the opening of an 8-member ring at an appropriate off-center position for a charge balancing cation.

However, distances from framework oxygen and water molecules are consistent with only one cation, Mg^{2+}. Attempts to force refinement to coordinates with longer bonds from cation to oxygens and waters failed.

If the coordinates of the *X* site and the bond distances around it are correct then the formula for the stilbite approximates

$$Na_{2.68}Ca_{3.36}Mg_{.24}Al_{9.88}Si_{25.12}O_{72}\cdot 24.5H_2O.$$

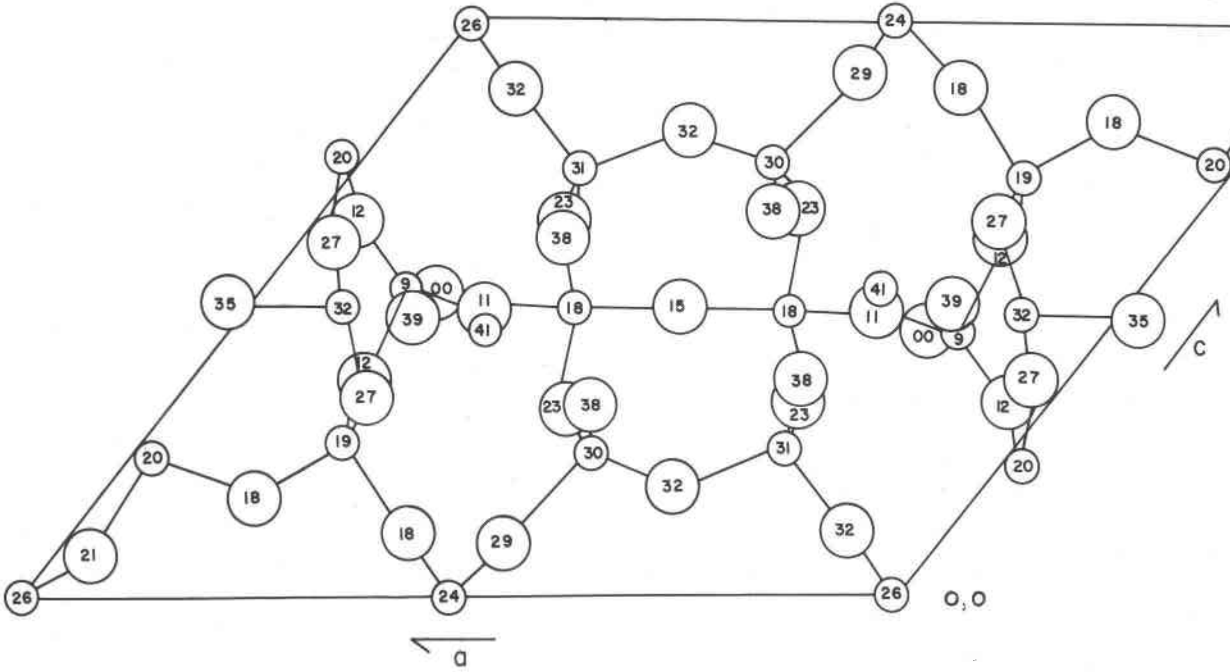

FIG. 3. Projection of silica-alumina framework on *ac* plane including atoms in lower half of the cell. Small circles are silicons; large circles are oxygens. Numbers in circles denote *y*-coordinates in hundreths.

If the X site is actually a Na site then the formula approximates

$$Na_{2.92}Ca_{3.36}Al_{9.64}Si_{25.36}O_{72}\cdot 24.5H_2O.$$

Cation-water-framework Relationships. All channel cavities and channel openings in the stilbite structure are occupied by cations.

The main cation site, the Ca, Na site is located in the center of the largest part of a relatively large cavity or cage in the silica-alumina framework. Each of the stippled areas of Figure 1 schematically defines the largest portion of a cage. The other half of the cage is the center portion of Figure 1 inverted and placed over the stippled area. The largest portion of the cavity contains the equant 8-member ring and the smaller half of the cage contains the narrow, elongate 8-member ring.

The positions of the site Na(1) are in the main 10-member ring channel parallel to a, but above and below the mirror plane (Figure 4). The largest portion of the main channel zig-zags along a and Ca, Na and Na(1) lie about on the main channel center line.

The Na(2) site is on the opposite side of the large cage from the Ca, Na site and lies just inside a small cage formed by the elongate 8-member ring. The Na(3) site is almost centered in the same cage as the Na(2) site. Both Na(2) and Na(3) lie above and below the mirror. The X site is near the center of the equant 8-member ring.

All four cation sites lie on a line parallel to the pseudoorthorhombic c.

Each Ca, Na site is surrounded by eight water molecules (Figure 4). The water molecules surrounding the Ca, Na position constitute all waters found in the structure and the other cations share these waters with the Ca, Na ions. Although the eight water sites are not completely filled under room humidity conditions, occupancy of these sites is probably more nearly complete when the mineral is saturated with water or when the Ca, Na site is filled with Ca only. With all eight sites filled the cell would contain 32 H_2O. With Ca filling the Ca, Na site under room humidity conditions there would be about 28 H_2O per cell.

The effect of sharing of waters among cations on partially occupied sites causes displacement of the waters around the positions the waters would occupy if Ca were the only cation. The displacement was illustrated in the Fourier maps by a smearing of the electron density at the water sites. The coordinates of the water molecules and bond distances between cation and water molecules are therefore approximate and coordinates of each H_2O represent the best single site.

The Na(1), Na(2), Na(3) and X sites have a maximum occupancy of 0.25 each because of closeness of the sites to twofold axes and mirror planes. More than 0.25 occupancy of sites would place symetrically related cations closer than permitted for a stable configuration. The oc-

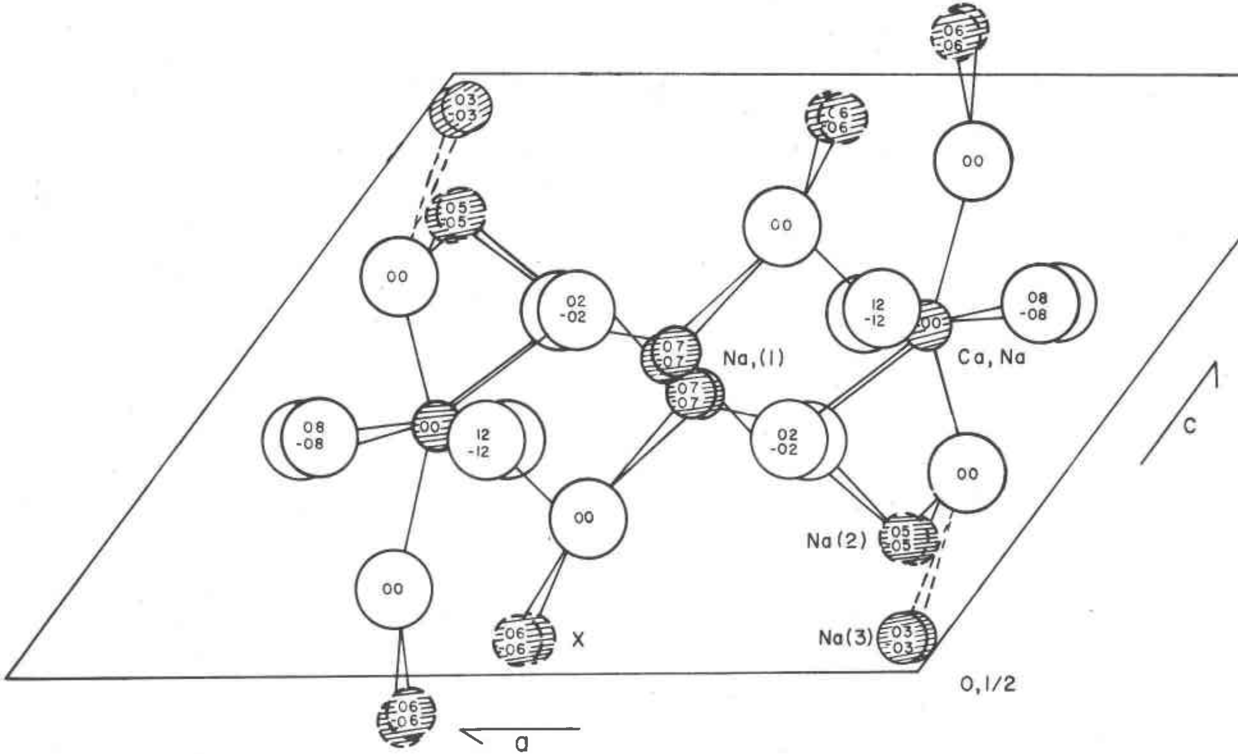

FIG. 4. Projection of cations and water molecules on *ac* plane. Small circles are cations; large circles are water molecules Numbers in circles denote *y*-coordinates in hundreths. The projection is displaced 1/2 along *c* from the projection of Figure 3.

cupancy of the X site is further limited because of its short Ca, Na distance to cells where Ca is not present. Therefore, the X site cannot have an occupancy in excess of 0.04. The Na(2) site is also not likely to be occupied when Ca is in the Ca, Na position. There should be an effective restriction of 0.04 occupancy for this site also.

The maximum occupancy of the subsidiary cation sites are summarized as follows:

Na(1)	−0.25
Na(2)	−0.04
Na(3)	−0.25
X	−0.04

Although Na(1) site occupancy of 0.2 approaches the maximum of 0.25, the Na(3) site has not more than 0.04 occupancy, even though cation-cation repulsion is lower at Na(3) than at Na(1). The low occupancy at Na(3) seems to be the result of a small attractive potential because there are no tightly bound water molecules surrounding the site. There are at Na(3) three bonds at larger distances than bonds to Na(1), Na(2) and X which have four bonds each. Ions at Na(1), Na(2), and X are bound to four waters and oxygens (Table 3). Ions at Na(3) are bound to two oxygens and very loosely bound to one water.

CONCLUSION

Stilbite differs from other related zeolites, heulandite, clinoptiloite, epistilbite, dachiardite, ferrierite, and brewsterite in that stilbite has a relatively large cage formed by the silica aluminum framework. The center of the largest portion of the cage is occupied by Ca ions completely surrounded by water molecules rather than the Ca being directly bonded to one or more framework oxygens.

Preliminary calculations of cation-water, cation-framework bonding in these related zeolites suggest that one of the important parameters in determining which zeolite will form in a given environment is the strength of cation-water bond coupled with the activity of water. Differences in the structure of the framework seem to be of secondary importance. Stilbite seems to require relatively high activity of water for stability.

We are now beginning systematic calculations of cation-water and cation-framework bonding approximations in the rockforming zeolites with the hope that we can answer some of the puzzling questions about their structure and stability.

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