

The crystal structure of gottardiite, a new natural zeolite

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Abstract: Gottardiite is a new high-silica zeolite found in the Jurassic dolerites of Mt. Adamson (Victoria Land, Antarctica). Its unit-cell content is: $\text{Na}_{2.5}\text{K}_{0.2}\text{Mg}_{3.1}\text{Ca}_{4.9}\text{Al}_{18.8}\text{Si}_{117.2}\text{O}_{272} \cdot 93 \text{H}_2\text{O}$. The mineral is orthorhombic with $a = 13.698(2)$, $b = 25.213(3)$, $c = 22.660(2)$ Å, topological symmetry Fmmm and real symmetry Cmca. In the Fmmm symmetry there are oxygens on centres of symmetry, which cause energetically unfavourable T-O-T angles of 180° ; in the Cmca symmetry the sets of $\bar{1}$, on which these oxygens lie, disappear. The topology of gottardiite, which has not been found in other natural zeolites, is the same as that of synthetic zeolite NU-87; the latter, however, is characterized by a monoclinic symmetry $\text{P}2_1/c$ ($a = 14.32$, $b = 22.38$, $c = 25.09$ Å, $\beta = 151.5^\circ$). The framework of gottardiite can be described by the polyhedral units $5^4 6^2$ and 5^4 . These units developing along [010] give rise to chains which, sharing edges with other analogous chains, form impermeable sheets parallel to (001). Each sheet is bonded to other analogous sheets through 4-rings of tetrahedra between, and parallel to the sheets. A 2-D channel system parallel to (001) is present in gottardiite. Straight 10-ring channels run parallel to [100], whereas 12-ring channels "snake" in the [010] direction. 10-ring and 12-ring channels are connected through 10-ring windows. The ion sites localized in the channels all have weak electron density and large distances (> 2.7 Å) from framework oxygens. An enrichment in Al in the tetrahedra of 4-rings can be envisaged.

Key-words: gottardiite, zeolite, crystal structure.

1. Introduction

Synthetic aluminosilicate zeolites are extensively used in many industrial processes; in the petrochemical industry in particular, they are mainly used as catalysts. Medium-large pore materials (with intersecting channels delimited by 10-ring and/or 12-ring windows) are particularly suited to processing quite large molecules, such as the aromatic ones.

Gottardi & Galli (1985) and Pluth & Smith (1990) clearly demonstrated the fruitful symbiosis among mineralogists, crystal chemists, industrial scientists and engineers in zeolite science. The crystal structures of faujasite (Bergerhoff *et al.*, 1958) and mordenite (Meier, 1961) were resolved many years before their synthetic analogues became important in the chemical industry; the dis-

covery and determination of the crystal structure of mazzite demonstrated that the proposed framework of its synthetic counterpart, zeolite omega, was wrong (Galli, 1974). Recently, Pluth & Smith (1990) determined the crystal structure of boggsite, a new high-silica natural zeolite without a synthetic counterpart, which is very interesting due to the presence of a 3-D channel system with 10-ring and 12-ring windows. Its prospective use as a molecular sieve and catalyst is therefore extremely promising. Tschernichite, the natural counterpart of the synthetic zeolite Beta, has recently been found, in close association with boggsite, both in basalts near Goble, Oregon (Smith *et al.*, 1993) and in dolerites of Mt. Adamson (Victoria Land, Antarctica) (Galli *et al.*, 1995). Zeolite Beta and tschernichite are interpreted as the intergrowth of two distinct but close-

ly related polymorphs, both with 3-D mutually intersecting 12-ring channel systems. The occurrence of tschernichite is important because it suggests that the Beta structure type may be synthesized with a lower Si/Al ratio (Si/Al ~ 3.0) than synthetic Beta (Si/Al ~ 10), and in absence of an organic molecule acting as a template. Moreover, single-crystal X-ray data on a crystal from Antarctica suggest it is possible to clarify the problems still related to the crystal structure of Beta-type zeolites. It is worth noting that the dimensions of natural zeolite crystals are usually large enough for single crystal study, whereas this is rarely true for synthetic zeolites.

Recently, Galli *et al.* (submitted) described the new natural zeolite gottardiite (the new mineral and its name have been recently approved by the IMA NMMN commission) found, in close association with boggsite and tschernichite, in the Jurassic dolerites of Mt. Adamson (Northern Victoria Land, Antarctica); its chemical formula is reported in Table 1. The framework topology of gottardiite is the same as that of the synthetic zeolite

NU-87 (Shannon *et al.*, 1991), even if the two phases have different space groups: Cmca ($a = 13.698$, $b = 25.213$, $c = 22.660$ Å) for gottardiite and $P2_1/c$ ($a = 14.324$, $b = 22.376$, $c = 25.092$, $\beta = 151.515^\circ$) for NU-87 or $P2_1/b$ ($a = 14.324$, $b = 25.092$, $c = 22.376$, $\gamma = 151.515^\circ$) for NU-87 with axes oriented as in gottardiite.

2. Structure determination

A single crystal from the type locality (Mt. Adamson, Northern Victoria Land, Antarctica), measuring 0.14 mm along a , 0.12 mm along b and 0.02 mm along c , was used in the structural analysis.

Rotating [001] and Weissenberg (hk0) photographs indicated an orthorhombic symmetry with $a = 6.86$, $b = 12.60$, $c = 22.71$ Å. These parameters, however, did not fit all the peaks of the X-ray diffraction pattern obtained by a Gandolfi camera; this pattern can be completely indexed only if cell parameters a and b are doubled. The crystal was then mounted on a Siemens four-circle diffractometer, using a rotating anode X-ray gener-

Table 1. Chemical, experimental and refinement data for gottardiite.

Chemical formula ^a :	
(Na _{2.53} K _{0.17} Mg _{3.13} Ca _{4.84} Sr _{0.04} Ba _{0.02})Σ = 10.73(Fe _{0.13} Al _{18.75} Si _{117.17})Σ = 136.05O ₂₇₂ ·92.80 H ₂ O	
Unit cell parameters (Å)	$a = 13.698(2)$, $b = 25.213(3)$, $c = 22.660(2)$
Cell volume (Å ³)	$V = 7827(2)$
Dimensions of the crystal (mm)	$0.14 \times 0.12 \times 0.02$
Instrument	Siemens XP-18RA
Operating conditions	40 kV 150 mA
Radiation	Mo K α
Monochromator	graphite crystal
Scan type	ω
Scan width	1.2°
Maximum 2θ	56°
Unique reflections	3294
Refinement space group	Cmca
Refls. used in the refinement ($I > 4\sigma(I)$)	2326
$R\%$ ^b	11.95
$R_w\%$ ^c	9.68
N ^o of e ⁻ in extraframework cation sites:	
– chemical analysis	910
– structure refinement	534

^a Electron microprobe analysis; H₂O content from thermal gravimetric analysis.

$$^b R\% = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100$$

$$^c R_w\% = \frac{\sum \sqrt{w} (|F_o| - |F_c|)}{\sum \sqrt{w} |F_o|} \times 100, \quad w = \frac{k}{\sigma^2(F_o)}$$

ator (MoK α radiation). Refinement of unit cell parameters using 43 diffractions confirmed the orthogonal symmetry, with $a = 13.698$, $b = 25.213$, $c = 22.660$ Å. A data collection in the $4-25^\circ 2\theta$ range indicated a C-centered lattice; intensities were therefore collected with this lattice in the $4-56^\circ 2\theta$ range. Table 1 reports the unit cell parameters, and summarizes the experimental conditions used.

Systematic absences indicated Cmca and C2ca as possible space groups; centricity tests suggested the centrosymmetric one as the more probable. Direct methods in the centric space group, using

SHELX-86 (Sheldrick, 1986), gave a partially correct model, nevertheless clearly indicating a pentasil-type structure.

A comparison of the framework topology of synthetic zeolite NU-87 (Shannon *et al.*, 1991) (whose pseudoorthorhombic parameters calculated from the monoclinic cell: $a = 13.663$, $b = 25.092$, $c = 22.376$ Å, $\gamma = 90.37^\circ$, are very similar to those of gottardiite) with that resulting from direct methods, confirmed the same topology for both phases. This model gave the starting parameters of the framework for structural refinement, which was carried out using a combination of

Table 2. Atomic coordinates, occupancy and temperature factors for gottardiite.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>Occ.</i>	<i>U11</i>	<i>U22</i>	<i>U33</i>	<i>U23</i>	<i>U13</i>	<i>U12</i>	<i>Beq</i> *
T1	.0000	.0804(2)	.1973(3)	1.0	.013(3)	.013(3)	.019(3)	-.002(2)	.000	.000	1.18
T2	.0000	.1784(2)	.2828(3)	1.0	.014(3)	.021(3)	.021(3)	-.004(2)	.000	.000	1.47
T3	.0000	.2884(2)	.2204(3)	1.0	.021(4)	.015(3)	.017(3)	-.003(2)	.000	.000	1.39
T4	.0000	.3841(3)	.3023(3)	1.0	.012(3)	.022(3)	.017(3)	-.007(3)	.000	.000	1.34
T5	.0000	.4818(2)	.2235(3)	1.0	.030(4)	.019(3)	.015(3)	.004(2)	.000	.000	1.68
T6	.2102(3)	.0023(2)	.3160(2)	1.0	.020(2)	.030(2)	.024(2)	.004(3)	-.005(2)	.001(3)	1.95
T7	.1934(5)	.0978(1)	.1253(2)	1.0	.014(3)	.019(3)	.018(3)	-.003(2)	.006(2)	-.005(2)	1.34
T8	.2122(4)	.1948(2)	.3174(2)	1.0	.011(3)	.014(2)	.017(2)	.001(2)	-.004(2)	.001(2)	1.11
T9	.2143(4)	.3111(2)	.1846(2)	1.0	.018(3)	.012(2)	.020(3)	.001(2)	.001(2)	-.005(2)	1.32
T10	.1873(5)	.4049(1)	.3752(2)	1.0	.015(3)	.015(2)	.015(3)	-.004(2)	.004(2)	.002(2)	1.18
T11	.1151(3)	.0634(1)	.0009(2)	1.0	.025(2)	.019(2)	.014(1)	-.004(2)	.005(3)	-.007(1)	1.53
O1	.0000	.0208(6)	.2214(9)	1.0	.088(16)	.015(8)	.046(11)	-.004(8)	.000	.000	3.92
O2	.0969(17)	.0897(7)	.1594(12)	1.0	.025(9)	.084(12)	.113(19)	.009(11)	.049(11)	.002(9)	5.84
O3	.0000	.1213(7)	.2499(9)	1.0	.075(14)	.041(11)	.027(9)	-.015(9)	.000	.000	3.76
O4	.0955(11)	.1833(6)	.3238(6)	1.0	.020(8)	.059(8)	.021(6)	-.012(5)	.001(6)	-.001(6)	2.63
O5	.0000	.2249(6)	.2361(9)	1.0	.046(11)	.012(7)	.060(14)	-.014(8)	.000	.000	3.11
O6	.0928(11)	.3040(6)	.1810(6)	1.0	.017(8)	.054(8)	.038(8)	.010(6)	.007(6)	-.008(6)	2.87
O7	.0000	.3225(6)	.2802(7)	1.0	.055(12)	.017(8)	.024(9)	-.003(7)	.000	.000	2.53
O8	.0840(19)	.3950(8)	.3443(10)	1.0	.050(13)	.110(15)	.082(14)	-.041(10)	-.044(11)	-.001(9)	6.37
O9	.0000	.4225(7)	.2462(10)	1.0	.205(31)	.008(8)	.036(11)	-.016(9)	.000	.000	6.55
O10	.0928(8)	.4920(7)	.1818(5)	1.0	.033(6)	.076(11)	.033(6)	-.006(8)	.010(5)	.003(8)	3.74
O11	.2280(11)	.1576(5)	.1350(7)	1.0	.027(7)	.038(7)	.036(8)	-.006(5)	-.007(6)	-.002(6)	2.66
O12	.2242(11)	.0598(5)	.3504(7)	1.0	.042(8)	.027(6)	.068(10)	.005(7)	-.009(8)	-.003(6)	3.61
O13	.2381(14)	.4586(5)	.3559(8)	1.0	.094(14)	.032(7)	.098(13)	.014(8)	.073(11)	-.012(8)	5.90
O14	.1754(12)	.0893(6)	.0555(6)	1.0	.026(7)	.079(9)	.009(6)	-.014(6)	-.001(5)	-.010(7)	3.00
O15	.2329(12)	.2564(5)	.3357(5)	1.0	.055(11)	.028(6)	.037(6)	-.004(6)	.003(7)	-.015(7)	3.16
O16	.2500	.1829(6)	.2500	1.0	.037(10)	.031(9)	.009(8)	.000	.004(8)	.000	2.03
O17	.2381(10)	.3553(5)	.1332(6)	1.0	.049(10)	.036(6)	.021(6)	.012(5)	-.016(6)	-.031(6)	2.79
O18	.2500	.3290(6)	.2500	1.0	.029(9)	.017(7)	.026(9)	.000	.003(8)	.000	1.89
O19	.2500	.0050(16)	.2500	1.0	.033(9)	.146(22)	.036(9)	.000	.003(8)	.000	5.66
O20	.0000	.0807(5)	.0048(10)	1.0	.036(8)	.029(7)	.042(10)	-.003(10)	.000	.000	2.82
O21	.1276(10)	.0000	.0000	1.0	.033(8)	.021(7)	.070(10)	-.005(10)	.000	.000	3.26
O22	.1627(19)	.4084(6)	.4406(8)	1.0	.102(17)	.058(9)	.043(10)	.004(7)	.025(10)	.050(10)	5.34
X1	.000	.386(1)	.999(2)	.48(3)							1.7(5)
X2	.000	.183(1)	.430(1)	.77(5)							4.6(6)
X3	.000	.263(2)	.996(3)	.45(3)							3.9(8)
X4	.000	.081(2)	.404(2)	.64(6)							6.5(12)
X5	.067(4)	.281(2)	.421(2)	.59(4)							9.1(11)
X6	.121(4)	.458(2)	.019(2)	.24(3)							3.9(13)
X7	.000	.192(3)	.071(3)	.57(7)							11.0(23)
X8	.151(3)	.349(2)	.994(3)	.40(3)							6.6(11)
X9	.000	.390(2)	.103(3)	.63(8)							8.9(16)
X10	.120(4)	.268(2)	.558(2)	.56(4)							9.4(13)
X11	.193(6)	.271(3)	.473(4)	.36(4)							12.3(20)
X12	.000	.301(3)	.064(3)	.51(8)							8.9(22)

* $Beq = 8/3 \pi^2 (U11 + U22 + U33)$ Biso for all extraframework sites.

three-dimensional electron density synthesis and full matrix least-square techniques. Twelve extra-framework sites were located in the channels; they account only for 59% of the electrons obtained from chemical analysis. The occupancies and distances from the framework of these sites precluded any chemical interpretation, as will be discussed later.

Neutral scattering factors were used for framework atoms; a scattering curve $\text{Si}_{0.85}\text{Al}_{0.15}$ was used for all T atoms; extraframework site occupancies were refined using the neutral oxygen curve. Extinction and anomalous scattering corrections were not applied. The intensities were corrected on the basis of shape of the crystal using SHELX-76 (Sheldrick, 1976). As expected, considering the small size of crystal used and the low absorption factor value ($\mu = 6.85$), no appreciable differences were found with the results of the refinement performed with the intensities not corrected for absorption: hence the discussion of the crystal structure concerns the refinement carried out without absorption correction.

At the end of structure refinement (framework atoms refined with anisotropic displacement parameters, and extraframework atoms with isotropic ones), the R and R_w indices were 11.95 and 9.68 respectively. These values are high, but high error indices are often found in zeolites with large channel systems and poorly defined extraframework sites.

Positional and thermal parameters are reported in Table 2, and bond distances for framework atoms in Table 3. A list of observed and calculated

structure factors can be obtained from the authors upon request.

3. Topology

As said before, gottardiite has the same topology as synthetic zeolite NU-87 (Shannon *et al.*, 1991) (structure-type code NES, as assigned by the IZA Structure Commission, Meier & Olson, 1992). The framework can be described by the polyhedral subunit 5^26^2 **pes** (penta-edge-stellated-tetrahedron) found in boggsite and in many other pentasils (Pluth & Smith, 1990). Two **pes** units share a 6-ring to give a 5^46^2 unit, which is also present in boggsite (**eun** unit after Pluth & Smith, 1990). Two **eun** units are linked together by sharing three of their edges. This more complex unit is related by an inversion center, through T-O-T bridges, to another analogous unit. In this manner a 5^4 poly-

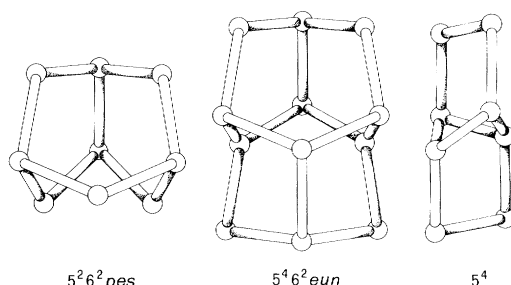


Fig. 1. Polyhedra subunits in gottardiite.

Table 3. Gottardiite framework interatomic distances (Å).

T1-O1	1.60(2)	T2-O3	1.62(2)	T3-O5	1.64(2)	T4-O7	1.63(2)
O2	1.60(2) x2	O4	1.61(2) x2	O6	1.60(2) x2	O8	1.52(2) x2
O3	1.58(2)	O5	1.58(2)	O7	1.61(2)	O9	1.60(2)
mean	1.60	mean	1.61	mean	1.61	mean	1.57
T5-O1	1.59(2)	T6-O10	1.63(1)	T7-O2	1.55(2)	T8-O4	1.63(2)
O9	1.58(2)	O12	1.66(1)	O11	1.60(1)	O11	1.65(1)
O10	1.61(1) x2	O13	1.59(2)	O12	1.58(2)	O15	1.63(1)
mean	1.60	O19	1.59(1)	O14	1.62(1)	O16	1.64(1)
mean	1.60	mean	1.62	mean	1.59	mean	1.64
T9-O6	1.68(2)	T10-O8	1.60(3)	T11-O14	1.63(2)		
-O15	1.62(1)	-O13	1.58(2)	-O20	1.64(1)		
-O17	1.65(1)	-O17	1.63(1)	-O21	1.61(1)		
-O18	1.63(1)	-O22	1.52(2)	-O22	1.67(2)		
mean	1.65	mean	1.58	mean	1.64		

Fig. 2. Projection of gottardiite framework along the [001] direction. 12-ring windows are shown by heavy full lines; 10-ring windows by heavy dashed lines; 4-rings between, and parallel to, the sheets by dotted lines.

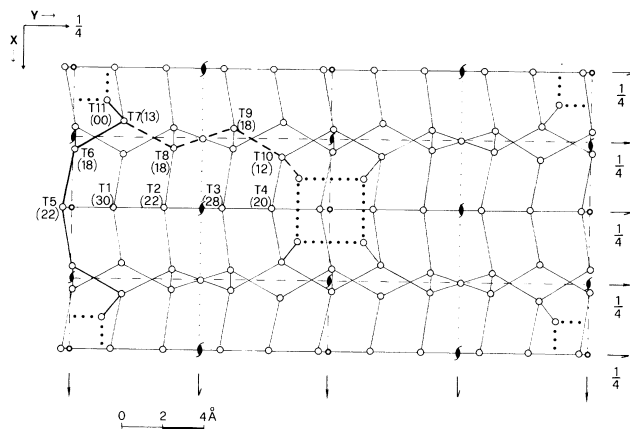
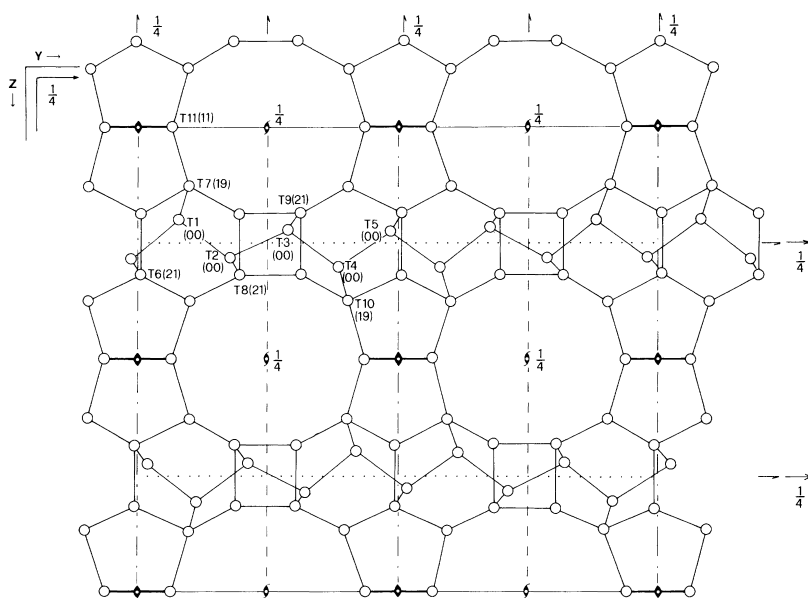


Fig. 3. Projection of gottardiite framework along the [100] direction. x axis down.



hedral subunit is generated (see Fig. 1). As a consequence, a chain $5^46^2 - 5^46^2 - 5^4 - 5^46^2 - 5^46^2 - 5^4 \dots$ of units develops in the [010] direction. This chain shares two edges each **eun**, and one edge each 5^4 unit, with analogous chains related by mirror planes parallel to (100). In such a way, impermeable sheets parallel to (001) are formed (see Fig. 2). Each sheet is bonded to other analogous sheets through 4-rings of tetrahedra between, and parallel to the sheets. The structure can therefore be seen as a pillared framework. The topological symmetry of this framework is Fmmm.

4. Channel system

The crystal structure of gottardiite is characterized by a two-dimensional channel system parallel to the *ab* plane. Straight 10-ring channels run parallel to [100] (see Fig. 3), and through 10-ring windows link 12-ring channels parallel to [010] (see Fig. 4). These 12-ring channels are interrupted every 25 Å (the value of parameter *b*) by the 4-rings of tetrahedra inserted between the sheets (see Fig. 2). Therefore, these channels are not straight but “snake” in the [010] direction. The 10-ring channel has a free diameter of about $4.8 \times$

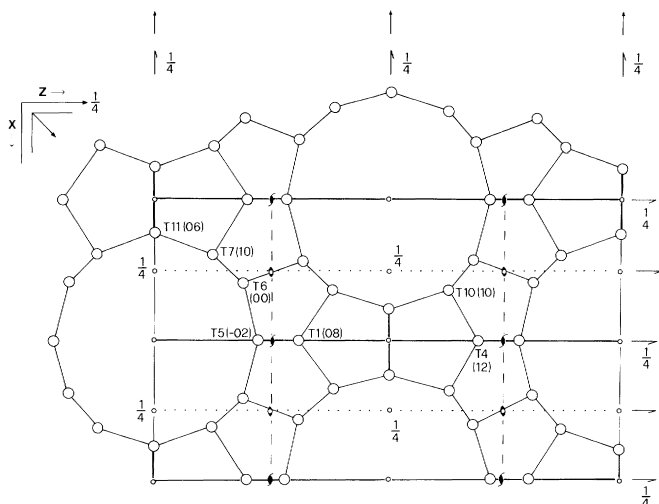


Fig. 4. Projection of gottardiite framework along the [010] direction, y axis down.

5.8 Å, and the 12-ring channel, nearly circular, a free diameter of about 6.3 Å.

The ac projection of gottardiite shows similarities with the ca projection of boggsite. In both structures, chains of 5-rings run parallel to the shortest axis (axis a in gottardiite, axis c in boggsite, both ~13 Å). These chains are linked through 6-rings in boggsite, and through double 5-rings in gottardiite. Consequently, the 10-rings of boggsite become 12-rings in gottardiite (see Fig. 4), and the parameter orthogonal to the 5-ring chains grows longer by about 2 Å.

5. Real symmetry of the framework

As said before, the topological symmetry of gottardiite is Fmmm, whereas its real symmetry reduces to Cmca. In the Fmmm space group there are five non-symmetry-related sites on centers of inversion. In the topological symmetry of gottardiite, oxygen atoms O5 (with coordinates 0, 1/4, 1/4) and O19 (with coordinates 1/4, 0, 1/4) lie on two of these $\bar{1}$, both with site symmetry 2/m. In the Cmca space group, the two inversion centers on which O5 and O19 lie disappear, whereas the other three remain. O5 is now on a mirror plane, O19 on a diad. Alberti (1986) showed that, in all natural zeolites where there are framework oxygens on centers of inversion in the topological symmetry, the real symmetry is lower than the topological one, and the centers of inversion on which the oxygen atoms lie disappear. This was attributed by Alberti (1986) to the disappearance of the energetically unfavourable T-O-T angles of

180° in the change of symmetry. The lowering of symmetry from the topological Fmmm to the real Cmca is therefore in agreement with this interpretation.

Gottardiite is characterized by a very high Si/Al ratio (~6.2), the highest value found so far in natural zeolites. The high errors of the T-O distances found in gottardiite preclude any reliable scheme of (Si,Al) distribution in the tetrahedral sites. It should be noted, however, that the largest tetrahedra are those of the 4-rings. An enrichment in Al-content in the tetrahedra of the 4-rings was found in the other natural pentasils: mordenite, dachiardite, and epistilbite. Also in boggsite one of the two 4-rings seems to accommodate a higher content of Al. These results could strengthen the hypothesis that, in gottardiite as well, there is an enrichment of Al in the tetrahedra of the 4-rings.

It is to be noted that both cations and oxygens of the framework have very high displacement parameters, as also found in boggsite (Pluth & Smith, 1990). It is impossible to establish whether this is really dynamic disorder, or a consequence of static disorder.

6. Extraframework ions

Twelve extraframework sites have been localized; they are distributed on the whole channel space and are characterized by weak electron densities and by distances from framework oxygens greater than 2.7 Å. The partial occupancies of all ion sites and their reciprocal distances prevent an unambiguous distinction between cation and water mole-

cule sites. The obvious conclusion is that only a weak interaction exists between framework and extraframework atoms.

Acknowledgements: C.N.R., MURST and P.N.R.A. (ENEA 3.1.1) are acknowledged for financial support. The CIGS of Modena University is also acknowledged for the assistance in the X-ray data collection.

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Received 22 March 1995

Accepted 7 September 1995