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CRYSTAL STRUCTURE REFINEMENT OF MAZZITE**

RIASSUNTO. — La mazzite, $\text{Na}_{0.90.2}\text{K}_{2.0}\text{Ca}_{1.4}\text{Mg}_{2.1}[\text{Al}_{10.0}\text{Si}_{20.0}\text{O}_{72}]\cdot 28\text{H}_2\text{O}$, probabile corrispondente naturale della zeolite Ω , cristallizza nel sistema esagonale con $a = 18,392$ e $c = 7,646$ Å. La sua struttura è stata raffinata nel gruppo spaziale $P6_3/mmc$ fino ad un $R = 0,049$ per i 681 riflessi osservati. L'impalcatura è caratterizzata dalla presenza di gabbie tipo gmelinite che si sovrappongono dando luogo a colonne parallele a c . Queste, sfasate di $c/2$ per la presenza di uno slittopiano, sono legate lateralmente tra di loro e delimitano due tipi di canali, pure paralleli a c . I cationi scambiabili sono distribuiti in tre posizioni diverse: il Mg^{++} , completamente circondato da acqua, è posto al centro delle cavità tipo gmelinite; gli ioni (K^+ , Na^+ , Ca^{++}), legati sia ad ossigeni dell'impalcatura sia a molecole d'acqua, si trovano nelle cavità tra le gabbie; il Ca^{++} completamente circondato da molecole d'acqua, si trova al centro dei grandi canali delimitati da anelli di 12 tetraedri.

ABSTRACT. — Mazzite, $\text{Na}_{0.90.2}\text{K}_{2.0}\text{Ca}_{1.4}\text{Mg}_{2.1}[\text{Al}_{10.0}\text{Si}_{20.0}\text{O}_{72}]\cdot 28\text{H}_2\text{O}$, probably the natural counterpart of the synthetic zeolite Ω , crystallizes in the hexagonal system with $a = 18.392$ and $c = 7.646$ Å. Its crystal structure was refined in the space group $P6_3/mmc$ to a residual R of 0.049 for the 681 observed reflections. The aluminosilicate framework consists of gmelinite-type cages superimposed to form columns parallel to c . The columns, shifted by $c/2$ in accord with a c glide plane, are cross-linked to form two different types of channels parallel to c . The exchangeable cations are distributed into three positions: Mg^{++} is completely surrounded by water molecules in the gmelinite-type cages; (K^+ , Na^+ , Ca^{++}) ions are coordinated both to framework oxygens and water molecules between the cages; and Ca^{++} is completely surrounded by water molecules in the middle of the largest channels formed by rings of 12-tetrahedra.

Introduction

The zeolite, mazzite described as a new mineral by GALLI et al. (1974), is closely related to the synthetic molecular sieve Ω (UNION CARBIDE Co., 1967); they probably have the same framework.

The present study was undertaken to determine the details of the crystal structure of mazzite, and to compare it with the structure proposed by BARRER and VILLIGER (1969) for molecular sieve Ω . A preliminary report on the structure determination was published elsewhere (GALLI, 1974). The crystal structure of mazzite dehydrated at 600°C has been recently described (RINALDI et al., 1975).

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Experimental

A regular hexagonal prism, *ca* 0.6 mm long and 0.04 mm wide, was removed from the holotype of GALLI et al. (1974) from Mont Semiol, Montbrison, Loire, France, the original locality for offretite. It was mounted parallel to the elongation (*c*-axis). Unit cell dimensions obtained with a 4-circle automatic diffractometer agree with those accurately determined by GALLI et al. (1974) from powder diffractometry:

$$a = 18.392 \pm 0.008, \quad c = 7.646 \pm 0.002 \text{ \AA}$$

The systematically absent reflections (1 odd in $hh\bar{2}hl$) indicate $P6_3/mmc$, $P\bar{6}2c$ or $P6_3mc$ as possible space-groups.

Chemical analysis from new electron probe data (RINALDI et al., 1975) yielded a unit cell content of:



Intensity data were collected with a Picker FACS-1 automatic four-circle diffractometer of the Department of the Geophysical Sciences of the University of

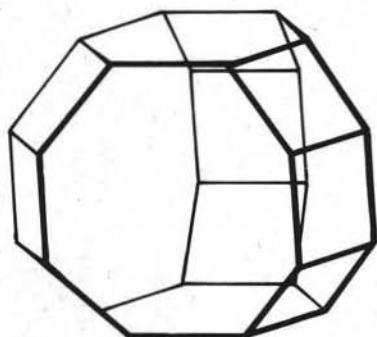


Fig. 1. — Structural scheme for the « gmelinite-type » cage. T atoms lie at the intersections and the O-atoms near the mid-points of each line.

Chicago with ϑ - 2ϑ scans (1° min^{-1}) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Four sets of equivalent diffraction ($\sin \vartheta / \lambda_{\text{max}} = 0.562$) were averaged to 759 independent reflections, of which 78 were considered to be unobservable, having $F_0 \leq 2\sigma_{F_0}$. Data processing was carried out in the manner described by RINALDI et al. (1975) to yield $|F_0|$ and $\sigma_{|F_0|}$. No correction for absorption was applied because of the low absorption coefficient and the small dimensions of the crystal.

Some difficulties were experienced during data collection due to instability of the intensities of the standard diffractions. This problem was overcome by applying at the free end of the crystal a second drop of epoxy resin, similar to that used to fix it on the side of the goniometer head. Perhaps water molecules were moving

in response to changes of relative humidity and the epoxy sealed the one-dimensional channel system. The structure was solved starting from the « gmelinite-type » cage (Fig. 1) which was assumed by BARRER and VILLIGER (1969) to be part of the structure of zeolite Ω . Space group $P6_3/mmc$ requires that the cages be staggered by $c/2$, whereas BARRER and VILLIGER (1969) placed all of them at the same height. Refinement of F's was carried out with a modified ORFLS full-matrix least-squares

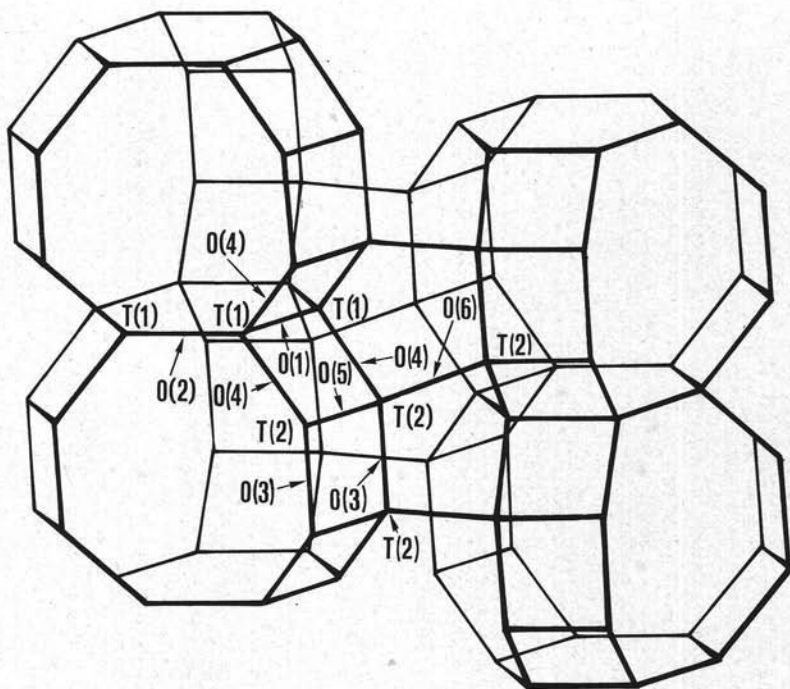


Fig. 2. - The superimposing and cross linking of « gmelinite-type cages » in the mazzite structure, represented as in Fig. 1. Atoms are coded as in Table 1.

program (BUSING et al., 1962) and by Fourier syntheses. Atomic scattering factors (CROMER and MANN, 1968) were used for Mg^{++} , K^+ , Ca^{++} , Na^+ and $[1/4 Al^{++} + 3/4 Si^{++}]$ (for which Al^+ was interpolated between Al and Al^{3+} and Si^{++} between Si and Si^{++}). The final model, checked by difference Fourier synthesis, did not show any significant residual electron density. Attempts to refine the structure in $P\bar{6}2c$ and $P6_3mc$ resulted in worse R values than for the centric space-group. The lowest R-value ($R = \frac{\sum ||F_o - F_c||}{\sum |F_o|}$) with framework atoms only was 0.37. Introduction of exchangeable cations and water molecules (detected with three dimensional electron density maps) resulted in $R = 0.075$ with isotropic temperature factors. Partial anisotropic refinement on all atoms excluding Ca in

TABLE 1

Atomic coordinates, thermal parameters and occupancy factors with e.s.d.'s on the last digit in parentheses. The form of the anisotropic temperature factors ($\times 10^4$) is:

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$$

Atom	Symmetry*	x/a	y/b	z/c	β_{11} or $B(\text{\AA})^2\beta_{22}$	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy %	
T(1)	12(j)	.1584(1)	.4902(1)	1/4	9(1)	9(1)	60(3)	5(1)	0	0	100
T(2)	24(l)	.3536(1)	.0933(1)	.0444(2)	10(1)	7(1)	59(2)	4(1)	2(1)	-0(1)	100
O(1)	6(h)	.2589(2)	.5178	1/4	14(2)	20(4)	166(18)	10	0	0	100
O(2)	6(h)	.4249(2)	.8498	1/4	14(2)	16(3)	116(16)	8	0	0	100
O(3)	12(j)	.3822(3)	.1004(3)	1/4	24(2)	27(3)	78(9)	17(2)	0	0	100
O(4)	24(l)	.4352(2)	.1114(2)	-.0721(5)	21(2)	25(2)	106(8)	14(1)	9(3)	8(3)	100
O(5)	12(k)	.1614(2)	.3228	-.0016(6)	14(1)	22(2)	107(11)	11	4(2)	8	100
O(6)	12(i)	.2741(3)	0	0	20(2)	12(2)	153(14)	6	-3(2)	-6	100
K, Na, Ca	6(g)	1/2	0	0	19(2)	30(3)	217(17)	15	20(3)	40	50(1)
Mg	2(d)	1/3	2/3	-1/4	32(2)	32	93(14)	16	0	0	100
Ca	4(e)	0	0	.072(8)	23.2(32)						22(1)
H ₂ O(1)	12(k)	.467(1)	.934	.661(2)	6.4(4)						50(1)
H ₂ O(2)	4(f)	1/3	2/3	.016(1)	4.3(3)						100
H ₂ O(3)	6(h)	.271(1)	.542	-1/4	5.4(6)						44
H ₂ O(4)	12(j)	.566(1)	.355(1)	1/4	6.9(5)						44
H ₂ O(5)	24(l)	.028(2)	.148(1)	.030(4)	7.7(11)						23(1)
H ₂ O(6)	6(h)	.088(1)	.176	1/4	21.8(19)						89(5)
H ₂ O(7)	6(h)	.076(1)	.152	-1/4	31.2(30)						45(3)

* Number of position and Wyckoff notation for $P6_3/mmc$.

Occupancy of the T(1) and T(2) sites: Si = 73 %, Al = 27 %.

Occupancy of the K, Na, Ca site: K = 42 %, Na \approx 5 %, Ca \approx 3 %, and empty = 50 %.

TABLE 2

Analysis of anisotropic thermal parameters. Root mean square thermal vibrations (\AA) along the ellipsoid axes and angles ($^\circ$) between the principal axes (U_i) of the vibration ellipsoid and the $[100]$, $[120]$ and $[001]$ directions

Atom	Principal axis	R.m.s. amplitude	\mathcal{J}_1	\mathcal{J}_2	\mathcal{J}_3
T(1)	1	.10(1)	28(40) $^\circ$	62(40) $^\circ$	90 $^\circ$
	2	.11(1)	118(40)	28(40)	90
	3	.13(1)	90	90	0
T(2)	1	.09(1)	101(6)	169(6)	93(4)
	2	.12(1)	160(7)	79(6)	107(7)
	3	.13(1)	73(7)	90(4)	163(7)
O(1)	1	.12(4)	0	90	90
	2	.16(2)	90	0	90
	3	.22(1)	90	90	0
O(2)	1	.13(2)	0	90	90
	2	.15(1)	90	0	90
	3	.19(1)	90	90	0
O(3)	1	.15(1)	21(9)	69(9)	90
	2	.15(1)	90	90	0
	3	.19(1)	69(9)	159(9)	90
O(4)	1	.15(1)	22(13)	91(13)	68(13)
	2	.17(1)	74(16)	42(9)	128(12)
	3	.19(1)	74(7)	132(9)	133(8)
O(5)	1	.12(1)	0	90	90
	2	.15(1)	90	33(12)	123(12)
	3	.19(1)	90	123(12)	147(12)
O(6)	1	.13(2)	90	172(5)	98(5)
	2	.17(2)	0	90	90
	3	.21(1)	90	82(5)	172(5)
K, Na, Ca	1	.14(1)	0	90	90
	2	.15(1)	90	31(3)	121(3)
	3	.28(1)	90	121(3)	149(3)
Mg*	1	.17(1)	90	90	0
	2	.20(1)			
	3	.20			

* Being a rotation ellipsoid, only the angles relative to the rotation axis are given.

the large channels and all water molecules, converged to a final $R = 0.049$ (omitting zeros) and $R = 0.054$ (including zeros). The weighted R_w ($R_w = [\sum w|F_o - F_c|^2 / \sum w|F_o|^2]^{1/2}$ where $w = (1/\sigma_{F_o})^2$) was 0.052.

Population refinement of $H_2O(3)$ and $H_2O(4)$ showed anomalously high values ($54 \pm 3\%$) which were consequently held fixed at 44% in accordance with statistical occupancy of geometrically related positions. In the last stages of the refinement the position of $H_2O(7)$ was held fixed at $z/c = -1/4$ after it had refined to a value of $z/c = -264(14)$.

Positional and thermal atomic parameters are given in Table 1 and 2. The observed and calculated structure factors are listed in Table 3. Tables 4 and 5 contain the interatomic distances.

Structure refinement and discussion

Description of the structure may begin with the «gmelinite cage», which is represented clinographically in Fig. 1; in this Figure each nodal point represents a tetrahedral-atom, oxygens being placed near the midpoint of the lines so that each line represents a T-O-T bridge. These cages are superimposed to build columns parallel to c , with the upper and the lower hexagonal rings in common between cages. Adjacent columns of cages are shifted by $c/2$ and interconnected as shown in Fig. 2. A projection of the whole structure along c is represented in Fig. 3, where one may note that: (a) cross linking of the cages forms large channels delimited by 12-membered rings and surrounded by 6 cages, and smaller ones delimited by distorted 8-membered rings between adjacent pairs of cages; (b) the exchangeable cations are distributed into three positions, (I) inside the cages, (II) in the channels between the cages, and (III) in the middle of the larger channels.

The free diameter of the large channels formed by 12-rings of tetrahedra is 7.4 Å assuming the effective radius of oxygen to be 1.35 Å. Channels of the same order of magnitude are rather rare in zeolites, being present only in faujasite, gmelinite, mordenite and offretite.

The analysis of the anisotropic temperature factors (Table 3) revealed small deviation from isotropy for all atoms, the maximum anisotropy occurring in the thermal parameters of (K, Na, Ca) in site II.

The mean T-O distances for mazzite are consistent with Si, Al disorder (Table 4).

The topological difference between this structure and that proposed by BARRER and VILLIGER (1969) for zeolite Ω lies in the interconnection of the columns of cages, and it is a result of the different space group, $P6_3/mmc$ assumed from single crystal data for mazzite, compared to $P6/mmm$ assumed from powder data for phase Ω . The difference between the two is revealed by the absence of diffractions

of the type $hh2hl$ with $l = \text{odd}$ in $P6_3/mmc$. The same diffraction however are missing also in the powder data of phase Ω (AIELLO and BARRER, 1970). Hence the two zeolites could have the same space group and the same framework.

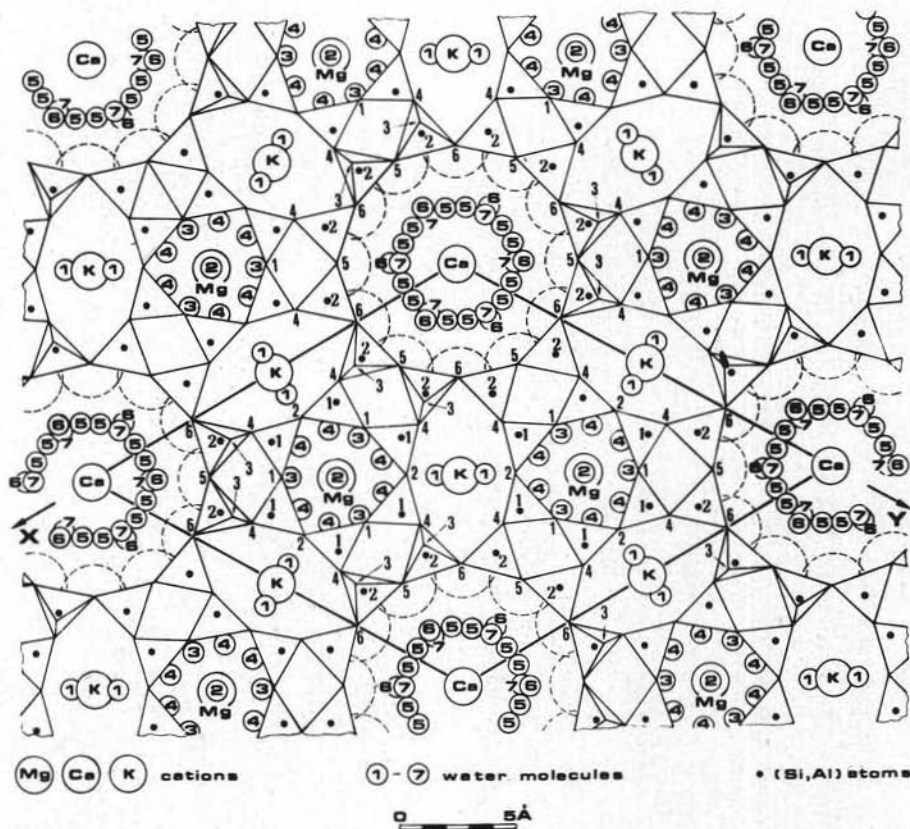


Fig. 3. — The structure of mazzite projected along c . TO_4 tetrahedra pointing up are easily recognizable whereas those pointing down are shown only as triangles. Those with an edge normal to the projection plane can be distinguished because they form hexagonal rings around Mg. The positions and coordinations of the exchangeable cations may be better understood by comparing this Figure with Figs. 4, 5 and 6. Broken circles represent the dimensions of oxygens atoms, and indicate the free aperture of the main channels.

One of the characteristic features of mazzite as a zeolite is its high Mg-content. Mg^{++} -ions occur in site I at the center of all the «gmelinite-type» cages (Fig. 4). Above and below each Mg^{++} -ion has two $\text{H}_2\text{O}(2)$ molecules (100% occupancy) and nine positions for water molecules [$\text{H}_2\text{O}(3)$ and $\text{H}_2\text{O}(4)$] surround the Mg^{++} -ion at its own level, but only four out of these nine positions can be occupied at the same time; as for instance, those joined to Mg^{++} by a dashed line in Fig. 4. The

TABLE 3
 Observed and calculated structure factors ($X 10$). Unobserved reflections
 are marked with an asterisk

h k l	PO	PC	h k l	PO	PC	h k l	PO	PC	h k l	PO	PC	h k l	PO	PC	h k l	PO	PC	
1 0 0	648	-643	3 2 2	738	-736	5 4 0	208	216	9 2 0	64	82	12 9 10	81	86	15 4 4	295	294	
1 1 0	948	-1041	3 3 2	887	-889	5 4 0	211	215	9 2 0	27	33	13 0 10	32	-44	16 0 4	845	842	
2 0 0	719	-732	4 0 2	57	-2	6 0 0	981	960	9 2 0	75	-87	13 1 10	81	-83	16 0 4	225	228	
2 1 0	756	772	4 1 2	36	-51	6 0 0	395	-391	9 5 0	155	-155	13 2 1	296	-295	16 2 4	87	84	
3 0 0	607	604	4 2 2	367	383	6 0 0	330	-328	9 5 0	71	-95	13 3 1	263	-266	17 0 4	52	-19	
3 1 0	826	847	4 3 2	71	31	6 3 0	404	-389	9 7 0	153	-155	14 4 1*	38	377	17 0 4	140	-144	
3 2 0	1163	-1160	4 4 2	789	760	6 3 0	454	-299	10 0 0	70	96	13 5 1	171	-277	1 0 2	225	-188	
4 0 0	852	-849	5 1 2*	988	-955	6 3 0	862	-871	10 0 0	267	-271	13 6 1	56	-82	1 0 2	863	857	
4 1 0	1009	-1045	5 2 2*	137	182	6 3 0	55	45	10 3 0	217	-205	13 7 1	129	-135	2 0 2	363	-356	
4 2 0	1317	1318	5 3 2*	161	85	6 6 0	1248	1264	10 2 0*	32	-7	13 8 1	199	-212	3 0 2	363	-338	
4 3 0	277	-213	5 4 2*	211	-189	7 2 0	164	-160	10 5 0	152	135	14 1 1	143	149	3 2 2	50	59	
4 4 0	1623	1757	5 5 2*	271	-189	7 3 0	211	261	10 5 0	152	187	14 2 1	103	-177	4 0 2	101	-102	
5 0 0	2694	-2688	6 1 2	806	674	7 3 0	455	-462	11 2 0*	58	-68	14 3 1	159	153	4 2 2	262	267	
5 1 0	325	594	6 2 2	218	-236	7 3 0	285	283	11 3 0	59	-21	14 4 1	190	190	4 2 2	111	85	
5 2 0	1120	1136	6 3 2	619	-632	7 6 0	196	197	11 4 0	247	136	14 5 1	247	-265	4 2 2	197	187	
5 3 0	212	-213	6 4 2	433	388	8 0 0	701	720	12 0 0	327	-364	14 7 1	271	246	5 0 2	243	-295	
5 4 0	11	4	6 5 2	795	-764	8 1 0	128	149	12 1 0	124	121	15 0 1	112	116	5 2 2	193	177	
6 0 0	886	816	7 1 2	15	-21	8 3 0	954	632	12 3 0	142	202	15 2 1	112	96	5 4 2	576	-555	
6 1 0	277	-311	7 2 2	136	136	8 3 0	173	133	13 0 0	242	260	15 3 1	173	-172	6 0 2	736	-746	
6 2 0	572	-593	7 3 2	764	-729	8 6 0	704	-753	13 1 0	125	-124	15 4 1	231	245	6 2 2	262	-213	
6 3 0	794	-796	7 4 2	229	173	8 6 0	119	-155	13 2 0	355	308	15 5 1	216	213	6 3 2	1939	1944	
6 4 0	213	-262	8 1 2	398	-459	8 6 0	225	-23	13 3 0	148	113	15 6 1	119	-127	6 4 2	526	-526	
6 5 0	1263	-1191	8 2 2	554	-331	8 6 0	71	-2	1 1 0	299	293	16 2 1	157	116	6 5 2	197	166	
6 6 0	1379	1424	8 3 2	935	936	9 0 0	406	-405	2 2 0*	50	42	16 2 1	69	92	6 5 2	640	640	
7 0 0	415	304	8 4 2	589	-578	9 0 0	351	-362	2 3 0*	45	-55	16 3 1	152	126	7 0 2	1036	-1043	
7 1 0	88	76	8 5 2	613	607	9 2 0	188	-191	2 4 0*	45	-55	16 4 1	211	211	7 0 2	842	811	
7 2 0	309	-297	8 6 2	38	-16	9 3 0	159	-152	3 0 0	266	-256	17 0 1	261	258	7 2 2	115	-113	
7 3 0	948	-937	8 7 2	1042	976	9 3 0	37	-36	3 1 0	112	126	17 1 1	271	-292	7 3 2	261	-214	
7 4 0	296	-235	8 8 2	884	557	9 3 0	1	2	3 2 0	119	161	17 2 1	191	161	7 4 2	472	-499	
7 5 0	948	-937	8 9 2	71	52	9 6 0	61	-64	3 3 0	132	131	17 3 1	56	-70	7 5 2	719	692	
7 6 0	963	953	9 0 2	208	-208	9 6 0	27	-26	3 4 0	148	113	18 0 1	110	-110	7 6 2	161	-100	
7 7 0	379	422	9 1 2	128	-50	9 6 0	53	-2	4 0 0	1	8	1 5 2	273	263	8 0 2	365	380	
7 8 0	1059	1051	9 2 2	581	-575	9 9 0	356	-353	4 2 0	242	-247	2 1 1	516	525	8 1 2	311	-317	
7 9 0	815	764	9 3 2	276	281	9 9 0	226	-229	4 3 0	115	-115	2 2 1	458	-467	8 2 2	319	-166	
8 0 0	391	324	9 4 2	672	693	10 1 0	399	399	4 4 0	242	242	3 1 1	185	136	8 3 2	255	-257	
8 1 0	1423	1426	9 5 2	959	-978	10 2 0	950	-918	5 0 0*	50	26	3 1 1	208	253	8 4 2	518	-518	
8 2 0	63	113	9 6 2	210	-210	10 2 0	311	-255	5 1 0*	311	-255	4 1 1	231	245	8 5 2	73	-73	
8 3 0	884	-864	9 7 2	6	-6	10 5 0	214	-208	5 2 0	188	-191	4 5 1	1074	-1071	8 6 2	53	-108	
8 4 0	148	-262	9 8 2	316	-321	10 5 0	50	-53	5 3 0	88	92	4 1 1	53	-61	8 7 2	469	413	
8 5 0	375	-417	9 9 2	1017	-1047	10 7 0	327	-319	5 4 0	745	741	4 3 1	137	-96	8 8 2	497	-502	
8 6 0	30	-18	10 0 2	398	439	10 8 0	167	159	6 0 0	187	-176	5 0 1	1006	1076	9 0 2	775	84	
8 7 0	676	-611	10 1 2	62	-25	10 8 0	123	-119	6 1 0	49	-39	5 1 1	113	113	9 1 2	367	-376	
8 8 0	528	-493	10 2 2	137	-121	11 0 0	363	351	6 3 0*	49	-11	5 2 1	429	-434	9 2 2	821	-811	
8 9 0	226	255	10 3 2	111	-105	11 1 0	231	-249	7 0 0	149	191	5 3 1	630	629	9 3 2	35	39	
9 0 0	264	-264	10 4 2	119	-126	11 1 0	192	-206	7 1 0	219	219	5 4 1	429	-432	9 4 2	379	385	
9 1 0	384	-464	10 5 2	217	-216	11 3 0	217	214	7 2 0	96	92	6 0 1	249	-249	9 5 2	91	-74	
9 2 0	199	-188	10 6 2	382	-392	11 3 0	141	170	8 0 0	6	-6	6 1 1	937	-913	9 6 2	339	-335	
9 3 0	468	-468	10 7 2	1284	1286	11 3 0	195	-191	8 1 0	417	417	6 2 1	514	-514	9 7 2	487	-487	
9 4 0	238	-246	10 8 2	399	385	11 6 0	494	-485	8 2 0	6	6	6 3 1	83	-58	10 0 2	254	224	
9 5 0	362	-371	10 9 2	662	594	11 7 0	298	-295	8 3 0	717	742	6 4 1	430	-433	10 1 2	262	261	
9 6 0	846	-846	11 0 2	88	-89	11 7 0	171	-171	8 4 0	136	136	6 5 1	1163	-1162	10 2 2	541	-541	
9 7 0	73	98	11 1 2	141	-155	12 0 0	1277	1286	8 5 0	1	1165	-1162	7 5 1	601	-612	10 3 2	92	-126
9 8 0	682	-684	11 2 2	58	-58	12 1 0	369	-364	8 6 0	2	222	267	7 1 1	254	266	10 4 2	176	-176
9 9 0	189	-189	11 3 2	118	-126	12 2 0	136	-132	8 7 0	136	136	7 2 1	657	-647	10 5 2	367	-367	
10 0 0	1488	715	11 4 2	1278	1297	12 3 0	78	-91	8 8 0	2	172	166	7 3 1	267	-662	10 6 2	150	-156
10 1 0	109	-133	11 5 2	786	-802	12 4 0	467	-467	8 9 0	2	214	-237	7 4 1	706	725	11 0 2	437	431
10 2 0	955	-955	11 6 2	416	-421	12 5 0	276	-274	9 0 0	276	276	7 5 1	641	641	11 1 2	312	-318	
10 3 0	535	545	11 7 2	417	316	12 6 0	442	428	9 1 0	1875	1860	7 6 1	841	154	11 2 2	817	-819	
10 4 0	98	-81	11 8 2	772	-798	12 7 0	331	-337	9 2 0	1	655	-667	8 0 1	967	953	11 3 2	117	-128
10 5 0	298	-236	11 9 2	66	-66	13 0 0	127	-127	9 3 0	2	460	-460	8 1 1	256	-272	11 4 2	359	-349
10 6 0	1175	1175	12 0 2	48	-48	13 1 0	112	-108	9 4 0	1	404	-408	8 2 1	55	-25	11 5 2	957	811
11 0 0	752	-752	12 1 2	295	337	13 2 0	408	-408	9 5 0	1	146	-151	8 3 1	593	-551	12 0 2	52	29
11 1 0	811	-810	12 2 2	93	82	13 3 0	98	92	9 6 0	1	146	-151	8 4 1	593	-551	12 1 2	52	29
11 2 0	518	-495	12 3 2	118	-126	13 4 0	210	-213	9 7 0	6	2	181	204	12 2 2	179	-179		
11 3 0	508	579	12 4 2	424	436	13 5 0	115	130	9 8 0	3	213	-213	8 5 1	181	204	12 3 2	312	-312
11 4 0	194	-120	12 5 2	365	-367	14 0 0	182	130	9 9 0	4	291	326	9 0 1	147	-283	12 4 2	176	-173
11 5 0	178	-168	12 6 2	416	-421	14 1 0	59	32	10 0 0	1	62	46	9 1 1	174	130	12 5 2	625	-622
11 6 0	545	-534	12 7 2	329	317	14 2 0	125	-90	10 1 0	291	284	9 2 1	282	-282	12 6 2	118	-114	
11 7 0	350	341	12 8 2	314	-397	14 3 0	86	115	7 1 1	494	511	9 3 1	35	-7	13 0 2	91	94	
11 8 0	454	-454	12 9 2	308	308	14 4 0	48	-48	7 2 1	524	-494	9 4 1	462	462	13 1 2	150	-150	
11 9 0	215	-202	12 10 2	318	-283	14 5 0	3	46	7 3 1	276	-276	9 5 1	366	-521	13 2 2	367	-367	
12 0 0	4135	-2127	12 11 2	78	-90	15 0 0	62	50	7 4 1	155	148	9 6 1	146	133	13 3 2	50	45	
12 1 0	768	-822	12 12 2	131	-138	15 1 0	131	-138	7 5 1	344	365	9 7 1	140	133	13 4 2	105	83	
12 2 0	107	103	12 13 2	102	-109	15 2 0	308	-337	7 6 1	41	-47	9 8 1	162	-163	13 5 2	162	-151	
12 3 0	421	-231	13 0 2	458														

same figure shows also the positions of the framework oxygens relative to the Mg^{++} -water complex. In the dehydrated form Mg bonds to the three $O(1)$'s of these rings and to one residual water molecule (RINALDI et al., 1975).

Occupancy of $H_2O(3)$ and $H_2O(4)$ must not be higher than $4/9 = 0.44$, and the multiplicity factor was fixed at this value in the last cycles of the refinement, as said above. Essentially the Mg^{++} -ions are octahedrally coordinated.

Further studies on the crystallization kinetics of zeolites containing the same building units as mazzite may well lead to the conclusion that the Mg-water complex acts as a template to the formation of «gmelinite-type cages». The same role would be played by the large organic TMA-ions in the crystallization of zeolite Ω .

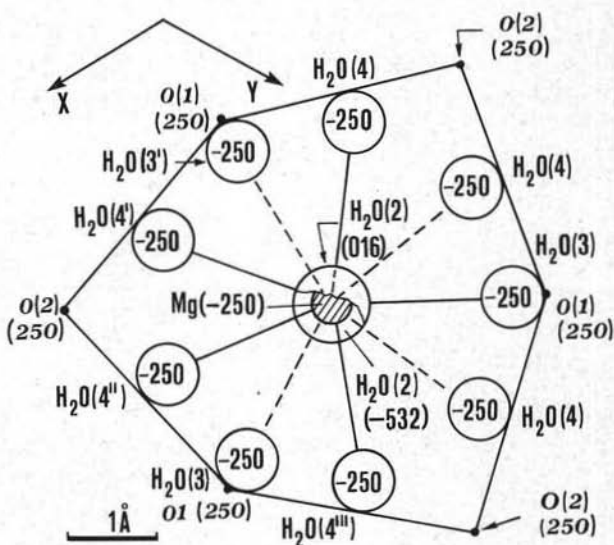


Fig. 4. — Coordination of water molecules around Mg in site I shown in projection along c . Three-digit numbers give the height over the projection plane as permillage of c . $H_2O(2)$ is always present. Only four of the nine $H_2O(3)$ and $H_2O(4)$ molecules are present at the same time (for instance those joined to Mg with dashed lines). On the average, Mg coordinates octahedrally to 6 water molecules.

Site II is occupied about 50% by a mixture of ions (in order of abundance: $K \sim 42\%$, $Na \sim 5\%$, $Ca \sim 3\%$ and empty 50%). These cations (Fig. 5) coordinate mainly to framework-oxygens, two $O(2)$ and four $O(4)$, which form a rather distorted hexagon. The distances to $O(2)$ are slightly larger than those reported by SHANNON and PREWITT (1969) for 8-coordinated K^+ . The coordination is completed by two $H_2O(1)$ molecules, with an occupancy of 50%; the overly short distances of these water molecules to the cations may be easily explained, as done in the legend of Fig. 5.

Fig. 6 is a detail of the content of the larger channels, with cation site III. Here the situation is complicated by many low occupancies, the higher ones being 89 % for H₂O(6) and 45 % for H₂O(7), which determine the prevailing coordination pattern around Ca⁺⁺; this can be described as follows: the Ca cations are

TABLE 4

Interatomic distances (Å) and angles (°) within the framework with e.s.d.'s on the last digit in parentheses

T(1)-O(1)	1.655(3)	O(1)-T(1)-O(2)	109.1(4)
T(1)-O(2)	1.641(2)	O(1)-T(1)-O(4)	110.4(2) [x2]
T(1)-O(4)	1.658(4) [x2]	O(2)-T(1)-O(4)	108.3(2) [x2]
Average	1.653	O(4)-T(1)-O(4)	110.3(3)
O(1)-O(2)	2.685(5)	O(3)-T(2)-O(4)	106.4(2)
O(1)-O(4)	2.720(5) [x2]	O(3)-T(2)-O(5)	110.4(3)
O(2)-O(4)	2.674(4) [x2]	O(3)-T(2)-O(6)	111.3(2)
O(4)-O(4)	2.721(8)	O(4)-T(2)-O(5)	111.6(2)
T(2)-O(3)	1.642(2)	O(4)-T(2)-O(6)	110.5(2)
T(2)-O(4)	1.629(4)	O(5)-T(2)-O(6)	106.8(2)
T(2)-O(5)	1.645(2)		
T(2)-O(6)	1.640(2)	T(1)-O(1)-T(1)	149.2(5)
Average	1.639	T(1)-O(2)-T(1)	171.0(5)
		T(1)-O(4)-T(2)	144.6(2)
O(3)-O(4)	2.619(4)	T(2)-O(3)-T(2)	146.5(4)
O(3)-O(5)	2.699(5)	T(2)-O(5)-T(2)	138.0(3)
O(3)-O(6)	2.710(4)	T(2)-O(6)-T(2)	136.7(3)
O(4)-O(5)	2.708(5)		
O(4)-O(6)	2.685(5)		
O(5)-O(6)	2.637(2)		

located on the *c* axis at *z/c* = 0.072 with an occupancy of 23 %. Six water positions occupied by H₂O(6) and H₂O(7) occur above and below the Ca site at the vertices of a hexagonal prism. More water molecules [H₂O(5)] are located at approximately the same height as Ca and with an occupancy of 23 % in twelve positions of which only three can be occupied at the same time in accordance with statistical occupancy and possible distance restraints. The Ca position could actually be occupied by a random alternation of Ca and water molecules.

In short the walls of the wide channel are lined with water molecules, and the cations are set at regular intervals in the middle of these « water pipes ». This

configuration is the most plausible, however the distribution of cations and water molecules in these wide channels is not as well defined as it may be in smaller cavities due to the considerable freedom of movement of the atomic species as evidenced by their high thermal motions.

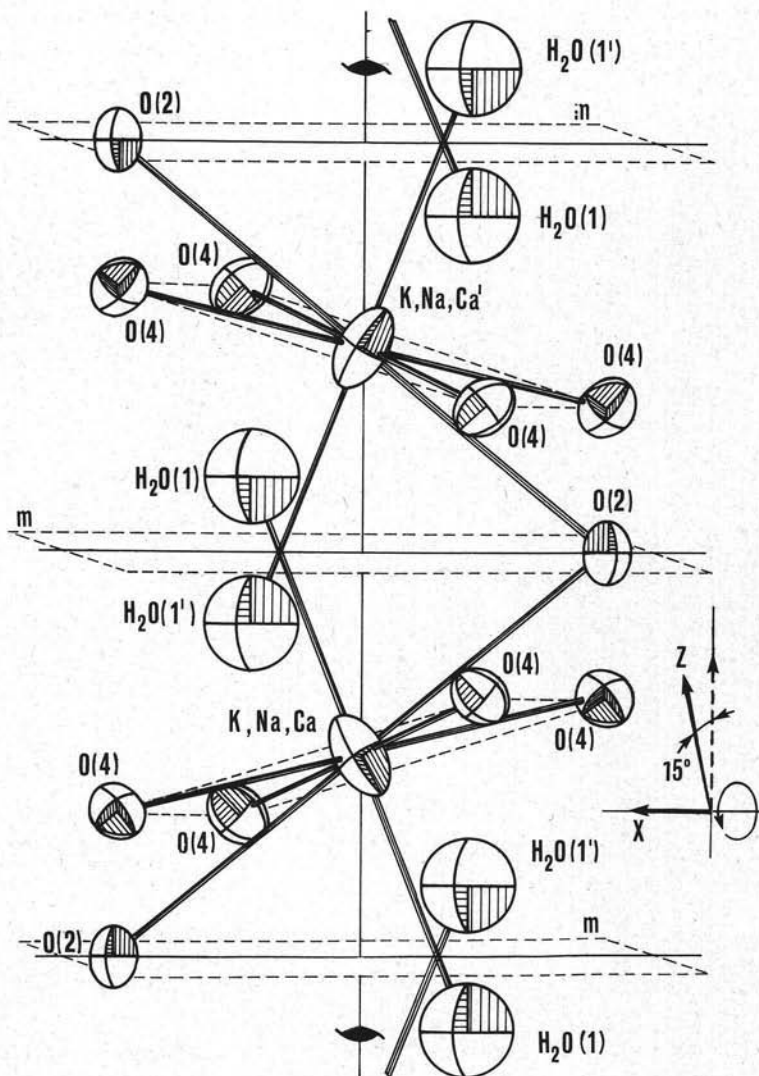


Fig. 5. — Coordination of framework-oxygens and water molecules around the (K, Na, Ca) site II (occupancy factor = 50%), shown in clinographic projection. The cation is at the center of a distorted hexagon with two O(2) and four O(4) at its corners. The distance from the lower cation to H₂O(1') (occupancy factor 50%) is 1.63 Å, hence forbidden. The following assumption is proposed: when the upper cation position is empty and the lower is occupied, the two H₂O(1) are present and the two H₂O(1') are absent, and vice-versa.

An interesting relationship exists between the structures of mazzite and offretite (GARD and TAIT, 1972), which are associated at Mont Semiol. Both zeolites contain the «gmelinite-type» cages occupied by the hydrated Mg-ion, and in both of them the superimposition of these cages forms columns parallel to c . Offretite contains large channels surrounded by 12-rings of tetrahedra too, but the positions and the connections between the «gmelinite-type» cages are different; a rotation of 60° and translation of $c/2$ of the columns is necessary to transform one structure into the other. Some similarities between the two could also be present in the distribution of the cations within the large channels.

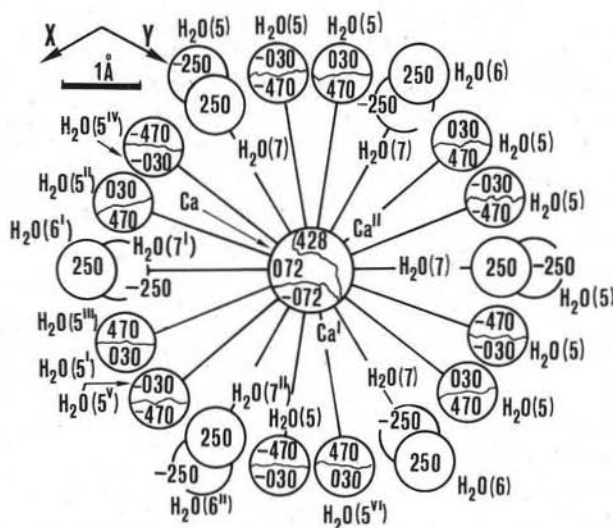


Fig. 6. — Coordination of water molecules around Ca in site III shown here in projection along c . Three digit numbers give the heights over the plane of projection as permillage of c . Most abundant are $H_2O(6)$ and $H_2O(7)$ placed at $z/c = 1/4$ and $-1/4$, hence giving a hexagonal prism configuration around Ca, which lies nearly at $z/c = 0$.

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TABLE 5

Cations, oxygens and water molecules: distances less than 3.40 Å, with e.s.d.'s on the last digit in parentheses

K, Na, Ca-O(2)	3.06(1)[x2]	H ₂ O(3)-O(3)	3.04(2)
K, Na, Ca-O(4)	2.89(1)[x4]	H ₂ O(3 ^I)-H ₂ O(4 ^I)	1.37(2)*
K, Na, Ca-H ₂ O(1)	2.80(1)[x2]	H ₂ O(3 ^I)-H ₂ O(4 ^{II})	2.63(2)
K, Na, Ca-H ₂ O(1 ^I)	1.63(1)[x2]*	H ₂ O(4)-O(3)	2.95(2)
Mg-H ₂ O(2)	2.03(1)[x2]	H ₂ O(4)-O(4)	3.29(1)
Mg-H ₂ O(3)	1.99(2)[x3]	H ₂ O(4 ^I)-H ₂ O(4 ^{II})	1.46(3)*
Mg-H ₂ O(4)	2.08(2)[x6]	H ₂ O(4 ^{II})-H ₂ O(4 ^{III})	2.64(3)
Ca-Ca ^I	1.10(13)*	H ₂ O(5)-O(5)	2.93(3)
Ca-Ca ^{II}	2.72(13)*	H ₂ O(5)-O(6)	2.62(2)
Ca-H ₂ O(5 ^I)	2.52(2)[x6]	H ₂ O(5 ^I)-H ₂ O(5 ^{II})	1.70(5)*
Ca-H ₂ O(5 ^V)	2.62(3)[x6]	H ₂ O(5 ^I)-H ₂ O(5 ^{III})	3.36(7)
Ca-H ₂ O(6 ^I)	3.11(4)[x3]	H ₂ O(5 ^I)-H ₂ O(5 ^{IV})	2.55(3)
Ca-H ₂ O(7 ^{II})	2.78(4)[x3]	H ₂ O(5 ^I)-H ₂ O(5 ^V)	1.00(5)*
H ₂ O(1)-O(3)	3.21(1)	H ₂ O(5 ^I)-H ₂ O(5 ^{VI})	3.23(5)
H ₂ O(1)-O(4)	2.93(1)	H ₂ O(5 ^I)-H ₂ O(6 ^I)	1.93(3)*
H ₂ O(1)-H ₂ O(1)	3.25(3)	H ₂ O(5 ^I)-H ₂ O(6 ^{II})	2.83(3)
H ₂ O(1)-H ₂ O(1 ^I)	1.36(3)*	H ₂ O(5 ^I)-H ₂ O(7 ^I)	2.31(3)*
H ₂ O(1)-H ₂ O(4)	2.51(2)	H ₂ O(5 ^I)-H ₂ O(7 ^{II})	2.38(3)*
H ₂ O(2)-O(1)	2.97(1)	H ₂ O(6)-O(5)	3.03(2)
H ₂ O(2)-H ₂ O(3)	2.84(2)	H ₂ O(6 ^I)-H ₂ O(7 ^{II})	2.63(2)
H ₂ O(2)-H ₂ O(4)	2.91(1)	H ₂ O(7)-O(5)	3.31(3)

The superscripts do not follow any specific rule, but are used solely to locate the corresponding atoms in Figs. 4, 5 and 6.

An asterisk indicates distances too short for simultaneous occupation of both sites.

The multiplier of the interatomic distances related by symmetry is given in square brackets for cation polyhedra only.

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