Mazzite-Na, a new zeolite from Boron, California: Its description and crystal structure

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ABSTRACT

Mazzite-Na, $Na_8Al_8Si_{28}O_{72}\cdot30H_2O$, is a new zeolite mineral species occurring in basalt at the bottom of the open pit of the U.S. Borax mine at Boron, California. It crystallizes as white, very thin, flexible fibers up to 2 mm in length, and commonly fills small cavities as satiny mats. The luster is vitreous, and the streak is white. The fineness of the fibers precludes the determination of the hardness and the observation of any cleavage. The observed and calculated densities are 2.16 and 2.18 g/cm^3, respectively. The mineral is uniaxial positive with $n_\varepsilon = 1.472(3)$ and $n_\omega = 1.471(3)$. Electron-microprobe analyses yielded (in wt%) SiO_2 57.65, Al_2O_3 14.35, Fe_2O_3 0.65, MgO 0.22, CaO 0.18, BaO 0.14, Na_2O 8.07, K_2O 0.03, and H_2O 18.70 (TG analysis), which gives the empirical cell contents $(Na_{7.52}K_{0.02}Mg_{0.16}Ca_{0.09}Ba_{0.03})[Fe_{0.24}Al_{8.13}Si_{27.71}O_{72}]\cdot29.98H_2O$. Mazzite-Na is hexagonal, $P6_3/mmc$, $a = 18.2343(7)$, $c = 7.6371(2)$ Å, $Z = 1$. The strongest seven measured X-ray lines [d in Å(I)(hkl)] are: 9.08(100)(110), 6.86(70)(101), 5.95(70)(210), 4.681(40)(211), 3.787(80)(002), 3.511(40)(112), and 3.150(70)(500).

The framework consists of columns of gmelinite cages parallel to **c**, cross-linked to form two types of channels; one has an elliptical 8-ring cross section and the other has a circular 12-ring cross section. The extra-framework Na cations are located at three different sites. NaI is at the center of the 6-ring between adjacent gmelinite cages and is coordinated by six framework oxygen atoms and two H_2O molecules. NaII lies on the centerline of the 8-ring channel and is coordinated by four framework oxygen atoms and two H_2O molecules. NaIII occupies sites along the walls of the 12-ring channel and is coordinated with two framework oxygen atom and four H_2O molecules.

With the naming of this mineral for its Na dominant composition the original mineral is renamed mazzite-Mg, and the name mazzite is raised to series status.

INTRODUCTION

Galli et al. (1974) named and described mazzite, $(Mg_{2.5}K_2Ca_{1.5})[Al_{10}Si_{26}O_{72}]\cdot30H_2O$, from outcrops of olivine basalt near the top of Mont Semiol, near Montbrison, Loire, France. Using X-ray powder diffraction data, they showed that mazzite has the same framework topology as the synthetic zeolite Ω, $(Na_{6.6}TMA_{1.8})[Al_{8.4}Si_{27.6}O_{72}]\cdot22.2H_2O$, where TMA is the tetramethylammonium ion (Flanigen and Kellberg 1967, 1980; Barrer and Villiger 1969). It was puzzling that the natural mineral had such a different composition of charge-balancing extra-framework cations, as well as a lower Si/Al framework content.

In the 1990s a mazzite-like mineral was found in cavities of basalt at Boron, California. Energy dispersive analysis of this material showed that it was Na-dominant, like zeolite Ω. Only recently were we able to obtain quantitative chemical analyses and crystal structure data of sufficient quality to support a proposal for a new mineral and mineral name.

The mineral data and the proposed mineral name, mazzite-Na (IMA 2003-058), have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Society. Following the recommendations of the Zeolite Subcommittee (Coombs et al. 1998), we also proposed that the name mazzite be raised to series status and that the name for the original mineral be changed to mazzite-Mg. These proposals were also approved by the Commission. In this paper we will describe the new mineral, and compare its composition and crystal structure with mazzite-Mg.

OCCURRENCE

Mazzite-Na was found in cavities in blocks of basalt on the waste dump at the U.S. Borax mine at Boron, 135 km northeast of Los Angeles, California. The blocks were exposed and removed by the ongoing quarrying operation. The basalt underlies basin fill deposits, consisting of sand, shale, tuff, and borate deposits, all comprising the Miocene Kramer beds. At the base of the section two subalkaline basalt flows about 10 m thick are overlain by several meters of silt and clay. These are in turn are overlain by 150 to 200 m of lacustrine deposits of silt and sodium borate with a few interbeds of rhyolite tuff. The borate-bearing beds are covered with 50 to 100 m of post-Miocene alluvial gravel.

All cavities and fractures in the basalt are lined with ferroan saponite about 0.5 mm thick. Other minerals in the cavities, zeolites along with some sulfide, borate, and carbonate minerals, grow on this clay layer (Wise and Kleck 1988). The zeolite minerals include phillipsite-Na, gmelinite-Na, mordenite,

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clinoptilolite-Na, chabazite-Na, heulandite-Na, analcime, and mazzite-Na. The crystals of the first four zeolites reveal an interrupted growth history. Early formed crystals show the effects of partial dissolution, and are coated with a thin layer of saponite. Epitaxial overgrowths of clear crystals are common. These relations suggest that many crystals grew before the formation of the sodium borate-rich lake, and after that lake was established Na-rich waters seeped into the underlying sediments and basalt. The early formed zeolites were cation-exchanged and partially dissolved. Some further zeolite crystallization occurred with the Na-rich solutions. There is no textural evidence to indicate whether mazzite-Na crystallized before or after the entrance of Na-rich waters, but some crystal structure evidence, to be presented below, suggests that it too was cation exchanged.

Mazzite-Na typically forms sprays of white, satiny fibers, which are so delicate that when the fluid drained from the cavity, the fibers collapsed into lustrous mats (Fig. 1). The fibers are extremely fine, typically about 10 μm wide, but up to 2 mm in length. As shown in Figure 1 analcime is the only other zeolite found to grow on or even in the same cavity with mazzite-Na.

FIGURE 1. Silky mazzite-Na fibers filling a cavity in basalt from the open pit of the U.S. Borax mine at Boron, California. The long dimension of the cavity is 5 mm. The mazzite-Na has grown on a saponite layer about 0.4 mm thick, and small crystals of analcime decorate the fibers on the lefthand side.

PHYSICAL PROPERTIES

Mazzite-Na crystallizes as colorless, transparent fibers, which have a vitreous luster and white streak. The fineness of the fibers precludes the determination of the hardness, and cleavage is not apparent even at high magnification. The fibers are flexible in contrast to those of mordenite and ulexite, which occur in cavities of the same basalt. The density, 2.16 g/cm³, was measured by flotation in an aqueous solution of potassium iodomercurate. This value agrees well the calculated density, 2.18 g/cm³. The calculated density of mazzite-Mg is 2.108 g/cm³. Optically mazzite-Na is very nearly isotropic. In immersion oils the thin needles are barely discernable, and the usual Becke line method results are only approximate, $n_\varepsilon = 1.472(3)$ and $n_\omega = 1.471(3)$. Determination of the sign of elongation, slow, verifies the positive optic sign. These values are substantially less than those of mazzite-Mg ($n_\varepsilon = 1.499$ and $n_\omega = 1.506$).

CHEMICAL COMPOSITION

Electron microprobe analysis was carried out using an ARL-SEMQ instrument in wavelength dispersive mode, operating at 15 kV and with a beam current of 20 nA and diameter of 15 μm. The standards used were Amelia albite for Si, Al, and Na, Asbestos microcline for K, paracelsian for Ba, and synthetic diopside Di85-JD15, AN70 glass, Sr-anorthite, and P140 olivine for Mg, Ca, Sr, and Fe, respectively. Iron was assumed to be in the ferric state. The data acquisition and processing were performed using the PROBE program (Donovan 1995). For most zeolites, in particular those with large channels, the electron bombardment and vacuum conditions in the microprobe sample chamber cause a loss of H_2O and extra-framework cation migration. To minimize these effects, a beam current of 20 nA and a defocused beam of 15 μm and short counting times (5, 10, and 5 sec on high background, peak, and low background, respectively) were used. It was not possible to use a larger beam because of the thinness of the mazzite-Na crystals. The water content was determined by thermogravimetric analysis of a 0.18 mg sample using a Seiko SSC/5200 instrument, operating at 10 °C/min from 18 to 800 °C in air. The weight loss was 18.70% and was used to normalize each microprobe point analysis to 100%, to correct for the undetermined loss of zeolitic water under the electron beam. Table 1 shows the average of six point analyses and the chemical formula calculated on the basis of 72 oxygen atoms, the number of framework oxygen atoms in the unit cell.

TABLE 1. Chemical composition and chemical formula (based on 72 oxygen atoms) of mazzite-Na and mazzite-Mg (Coombs et al. 1998)

Oxide	wt%	Range	Standard deviation	wt%	Element	Atoms in the formula	
	mazzite-Na			mazzite-Mg		mazzite-Na	mazzite-Mg
SiO_2	57.65	56.93–58.94	0.84	54.14	Si	27.71	26.03
Al_2O_3	14.35	13.36–15.34	0.68	17.87	Al	8.13	10.13
Na_2O	8.07	7.28–8.97	0.67	0.19	Na	7.52	0.18
K_2O	0.03	0.02–0.05	0.01	3.56	K	0.02	2.18
MgO	0.22	0.03–0.46	0.15	3.14	Mg	0.16	2.25
CaO	0.18	0.01–0.75	0.15	2.53	Ca	0.09	1.30
SrO	0.01	0.00–0.04	0.02	–	Sr	–	–
BaO	0.14	0.07–0.35	0.11	0.13	Ba	0.03	0.02
Fe_2O_3	0.65	0.07–1.14	0.42	0.02	Fe	0.24	0.00
H_2O	18.70			18.42	H_2O	29.98	29.53
					E%	3.3	6.5
					Si/Al	3.41	2.57

Notes: E% = 100 × [(Al + Fe) − (Li + Na + K) − 2(Mg + Ca + Sr + Ba)] / [(Li + Na + K) + 2(Mg + Ca + Sr + Ba)] (Passaglia 1970).

The reliability of the chemical analysis is supported by the low balance error E% (Passaglia 1970), which is less than 9% for the six point analyses and 3.3% for the average analysis, and by the number of tetrahedral atoms which is very close to 36 (half the 72 framework oxygen atoms).

The chemical analysis of mazzite-Mg from Mt. Semiol, obtained by microprobe analysis (G. Vezzalini, personal communication 1996) and reported in the recommended nomenclature for zeolite minerals (Coombs et al. 1998), is given in Table 1. Comparing the formulas of the two species, mazzite-Na has an Si/Al ratio of 3.41, higher than that of mazzite-Mg (2.57); moreover, in mazzite-Mg the extra-framework cations are Mg, K, and Ca in sub-equal quantities, while in mazzite-Na, sodium is dominant with very low amounts of Mg, Ca, K, and Ba.

Because of the very thin nature of the crystals, a reasonably random X-ray powder diffraction pattern could only be obtained by using a Gandolfi camera. This pattern and the unit-cell refinement are given in Table 2, where it is compared to that of mazzite-Mg.

THE CRYSTAL STRUCTURE OF MAZZITE-Na

Experimental methods

The diffraction pattern of a very thin fiber of Mazzite-Na (0.5×0.02 mm) was collected at beam line XRD-1 at the ELETTRA synchrotron radiation source (Trieste, Italy) with a single-axis goniostat system. A set of 60 frames was measured with a MAR 165 CCD detector, using a rotation width of 3° and an exposure time of 60 s/frame. The DENZO package (Otwinowski and Minor 1997) was used for refinement of the unit-cell parameters and data reduction. The total number of integrated reflections was 12 868, of which reflections $0.26° < θ < 31.97°$ (resolution between 100.00 and 0.85 Å) were used for unit-cell refinement. The unit cell and data collection parameters are reported in Table 3.

Structural refinement

Least-squares refinement was carried out in space group $P6_3/mmc$ using the SHELX-97 computer program (Sheldrick 1997) starting from the atomic coordinates reported by Galli (1975) for mazzite-Mg. Atomic scattering curves for neutral atoms Si, O, and Na were used for tetrahedral, oxygen and H_2O, and sodium sites, respectively. Anisotropic displacement parameters were used for all framework atoms and for the extra-framework cations NaI and NaII. However, because of the high number and closeness of partially occupied sites, isotropic displacement parameters were used for NaIII and H_2O oxygen atoms. The structural refinement parameters are reported in Table 3. The refinement converged to final discrepancy factors $R(F_o) = 4.5\%$ [for 612 $F_o > 4σ (F_o)$] and $R_w(I) = 13.2\%$. A table with anisotropic displacement parameters U_{ij} has been deposited with the MSA data depository.

Atomic coordinates, occupancy factors, and thermal parameters are reported in Table 4, and interatomic distances and angles in Tables 5 and 6 for framework and extra-framework atoms, respectively. The site labels are the same as those used by Galli (1975) for mazzite-Mg.

TABLE 2. X-ray powder diffraction pattern (Gandolfi camera 114.6 mm diameter, Cu$K\alpha$ radiation) of mazzite-Na

hkl	I	d_{calc} (Å)	d_{obs} (Å)	d (mazzite-Mg) (Å)
100	10	15.76	15.63	15.93
110	100	9.10	9.08	9.20
200	20	7.88	7.86	7.96
101	70	6.83	6.86	6.89
210	70	5.96	5.95	6.02
201	20	5.46	5.50	5.53
300	15	5.25	5.25	5.31
211	40	4.683	4.681	4.729
310	10	4.371	4.364	4.423
400	15	3.940	3.939	3.986
002	80	3.789	3.787	3.824
102	5	3.715	3.684	3.717
320	20	3.615	3.613	3.655
112	40	3.498	3.511	3.531
410				3.474
202	10	3.415	3.427	3.452
500	70	3.152	3.150	3.185
302	8	3.073	3.079	3.102
330	8	3.033	3.031	3.065
420	10	2.978	2.977	3.010
222	20	2.912	2.913	2.941
510	5	2.830	2.823	2.865
511	20	2.652	2.654	2.681
600	20	2.627	2.625	
322				2.643
520	20	2.524	2.523	2.552
601	3	2.482	2.480	2.511
431	3	2.452	2.447	
203	3	2.406	2.409	2.422
332	20	2.369	2.375	2.393
440	20	2.275	2.275	2.302
313	5	2.187	2.186	2.210
620		2.185		
432	5	2.139	2.137	
522,621	5	2.100	2.101	2.123
711	5	2.012	2.012	2.037
630	5	1.985	1.986	2.006
503,800	5	1.970	1.971	1.991
333	5	1.941	1.945	
513	5	1.886	1.885	
721	8	1.866	1.866	
603	3	1.821	1.824	

Notes: The d_{calc} (Å) values were obtained from the unit-cell refinement based on powder X-ray diffraction data, which gave $a = 18.20(2)$ Å and $c = 7.579(1)$ Å. Comparison mazzite-Mg data are from ICDD file 38-426.

TABLE 3. Unit-cell and structural refinement parameters for mazzite-Na

a (Å)	18.2343(7)
c (Å)	7.6371(2)
$γ$ (°)	120.00
V (Å)³	2199.1(1)
Space group	$P6_3/mmc$
Maximum 2θ	63.54
Measured reflections	12868
Unique reflections	718
R(int) %	1.75
$R1$(%) for all 718 data	5.2
$R1$(%) for 612 $F_o > 4σ(F_o)$	4.5
$wR2$(%)	13.23
No. of parameters	107

TABLE 4. Atomic coordinates, occupancy, and displacement parameters for mazzite-Na

Atom	x	y	z	Occupancy	U_{eq} or U_{iso}*
T1	0.15791(8)	0.49004(8)	1/4	1.0	0.0162(5)
T2	0.35457(6)	0.09295(6)	0.0457(1)	1.0	0.0162(4)
O1	0.2580(2)	0.5161((4)	1/4	1.0	0.032(1)
O2	0.4246(2)	0.8493(4)	1/4	1.0	0.037(1)
O3	0.3829(3)	0.0977(2)	1/4	1.0	0.0258(9)
O4	0.4357(2)	0.1092(2)	–0.0721(4)	1.0	0.0308(8)
O5	0.1625(1)	0.3250(2)	–0.0046(5)	1.0	0.0284(9)
O6	0.2727(2)	0	0	1.0	0.0275(9)
NaI	1/3	2/3	1/4	0.24(1)	0.06(1)
NaII	1/2	0	0	0.77(1)	0.119(4)
NaIII	0.032(1)	0.144(1)	0.040(3)	0.26(1)	0.19(1)*
W1	0.4658(4)	0.9316(9)	0.719(2)	0.44(1)	0.076(4)*
W2	1/3	2/3	0.963(7)	0.63(4)	0.18(2)*
W2A	1/3	2/3	0.056(5)	0.19(4)	0.021(7)*
W3	0.243(2)	0.680(3)	3/4	0.24(2)	0.13(2)*
W5*	0.130(3)	–0.004(3)	3/4	0.46(3)	0.25(2)*
W6	0.089(2)	0.177(3)	1/4	0.36(2)	0.15(2)*
W7	0.078(2)	–0.078(2)	3/4	0.12(2)	0.07(2)*
W8	0.437(2)	0.874(3)	0.704(5)	0.08(1)	0.03(1)*

* W4 is empty in mazzite-Na.

RESULTS AND DISCUSSION

Framework

The structure refinement shows that mazzite-Na has the same framework as mazzite-Mg (Galli 1975), framework-type code MAZ (Baerlocher et al. 2001), and is hence isotypic with the synthetic Zeolite Ω (Flanigen and Kellberg 1966, 1967, 1980; Barrer and Villiger 1969; Martucci et al. 2003) and ZSM-4 (Ciric 1968; Ciric and Ried 1969; Rubin et al. 1977). The space group of mazzite-Na is $P6_3/mmc$, and its structure can be described by gmelinite-type cages superimposed by sharing hexagonal rings to form columns parallel to **c**. Adjacent columns staggered by $c/2$ are cross-linked through ladders of non-planar 5-rings, to form two different types of channels parallel to **c**, a large diameter 12-ring channel and an elliptical 8-ring channel.

The mean T1-O and T2-O distances confirm that the Si and Al atoms are largely disordered at the two tetrahedral sites (Table 5), with a slight Al-enrichment at the tetrahedral T1 site of the 6-ring gmelinite cage. The same distribution of aluminum was observed in mazzite-Mg (Galli 1975) and in its dehydrated phase (Rinaldi et al. 1975). This slight enrichment was explained by Alberti and Vezzalini (1981) on the basis of crystal-energy calculations. In the synthetic zeolite Ω (Martucci et al. 2003) the uncertainty in powder refinements prevented an accurate determination of the Al distribution. The mean T-O values of mazzite-Na are smaller than those of mazzite-Mg reflecting the higher Si/Al ratio, which is 3.41 in mazzite-Na and 2.57 in mazzite-Mg.

The T1-O2-T1 angle in mazzite-Na (Table 5) has an unusually high value of 172°, which is consistent with the Martucci et al. (2003) observations of 171° for mazzite-Mg and 176° for zeolite Ω. These anomalous values will be discussed below.

Extra-framework species

Three extra-framework cation sites and eight H_2O sites were located during the structure refinement and all are partially occupied (see Table 4). As is shown in Figure 2 the extra-framework species distribution in mazzite-Na is somewhat different

TABLE 5. Selected interatomic distances (Å) and angles (°) within the framework of mazzite-Na

T1-O1	1.641(2)	gmelinite cage	
T1-O2	1.625(1)		
T1-O4	1.655(3) (×2)	O3-O3	6.05(1)
Average	1.644		
T1-O1-T1	151.0(4)	8-ring channel	
T1-O2-T1	172.0(5)		
T2-O3-T2	145.9(3)	O2-O2	6.10(1)
T1-O4-T2	142.9(2)	O4-O4	5.65(1)
T2-O5-T2	139.8(3)	O6-O6	8.29(1)
T2-O6-T2	133.7(2)		
T2-O3	1.632(1)	12-ring channel	
T2-O4	1.626(3)		
T2-O5	1.637(2)	O5-O5	10.26(1)
T2-O6	1.641(2)	O6-O6	9.95(1)
Average	1.634		

TABLE 6. Interatomic distances (≤3.2 Å) for extra-framework atoms of mazzite-Na

NaI-O1	2.378(6) (×3)	W1-O3	3.073(5) (×2)	W5-O6	3.20(3) (×2)
NaI-O2	2.884(7) (×3)	W1-O4	3.17(1) (×2)	W5-NaIII	1.70(3) (×2)*
NaI-W2	2.19(5) (×2)	W1-NaII	1.99(2)*	W5-NaIII	2.26(3) (×2)
NaI-W2A	1.48(4) (×2)*	W1-NaII	2.40(2)	W5-NaIII	2.56(4) (×2)
		W1-W1	0.48(4)*	W5-NaIII	2.91(4) (×2)
NaII-O2	3.050(5) (×2)	W1-W3	2.96(4) (×2)	W5-W5	2.30(9)*
NaII-O4	2.825(3) (×4)	W1-W8	0.92(5)*	W5-W5	2.52(9)
NaII-W1	1.99(2) (×2)*	W1-W8	1.09(5)*	W5-W6	1.46(5)*
NaII-W1	2.40(2) (×2)			W5-W7	1.20(6)*
Na II-W8	2.53(5) (×2)	W2-NaI	2.19(5)		
Na II-W8	3.01(4) (×2)	W2-W2A	0.71(5)*	W6-O5	3.04(4) (×2)
		W2-W3	2.41(5) (×6)*	W6-NaIII	1.83(3) (×4)*
NaIII-O5	2.97(2)			W6-NaIII	2.93(3) (×4)
NaIII-O6	2.71(2)	W2A-O1	2.80(2) (×3)	W6-W5	1.46(5) (×2)*
NaIII-W5	1.70(3)*	W2A-NaI	1.48(4) (×3)*	W6-W7	2.64(4) (×2)
NaIII-W5	2.26(3)	W2A-W2	0.71(5)*		
NaIII-W5	2.56(4)	W2A-W2A	2.96(7)	W7-NaIII	2.34(2) (×4)
NaIII-W5	2.91(4)	W2A-W3	2.94(4) (×6)	W7-NaIII	2.37(3) (×4)
NaIII-W6	1.83(3)*			W7-W5	1.20(6) (×2)*
NaIII-W6	2.93(3)	W3-O3	3.02(4)	W7-W6	2.64(4) (×2)
NaIII-W7	2.34(3)	W3-W1	2.96(4) (×2)		
NaIII-W7	2.37(4)	W3-W3	1.41(8)*	W8-NaII	2.53(5)
		W3-W3	2.16(6)*	W8-NaII	3.01(4)
		W3-W3	3.08(7)	W8-W1	0.92(5)*
		W3-W8	2.16(6) (×2)*	W8-W1	1.09(5)*
				W8-W3	2.16(6) (×2)*
				W8-W8	0.71(8)*

* Distances too short for simultaneous occupation of both sites.
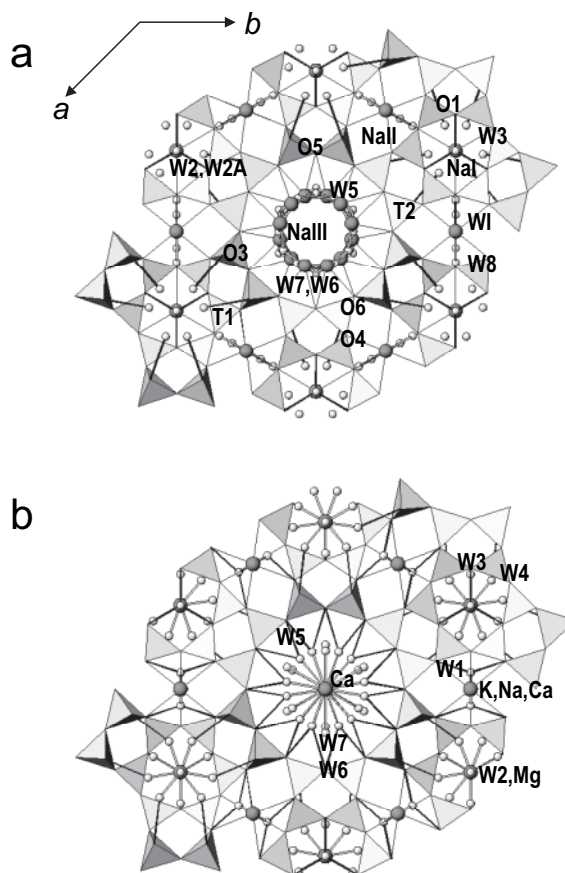

FIGURE 2. The structures of mazzite-Na (**a**) and mazzite-Mg (**b**) projected along **c**. In both drawings the larger and darker spheres represent extra-framework cations, and the smaller and lighter spheres, H_2O molecules. The thin lines are bonds between extra-framework cations and framework oxygen atoms with interatomic distances less than 3.2 Å. The double lines represent bonds between Na cations and H_2O molecules with interatomic distances less than 3.2 Å. Thick black lines are bonds between H_2O molecules and framework oxygen atoms with interatomic distances less than 3.0 Å.

from that in mazzite-Mg. Major differences are in the number and position of extra-framework species, in particular in the gmelinite-type cage and in the large 12-ring channel. One of the H_2O molecule sites (W4) found in mazzite-Mg is empty in the Na form, whereas two more sites (W8 and W2A) were located very near to W1 and W2, respectively.

Gmelinite cage. Na cations are located at the NaI site at the center of the 6-ring between superimposed gmelinite-type cages. NaI coordinates at shorter distances with three O1 oxygen atoms and two W2 H_2O molecules, and at longer distances with three O2 oxygen atoms, give a ditrigonal dipyramidal coordination (see Table 6 and Fig. 2). The W3 H_2O molecules are at the mirror plane at $z/c = 3/4$, and are disordered over six positions, of which only three are occupied simultaneously. These W3 H_2O molecules do not coordinate with the Na cation but are at a reasonable coordination distance only with O3 framework oxygen atoms. W2 and W2A are sites very near to the W2 site of mazzite-Mg, but cannot be occupied simultaneously by H_2O molecules, because they are too close. Moreover, the W2A-NaI distance is also too short; hence we can assume that either NaI and W2 or only W2A are occupied.

In mazzite-Mg (Galli 1975) the gmelinite cages are fully occupied by Mg atoms, which are sited at the center of the cage and octahedrally coordinated to six H_2O molecules. Analogously in zeolite Ω the TMA molecule substitutes for the Mg polyhedron at the center of this cage (Martucci et al. 2003), whereas in mazzite-Na the center of the gmelinite cage is empty. On the other hand, during dehydration of mazzite-Mg (Rinaldi et al. 1975), Mg moves to the top or the bottom of the cage in a position near to the plane of the 6-ring, with an occupancy of one-half. At this site Mg assumes a tetrahedral coordination with three O1 framework oxygen atoms and one residual H_2O molecule, W2. As observed by Martucci et al. (2003), in of all these phases the framework oxygen atom O1 bonds with the ions in the gmelinite cage (cations or H_2O molecules) and is responsible for the strong ditrigonal distortion of the 6-ring. This is true also for mazzite-Na, where Na atoms coordinate to both O1 and O2, but the distance to the first oxygen atom is much shorter (2.378 Å) than to the second one (2.886 Å). Notwithstanding the different atomic species and the different location of the cations in this cage, the T1-O2-T1 angle remains larger than T1-O1-T1 as observed in mazzite-Mg. In conclusion, looking at the O3-O3 distance, which is indicative of the gmelinite cage dimension, we observe that this value decreases from mazzite-Mg (6.18 Å), to mazzite-Na (6.05 Å), to zeolite Ω (6.00 Å), to dehydrated mazzite-Mg (5.83 Å). This trend is explained by the different contents of the gmelinite cage and is also shown by a change of the length of *a*, which decreases in the same order.

To summarize, the Na cations of mazzite-Na, with a lower hydration energy with respect to Mg, tend to occupy the center of the 6-ring between gmelinite cages (not the center of the cage) and to coordinate with framework oxygen atoms forming a different coordination polyhedron. The analysis of the thermal ellipsoid of NaI (see Fig. 3a) reveals that its major axis is parallel to **c**. Attempts to refine the NaI position out of the mirror plane gave poor results. However, we cannot exclude the possibility that the strongly anisotropic thermal factor of this atom is due to static disorder.
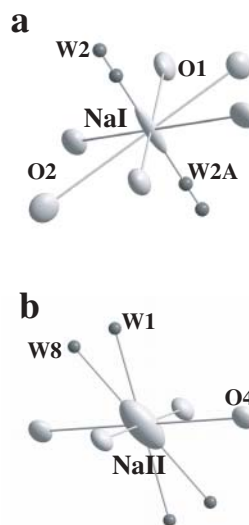

FIGURE 3. Coordination of NaI (**a**) and NaII (**b**) showing the anisotropic thermal ellipsoids of Na and framework oxygen atoms. In (**a**) W2 and W2A and in (**b**) W1 and W8 are alternately present in the bonding to Na atoms.

8-ring channel. The NaII site, at the center of the rings of 8 tetrahedra between the gmelinite-type cage chains, corresponds to site II in mazzite-Mg (Galli 1975), where it is occupied by (K, Na, Ca). In mazzite-Na this site has a similar coordination sphere with four O4 framework oxygen atoms at a shorter distance, two O2 oxygen atoms at a larger distance, and either two H_2O molecules at W1 or at W8 (Figs. 2a and 3b). The W1 and W8 sites cannot be simultaneously occupied, because the W1-W8 distance is too short (see Table 6). Considering only two H_2O molecules and only the nearer oxygen atoms, the NaII site has a distorted octahedral configuration. The size of the 8-ring channel and the distances of NaII from framework oxygen atoms are more similar to those of mazzite-Mg than that of zeolite Ω, even if the former site II is mainly occupied by K and in the latter by Na atoms. Like the NaI site, the thermal factor of the NaII site is strongly anisotropic with the major axis of the ellipsoid directed toward the H_2O molecules at the W8 site (see Fig. 3b).

12-ring channel. The Ca cations in mazzite-Mg and Na cations in zeolite Ω are located along the center line of this channel and are completely surrounded by H_2O molecules lining the channel walls. In mazzite-Na, on the contrary, this position is empty and four extra-framework sites (labeled NaIII, W5, W6, and W7) have been located in the channel. Na cations occupy the NaIII site along the channel walls and are at coordination distances from two framework oxygen atoms (O5 and O6) and six H_2O molecules. The H_2O molecules occur in three partially, but not simultaneously, occupied sites (W5, W6, and W7) as in mazzite-Mg. Similarly to mazzite-Mg, W5 and W6 form hydrogen bonds with framework oxygen atoms, but the distances in this case are longer and hence the bonds weaker. The proposed distribution of Na cations and H_2O molecules at the four sites was based on the shorter distances of NaIII from framework oxygen atoms. However, an unambiguous location of Na and H_2O molecules at these sites is not possible, owing to their low

occupancy and their large distances from framework oxygen atoms. The dimension of the 12-ring channel is similar to that of mazzite-Mg, whereas that of zeolite Ω is smaller and has a more circular shape. In fact the O5-O5 and O6-O6 distances are 10.28 and 10.08 Å, 9.88 and 9.89 Å, and 10.26 and 9.95 Å for mazzite-Mg, zeolite Ω, and mazzite-Na, respectively. It remains to be explained as to why the Na cations do not occupy the center of the 12-ring channel. We suggest that, as observed for the gmelinite cage, the Na cations have a hydration energy half that of Ca and hence tend to occupy a position nearer to the channel wall, to coordinate with framework oxygen atoms to obtain an even distribution of positive charge at both the O5 and O6 sites of the 12-ring. This result is in agreement with that reported by Yang and Armbruster (1996) and Stolz and Armbruster (2000) for exchanged heulandite, where small divalent cations are not coordinated by framework oxygen atoms and are preferentially surrounded by water molecules, whereas the Na atoms tend to shift toward the cavity walls. Nonetheless, all these arguments conflict with zeolite Ω, where the Na cations are completely hydrated at the center of the large channel.

On the whole, 125 electrons were localized at the cation sites and 166 at the H_2O molecule sites, in reasonable agreement with the 89 and 240 electrons given by the chemical analysis. This less-than-perfect correspondence is usual in zeolites, especially those with large channels, where many extra-framework sites with low occupancy are present, particularly in cation-exchanged forms.

Origin of mazzite-Na

The composition of mazzite-Na is the effect of an unusually Na-rich environment. The geologic setting of the basalt flow hosting the zeolite provides for a strongly Na-rich solution at some stage of zeolite crystallization. Morphological evidence from other zeolite species in the same flow suggests the influx of Na-rich waters occurred after most had crystallized. The strongly Na-rich composition of all zeolites at this locality (Wise and Kleck 1988) suggests extensive Na-cation exchange. Although we cannot find textural evidence that a mazzite phase had crystallized early, the presence of several extra-framework sites, all with low occupancy, supports the hypothesis of post-crystallization cation exchange (Yang and Armbruster 1996). The likelihood of a Ca→Na exchange is supported by the high Si/Al ratio of mazzite-Na. The high Si-content of the framework lowers the Coulombic force on the calcium cations and increases their diffusion coefficient (Yang et al. 1997).

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