

GARRONITE-Na, A NEW ZEOLITE SPECIES FROM MONT SAINT-HILAIRE, QUÉBEC

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ABSTRACT

Garronite-Na, ideally $\text{Na}_6(\text{Al}_6\text{Si}_{10}\text{O}_{32})\cdot 7\text{--}10\text{H}_2\text{O}$, a new mineral species, was found in the Mont Saint-Hilaire quarry, Québec. It occurs in vugs in sodalite syenite. The crystals are transparent to translucent, pale yellow in color, with a white streak and vitreous luster. Crystal aggregates are botryoidal masses up to 1.5 mm in size. The mineral is brittle with a good {011} parting. Associated minerals include aegirine, natrolite, gmelinite, and gonnardite. Garronite-Na is monoclinic, space group $I2_1$, with unit-cell parameters refined from single crystal X-ray diffraction data: a 9.990(2), b 10.032(2), c 10.036(2) Å, β 90.11(3)°, V 1005.8(7) Å³, and $Z = 1$. Electron microprobe analyses give (average of eight with ranges): Na₂O 14.28 (10.38–18.55), K₂O 1.10 (0.51–3.07), CaO 0.04 (0.01–0.11), MnO 0.02 (0.00–0.09), BaO 0.09 (0.00–0.44), FeO 0.02 (0.00–0.07), Al₂O₃ 26.89 (25.71–28.96), Nb₂O₅ 0.04 (0.00–0.10), SiO₂ 46.71 (42.65–49.32), TiO₂ 0.00 (0.00–0.02), H₂O 10.73 (10.22–11.22) (determined by crystal structure analysis), total 99.92 wt.%. The empirical formula, based on the crystal-structure analysis and ideally showing 16 (Si + Al) and 32 O atoms in the framework and 7.3 H₂O groups is: $(\text{Na}_{5.650}\text{K}_{0.286}\text{Ca}_{0.009}\text{Ba}_{0.007}\text{Mn}_{0.003}\text{Fe}_{0.003}\text{Nb}_{0.004})_{\Sigma 5.960}(\text{Al}_{6.468}\text{Si}_{9.532})_{\Sigma 16}\text{O}_{32}\cdot 7.3\text{H}_2\text{O} + (\text{O}_{0.67})$. Garronite-Na is biaxial positive, $\alpha = 1.489 \pm 0.001$, $\beta = 1.492 \pm 0.001$, $\gamma = 1.496 \pm 0.001$, $2V_{\text{meas.}} = 75(3)^\circ$, $2V_{\text{calc.}} = 82(7)^\circ$. The strongest eight reflections of the X-ray powder-diffraction pattern [$d(\text{obs.})$ in Å (hkl)] are: 7.098 (79) (011, 110), 5.026 (32) (002, 200), 4.101 (77) (112, $\bar{2}11$, $\bar{1}21$, 121), 3.172 (013, 031, 130, 310), 2.904 (14) ($\bar{2}22$, 222), 2.685 (64) (123, $\bar{3}21$), 1.9669 (14) (015, $\bar{1}43$, 341, 510), 1.7213 (11) ($\bar{3}34$, 053, 350, 433). The Mohs hardness is ~ 4 ; $D(\text{meas.}) = 2.19(2)$ and $D(\text{calc.}) = 2.071 \text{ g/cm}^3$. The structure has been refined to an R index of 0.056 for 2952 unique, observed reflections. The structure is a Si/Al–O framework like that of gismondine with Na atoms and H₂O groups in the cages.

Keywords: garronite-Na, new mineral species, crystal structure, zeolite, gismondine, non-centrosymmetric, infrared spectroscopy, hydrogen bonding, Mont Saint-Hilaire, Québec.

INTRODUCTION

Walker (1962) first described garronite from Glenariff Valley, County Antrim, Northern Ireland. This garronite is Ca-dominant and shall now be known as garronite-Ca to differentiate it from the present species description for garronite-Na. Garronite from Mont Saint Hilaire was described briefly by Horváth & Gault (1990) but was not fully characterized, although it was known to be Ca-deficient and Na-rich. A garronite-like mineral containing very little Ca was found in the Francon Quarry, Montreal (Tarassoff *et al.* 2006). The specimen was not fully analyzed so one cannot be certain that it is the same species. Artioli (1992) solved the crystal structure of garronite-Ca from a locality in Goble, Oregon, USA.

Garronite is a member of the zeolite group of minerals, which has 84 distinct species at this time. Within the group there are seven species with the same framework topology (GIS): amicitze, garronite-Ca, garronite-Na, gismondine-Ca, gismondine-Ba, and gobbinsite (Table 1). A great deal of effort has been invested in synthesizing GIS-type compounds due to the sorption properties of the crystal structures. As early as 1959 this product was synthesized (Barrer *et al.* 1959) and termed Na-P zeolite. Interest in the phase began as an early replacement in phosphate detergents, as it had very good adsorption properties for Ca cations with greatly reduced environmental impact.

The new mineral and its name have been approved by the Commission on New Minerals, Names and Classification (CNMNC), International Mineralogical

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TABLE 1. ZEOLITE SPECIES WITH THE GISMONDINE FRAMEWORK STRUCTURE (*gis*)

Type locality	amicite	garronite-Ca	garronite-Na	gismondine-Ca	gismondine-Ba	gobbinsite
Formula	Hegau, Germany $K_4Na_4(Al_6Si_8O_{32}) \cdot 10H_2O$	Antrim, Ireland $Na_{1.25}Ca_{2.50}(Al_6Si_{10}O_{32}) \cdot 14H_2O$	Mont Saint Hilaire, Canada $Na_6(Al_6Si_{10}O_{32}) \cdot 7.3H_2O$	Capo di Bove, Italy $Ca_4(Al_6Si_8O_{32}) \cdot 16H_2O$	Slag, Yorkshire, England $Ba_4(Al_6Si_8O_{32}) \cdot 12H_2O$	Bundoorra, Australia $Na_5(Al_6Si_{10}O_{32}) \cdot 12H_2O$
Space group	$I\bar{1}21$ (#5)	$\bar{1}4m2$ (#119)	$I121$ (#5)	$P2_1/c$ (#14)	monoclinic	$Pm\bar{m}b$ (#62)
<i>a</i> (Å)	10.226	9.927	9.990	10.02	14.896	10.104
<i>b</i>	10.422	9.927	10.032	10.62	9.951	9.782
<i>c</i>	9.884	10.303	10.036	9.84	7.613	10.152
α (°)	90	90	90	90	90	90
β	88.32	90	90.11	92.42	103.25	90
γ	90	90	90	90	95	90
<i>V</i> (Å ³)	1051.7	1015.3	1005.8	1046.2	1098.4	1003.4
<i>D</i> (g/cm ³)	2.15	2.20	2.07	2.28	2.37	2.15
Optics	α 1.485 β 1.490 γ 1.494	ε 1.500 ω 1.502	α 1.489 β 1.492 γ 1.496	α 1.525 β 1.531 γ 1.541	n (calc) 1.45	α 1.489 β 1.489 γ 1.494
Twin	None	Visible optically	$m\{011\}$ and $m\{10\bar{1}\}$	None	SEM visible	$m\{110\}$
Reference	Alberti <i>et al.</i> (1979)	Artoli (1992)	This work	Fischer (1963)	Braithwaite <i>et al.</i> (2001)	Gatta <i>et al.</i> (2010)

Association (IMA #2015–015). The species name is in keeping with the recommended nomenclature of zeolite minerals (Coombs *et al.* 1997). The holotype specimen (catalogue #CMNMC 86893) is housed in the collection of the Canadian Museum of Nature, Ottawa, Ontario, Canada.

OCCURRENCE

Garronite-Na was found in the Poudrette quarry, Mont Saint-Hilaire, La Vallée-du-Richelieu RCM, Montérégie, Québec, Canada (45° 33'N, 73° 08'W). Mont Saint Hilaire is an alkaline intrusive complex of Cretaceous age, approximately 40 km east of Montreal. Quarrying operations have exposed numerous pegmatites, miarolitic cavities, breccias, and xenoliths in that part of the intrusion described as the East Hill Suite (Currie 1989), which consists primarily of sodalite and nepheline syenites. Garronite was first found at Mont Saint-Hilaire in tiny vugs in tawite (sodalite-rich) segregations in nepheline syenite by László Horváth and Elsy Pfenninger-Horváth in 1984. It was recognized as a potential new member of the zeolite group from the X-ray powder diffraction pattern (XRPD) and preliminary electron microprobe data, but the material was not suitable for crystal-structure analysis. More suitable material was found in 1991 by Gilles Haineault in a hydrothermally altered zone in the so-called Poudrette pegmatite, which is the largest pegmatite exposed to date in the quarry. Here it occurs as opaque, white spheres and as aggregates or individual, opaque, white, frosted, crude to sharp pseudo-octahedral crystals up to 2 mm in diameter. Associated minerals in the same vug are natrolite, gmelinite, aegirine, and gonnardite, but more than 150 species have been identified in the pegmatite.

PHYSICAL AND OPTICAL PROPERTIES

Garronite-Na belongs to the monoclinic crystal system. It occurs as rough botryoidal aggregates up to 1.5 mm on grayish natrolite. Garronite-Na is transparent to translucent, pale yellow, with a white streak and vitreous luster. It is not fluorescent in either short-wave or long-wave ultraviolet light. It has an approximate hardness of 4 (Mohs hardness scale), is brittle, and has no apparent cleavage or parting when being broken. The density measured by sink/float in Clerici solution is 2.19(2) g/cm³ while a calculated density of 2.071 g/cm³ is obtained from the empirical formula using single-crystal unit-cell data.

Garronite-Na is biaxial positive, $\alpha = 1.489 \pm 0.001$, $\beta = 1.492 \pm 0.001$, $\gamma = 1.496 \pm 0.001$, $2V_{\text{meas.}}$ (from extinction curves) = 75(3)°, $2V_{\text{calc.}}$ = 82(7)°. Refractive indices were measured with a spindle stage using 590 nm incident light. Dispersion could not be

observed and pleochroism is absent. The optical orientations coincide with the cell vectors, but all are too similar to differentiate using precession photographs. The problem is compounded by multiple twin laws. Twinning is not definitively observed microscopically, but extinction is not sharp, which is probably a result of twinning.

CHEMICAL COMPOSITION

Electron-microprobe analysis

Microanalysis (Table 2) was carried out using a JEOL 8230 electron microprobe at the University of Ottawa. The accelerating voltage was 15 kV with a 10 nA beam current and a defocused beam size of 20 μm . Under these conditions, count rates were constant over the duration of the analyses (20s peak, 10s background). The following standards were used: SiK α , AlK α , and KK α , sanidine; CaK α , MgK α diopside; FeK α , hematite; MnK α , tephroite; TiK α , rutile; NaK α , albite; NbL α , columbite-(Mn); BaL α , sanbornite. Raw counting data was corrected for overlap using empirical correction factors, and matrix corrections were done using a PAP correction (Pouchou & Pichoir 1984). Eight analyses were obtained from two separate grains. One analysis with a very low total was eliminated. Grain #1 had spot analyses 8, 9, 10, 11, and 15 and grain #2 had spot analyses 12 and 13. The two grains have compositions that are similar enough for averaging.

Water analyses by direct weight-loss measure were not performed due to the small sample size, but we consider crystal-structure analysis a direct method for determining the amount of water in a mineral.

The empirical formula, based on the crystal-structure analysis and ideally having 16 (Al³⁺ + Si⁴⁺) cations total with 32 O atoms in the framework and 7.3 H₂O groups as determined in the crystal structure analysis is: (Na_{5.650}K_{0.286}Ca_{0.009}Ba_{0.007}Mn_{0.003}Fe_{0.003}Nb_{0.004}) Σ 5.960H_{0.50}[(Al_{6.468}Si_{9.532}) Σ 16O₃₂] \cdot 7.3H₂O. The 'excess' H in this calculation is for charge balance. The simplified formula is Na₆(Al₆Si₁₀O₃₂) \cdot 7.3H₂O. The ideal formula is Na₆(Al₆Si₁₀O₃₂) \cdot 7–10H₂O, where 10 H₂O groups would be the maximum allowable for the three water sites (O₉, O₁₀, O₁₁) found in this crystal structure.

Infrared analysis

The infrared spectrum (Fig. 1) of garronite-Na was obtained using a Bomen Michelson MB-120 Fourier-transform infrared spectrometer with a diamond-anvil cell microsampling device. The frequencies are well resolved. There is a major, broad peak in the high-frequency range 3500–3000 cm⁻¹ and centered at 3417

TABLE 2. GARRONITE-Na: CHEMICAL COMPOSITIONS

Spot #	8	9	10	11	12	13	15	Average	Min.	Max.
Na ₂ O (wt.%)	14.79	18.55	13.41	14.71	15.89	12.2	10.38	14.28	10.38	18.55
K ₂ O	1.46	0.51	1.22	0.82	1.42	1.37	0.91	1.10	0.51	3.07
CaO	0.04	0.01	0.03	0.05	0.03	0.05	0.04	0.04	0.01	0.11
BaO	0.16	0.05	0.18	0.02	0.07	0.12	0.00	0.09	0.00	0.44
FeO	0.00	0.07	0.00	0.00	0.03	0.05	0.00	0.02	0.00	0.07
MnO	0.00	0.09	0.00	0.00	0.00	0.05	0.00	0.02	0.00	0.09
MgO	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Al ₂ O ₃	26.26	28.96	26.4	26.03	25.71	27.07	27.77	26.89	25.71	28.96
SiO ₂	48.07	42.65	47.56	45.54	45.7	48.16	49.32	46.71	42.65	49.32
TiO ₂	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02
Nb ₂ O ₅	0.09	0.04	0.02	0.00	0.1	0.04	0.00	0.04	0.00	0.10
H ₂ O	10.81	10.50	10.76	10.43	10.40	10.63	11.22	10.73	10.22	11.22
Total	101.69	101.44	99.58	97.60	99.35	97.74	99.66	99.92	97.74	101.69

Note: Formula contents based on 16 (Al³⁺ + Si⁴⁺) in framework and 7.3 H₂O from the crystal structure analysis: (Na_{5.650}K_{0.286}Ca_{0.009}Ba_{0.007}Mn_{0.003}Fe_{0.003}Nb_{0.004})_{Σ5.960}H_{0.50}(Al_{6.468}Si_{9.532})_{Σ16}O₃₂·7.3H₂O
Excess H is added for charge balance.

cm⁻¹, due to [OH]⁻ stretching. There is a minor sharp peak at 2964 cm⁻¹ attributed to [H₂O] stretch, a medium-sharp peak at 1642 cm⁻¹ due to [H₂O] bend, and a medium-sharp peak at 1261 cm⁻¹ due to [OH]⁻ bending. Comparing the remaining part of the spectrum to spectra given in Farmer (1974), the following frequency regions are assigned modes: the large, strong peak centered at 992 cm⁻¹ with 1100 cm⁻¹ shoulder is the condensed [SiO₄] polyhedra stretching mode; medium-sharp peaks centered at 802, 741, and

668 cm⁻¹ are assigned to [SiO₄] and [AlO₄] bending modes for condensed polyhedra.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

X-ray powder diffraction

X-ray powder diffraction data (Table 3) were acquired with a Bruker D8-Discover instrument equipped with a Hi-Star 2D detector and using GADDS Software calibrated with a statistical ap-

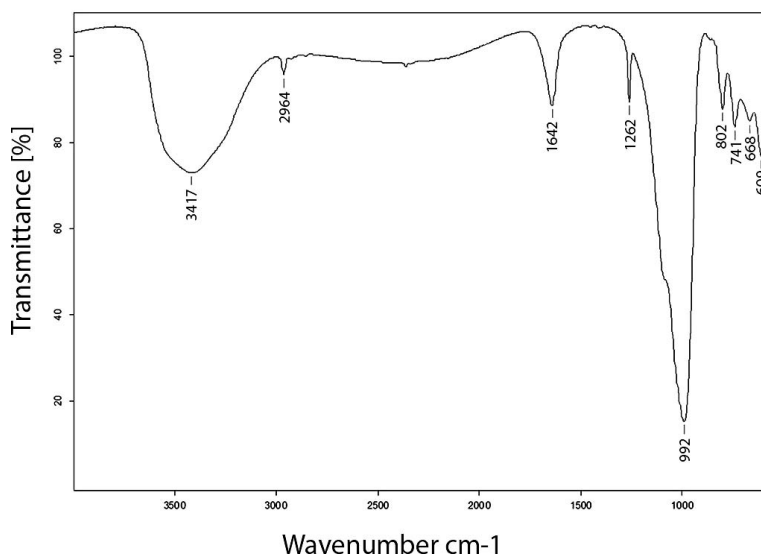


FIG. 1. The infrared spectrum for garronite-Na.

TABLE 3. GARRONITE-Na: X-RAY POWDER DIFFRACTION

<i>I</i> obs	<i>I</i> calc*	<i>d</i> obs	<i>d</i> calc**	<i>hkl</i>
79	87	7.098	7.112	011
	4		7.086	101
	100.0		7.082	110
32	36	5.026	5.048	002
	49		5.005	200
77	18	4.101	4.102	112
	14		4.101	211
	37		4.100	121
	33		4.091	121
	3		4.085	211
100	67	3.172	3.190	013
	25		3.171	031
	23		3.168	130
	63		3.166	310
14	9	2.904	2.905	222
	5		2.893	222
64	5	2.685	2.697	213
	9		2.694	123
	29		2.687	123
	3		2.685	132
	31		2.681	321
	2		2.681	132
	3		2.681	231
	3		2.676	231
	5		2.675	312
	10		2.674	321
5	9	2.505	2.505	040
9	7	2.363	2.381	114
	2		2.374	114
	2		2.364	411
	7		2.357	411
5	2	2.050	2.042	422
14	4	1.9669	1.9793	015
	7		1.9715	143
	7		1.9636	341
	4		1.9632	510
1	2	1.8363	1.8388	125
	2		1.8302	521
6	5	1.7768	1.7779	044
	5		1.7704	440
11	3	1.7213	1.7278	334
	6		1.7248	053
	6		1.7218	350
	3		1.7180	433
4	5	1.6755	1.6826	006
	2		1.6683	442
	5		1.6683	600
5	2	1.6298	1.6354	116
	2		1.6283	532
	2		1.6258	611
3	2	1.5870	1.5855	062
	2		1.5841	260
4	3	1.5478	1.5541	145

TABLE 3. CONTINUED.

<i>I</i> obs	<i>I</i> calc*	<i>d</i> obs	<i>d</i> calc**	<i>hkl</i>
	3		1.5444	541
	<2	1.5112	1.5123	262
	<2		1.5106	262
5	2	1.4784	1.4894	316
	2		1.4848	136
	2		1.4789	163
	2		1.4776	631
	2		1.4748	613
4	2	1.4199	1.4232	534
	2		1.4184	435
1	2	1.3946	1.3967	046
	2		1.3957	604
	2		1.3923	406
	2		1.3886	640
6	2	1.3650	1.3717	127
	3		1.3636	363
	3		1.3636	363
	2		1.3434	721
1	<2	1.3395	1.3400	642
1	3	1.3165	1.3212	037
	2		1.3163	730

* Calculated from the crystal structure determination.

** Calculated from XRPD Rietveld unit-cell refinement with $a = 10.010(2)$, $b = 10.020(2)$, $c = 10.096(2)$ Å, $\beta = 90.35(3)^\circ$, $V = 1012.6(3)$ Å³.

proach by Rowe (2009). This project was initiated based on very subtle differences in profile fitting for 2-theta values less than 35° to a relatively poor fit above the aforementioned value, when comparing the new species to the diffraction pattern of garronite-Ca. The search/match routine was expanded to a data base containing synthetic material, which indicated a more accurate match to the structure of a synthetic sodium aluminum silicate hydrate, therefore making it a new mineral species. The chemistry later confirmed this hypothesis. The pattern for garronite-Na was also compared to the diffractograms of minerals with similar structures, such as amicitte, gismondine, and gobbinsite, which displayed some similarities in peak distribution to that of the new species. A copper X-ray source was used for $K\alpha = 1.5418$ Å. Unit-cell parameters refined from the powder data using Bruker's Topas Rietveld software (Bruker 2010) are a 10.010(2), b 10.020(2), c 10.096(2) Å, β 90.35(3)°, V 1012.6(3) Å³. It should be noted that the Rietveld method was used only for unit-cell refinement in order to obtain a calculated value for the angle β , which was impossible to obtain through typical peak-indexing unit-cell refinement. The structure was actually solved with single-crystal X-ray diffraction data. The strongest eight reflections of the X-ray powder-diffraction

TABLE 4. GARRONITE-Na: DATA COLLECTION AND STRUCTURE REFINEMENT INFORMATION

Space Group	<i>I</i> 2 (SG # 5)	Merged measured reflections	5866
<i>a</i> (Å)	9.990(2)	Unique reflections	2952
<i>b</i> (Å)	10.032(2)	Observed reflections [> 4σ(<i>f</i>)]	2740
<i>c</i> (Å)	10.036(2)	<i>R</i> (int)	0.067
α (°)	90	Goodness of fit on <i>F</i> ²	1.038
β (°)	90.11(3)	<i>R</i> index for all data	0.068
γ (°)	90	<i>R</i> index for observed data	0.075
<i>V</i> (Å ³)	1005.8(7)	<i>R</i> for merged data	0.056

Ideal unit-cell contents: Na₆Al₆Si₁₀O₃₂·8H₂O

μ = 0.65 mm⁻¹

Refinement by full-matrix least squares on *F*²

pattern [*d*(obs.) in Å (*hkl*)] are: 7.098 (79) (011, 110), 5.026 (32) (002, 200), 4.101 (77) (112, $\bar{2}$ 11, $\bar{1}$ 21, 121), 3.172 (013, 031, 130, 310), 2.904 (14) ($\bar{2}$ 22, 222), 2.685 (64) (123, $\bar{3}$ 21), 1.9669 (14) (015, $\bar{1}$ 43, 341, 510), 1.7213 (11) ($\bar{3}$ 34, 053, 350, 433).

Single-crystal X-ray diffraction

To obtain a single crystal of garronite-Na, an aggregate was trimmed to a needle-like splinter, 20 × 20 × 70 μm. Intensity data were collected with a fully automated Bruker D8 three-circle diffractometer equipped with a rotating-anode generator operating at 50 kV, 24 mA, with MoKα radiation, multi-layer optics, and an APEX-II CCD detector. This setup yields a very intense X-ray beam. The detector is 5 cm from the crystal. Integrated intensities were collected up to 2θ = 60°, using 6 s frame counts and a frame width of 0.3°. A total of 17583 reflections were collected, of which 5866 were unique in *P*1. Unit-cell parameters for the single crystal were refined using 8157 indexed reflections. Due to problems with the choice of crystal system for garronite, as will be discussed later in the text, the cell parameters were refined in the triclinic crystal system as a starting point: *a* 8.6821(4) Å, *b* 8.6701(4) Å, *c* 8.6730(4) Å, α = 109.3191(7)°, β = 109.3428(7)°, γ = 109.7006(7)°, *V* = 502.88(7) Å³. Data pertinent to the intensity-data collection are given in Table 4.

Reduction of the intensity data, structure determination, and structure refinement were done with the SHELXTL (Sheldrick 1997) package of computer programs. Data reduction included corrections for background, scaling, and Lorentz-polarization factors. An empirical absorption correction (SADABS, Sheldrick 1998) was applied. The merging *wR*(int)² for the complete unique dataset (5866 reflections) decreased from 0.058 before the absorption correction

to 0.042 after the absorption correction. In the initial data reduction a list of 22 space groups in five crystal systems were given as possible choices for the crystal structure. This reduces to 15 space group choices if multiple orientations are ignored. The agreement factor for symmetry-related reflections, *R*(int), for a particular space group varied from 0.64 to 0.41 for 12 of the choices and was much better for the remaining three: *R*(int) values for monoclinic *I*, 0.067, (1389 unique reflections), for tetragonal *I*, 0.114, (2161 unique reflections), and for orthorhombic *I*, 0.409, (2085 unique reflections). The tetragonal space group is that of the initial garronite-Ca structure determined by Artioli (1992).

The choice of space group for garronite has always posed a problem and twinning compounds this problem. Space-group choice is discussed in detail by Artioli & Marchi (1999). Their resolution of the problem for garronite-Ca was space group *I*2/*a*. Their experiment used synchrotron powder diffraction data. In the present study on garronite-Na we used X-ray single-crystal diffraction data. To prevent making any false assumptions about the crystal system and space group, structure solution was begun in the triclinic crystal system. Assigning phases to a set of normalized structure factors gave a mean value |*E*² - 1| of 0.768, suggesting the non-centrosymmetric space group *P*1. The phase-normalized structure factors were used to construct an *E*-map on which were located positions for eight Si/Al atoms and 16 additional atoms which were assigned the O scattering curve. These initial sites were refined, and six new sites added in the framework cages. Eventually, the correct scattering curves could be assigned to each of the new sites, Na or O (water group). This structure model gave a residual of *R* = 0.073. This model was tested for higher symmetry using MISSYM (Le Page 1987). With just the framework atoms; *i.e.*, eight Si atoms and 16 O atoms, the added symmetry elements were a 4₁-screw axis and a center of symmetry. Ordering Si and Al in the framework based on BV calculations leaves a glide plane but no 4₁ screw axis. Including all atoms in the model, *i.e.*, eight Si atoms, 16 O atoms, four Na atoms, and two water groups, there is a two-fold axis. On the basis of these findings it was concluded that the best symmetry for these data was monoclinic.

Assigning phases to a set of normalized structure factors gave a mean value |*E*² - 1| of 0.751, suggesting the non-centrosymmetric space group *I*2. The phase-normalized structure factors were used to construct an *E*-map on which were located positions for four Si atoms and eight additional atoms which were assigned the O scattering curve. These initial sites were refined and new sites added. Eventually, the correct scattering curves could be assigned to each site. In the refinement

TABLE 5a. GARRONITE-Na: COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS AND BOND VALENCE SUMS (νu)

Atom	x/a	y/b	z/c	sof	$U_{eq.}/U_{ISO}$	BVS	BVS _{corr}
Si1	0.85957(6)	0.20483(5)	0.16817(5)	0.919(2)	0.01429(12)	3.91(1)	3.925
Si2	0.82952(5)	0.45345(5)	0.35748(5)	0.982(2)	0.01516(11)	4.18(1)	4.192
Si3	0.82915(6)	0.24197(5)	-0.14140(6)	0.892(2)	0.01375(13)	3.91(1)	3.925
Si4	0.85730(6)	0.49041(5)	0.66797(6)	0.936(2)	0.01555(13)	3.83(1)	3.846
O1	0.8179(2)	0.27428(18)	0.02211(16)	1	0.0318(4)	1.728(6)	1.73
O2	0.8042(2)	0.31329(16)	0.28674(17)	1	0.0341(5)	1.978(7)	1.98
O3	0.78726(19)	0.06500(19)	0.1966(2)	1	0.0363(5)	2.020(7)	2.02
O4	0.02454(19)	0.1780(2)	0.1852(2)	1	0.0360(5)	1.848(7)	1.85
O5	0.8152(2)	0.4363(2)	0.51828(19)	1	0.0338(5)	2.083(8)	2.08
O6	0.97663(17)	0.51362(19)	0.3199(2)	1	0.0306(4)	1.917(7)	1.92
O7	0.71283(17)	0.14512(17)	-0.1979(2)	1	0.0286(4)	1.949(6)	1.95
O8	0.79879(17)	0.39254(19)	-0.2159(2)	1	0.0311(4)	1.915(7)	1.92
Na1A	0.9733(7)	-0.1737(12)	0.4202(7)	0.349(2)	0.1428(16)	0.321(8)	0.349
Na1B	0.0167(5)	0.8354(9)	0.7152(6)	0.435(5)	0.1428(15)	0.559(11)	0.435
Na2	0.6509(4)	0.2568(4)	0.5803(4)	0.532(5)	0.0933(12)	0.939(9)	0.532
Na3	0	0.1433(11)	½	0.560(11)	0.240(8)	0.582(6)	0.560
O9A	0.7664(5)	0.0468(7)	0.4858(5)	0.6	0.0985(17)	1.037(5)	1
O9B	0.6584(4)	0.1024(6)	0.4813(5)	0.4	0.0985(17)	1.420(11)	1
O10	0.9256(3)	1.0019(4)	0.6615(3)	0.665(7)	0.05	1.249(11)	0.665
O11	0	0.8956(13)	0	0.298(9)	0.05	0.437(7)	0.298
H9A	0.7058(6)	0.0553(10)	0.4097(5)	0.6	0.05	0.877(4)	0.6
H9B	0.5708(5)	0.0620(12)	0.465(3)	0.4	0.05	0.492(3)	0.4
H10	0.8637(7)	0.0459(11)	0.6010(8)	0.9	0.05	1.125(5)	0.9

Note: BVS_{corr} = Bond valence sum corrected for site occupancy and Si/Al at tetrahedral sites. Bond valence calculations based on the constants of Brese & O'Keeffe (1991).

TABLE 5b. GARRONITE-Na: ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	$U_{eq.}$
Si1	0.0153(2)	0.0148(2)	0.0129(2)	-0.00236(18)	0.00109(18)	-0.00440(18)	0.01429(12)
Si2	0.0179(2)	0.0146(2)	0.0130(2)	-0.00206(17)	0.00065(17)	0.00360(18)	0.01516(11)
Si3	0.0105(2)	0.0115(2)	0.0193(3)	0.0012(2)	-0.0001(2)	0.00012(18)	0.01375(13)
Si4	0.0161(2)	0.0131(2)	0.0174(2)	0.00265(19)	0.0000(2)	-0.00013(19)	0.01555(13)
O1	0.0484(9)	0.0284(7)	0.0187(7)	0.0059(6)	0.0006(7)	0.0221(7)	0.0318(4)
O2	0.069(1)	0.0130(6)	0.0198(7)	-0.0023(5)	0.0074(8)	-0.0039(7)	0.0341(5)
O3	0.0287(8)	0.0280(8)	0.052(1)	0.0084(8)	-0.0030(8)	-0.0059(7)	0.0363(5)
O4	0.0265(7)	0.0406(10)	0.0410(9)	0.0060(8)	-0.0002(7)	-0.0030(8)	0.0360(5)
O5	0.0331(8)	0.0424(10)	0.0259(8)	0.0028(8)	0.0019(7)	0.0113(8)	0.0338(5)
O6	0.0178(6)	0.0351(9)	0.0390(9)	0.0097(8)	0.0013(7)	-0.0022(6)	0.0306(4)
O7	0.0275(7)	0.0187(6)	0.0395(9)	-0.0065(6)	-0.0108(7)	-0.0128(6)	0.0286(4)
O8	0.0193(7)	0.0298(8)	0.044(1)	0.0173(7)	0.0057(7)	-0.0024(6)	0.0311(4)
Na1A	0.067(3)	0.269(3)	0.093(3)	-0.073(2)	0.014(2)	-0.067(4)	0.1428(16)
Na1B	0.067(2)	0.269(3)	0.093(3)	-0.073(3)	0.014(2)	-0.067(2)	0.1428(15)
Na2	0.087(2)	0.0685(17)	0.124(3)	0.0492(16)	-0.0486(18)	-0.0401(15)	0.0933(12)
Na3	0.52(2)	0.107(6)	0.088(5)	0	-0.090(8)	0	0.240(8)

process, it became evident that two sites Na1 and O9 were best refined as split sites. In the last stages of refinement, there were electron residuals of +1.10 and -0.54 $e/\text{Å}^3$. In the final least-squares refinement, all non-H atom positions were refined with anisotropic

displacement parameters. The weighting scheme is inversely proportional to $\sigma^2(f)$. The addition of an isotropic extinction correction did not improve the refinement. The data did not yield a high-quality refinement due to problems with complex multiple

TABLE 6. GARRONITE-(Na) SELECTED BOND DISTANCES (Å)

Si1–O3	1.604(2)	Si2–O2	1.595(2)	Si3–O7	1.617(2)	Si4–O8	1.633(2)
Si1–O1	1.675(2)	Si2–O5	1.630(2)	Si3–O4	1.657(2)	Si4–O5	1.651(2)
Si1–O4	1.678(2)	Si2–O6	1.634(2)	Si3–O1	1.677(2)	Si4–O6	1.680(2)
Si1–O2	1.705(2)	Si2–O3	1.705(2)	Si3–O8	1.712(2)	Si4–O7	1.729(2)
<Si1–O>	1.666	<Si2–O>	1.641	<Si3–O>	1.666	<Si4–O>	1.673
Na1A–Na1B	1.366(9)	Na2–O9B	1.842(7)	Na3–O10 ×2	2.280(8)		
Na1A–Na1A	1.688(13)	Na2–O11	2.203(9)	Na3–O9A ×2	2.530(7)		
Na1A–O10	2.19(1)	Na2–O5	2.516(4)	Na3–O4 ×2	3.188(2)		
Na1B–O10	1.976(9)	Na2–O7	2.567(4)	Na3–O2 ×2	3.361(6)		
Na1B–Na2	2.765(7)	Na2–O9A	2.583(8)	Na3–O5 ×2	3.48(1)		
Na1B–O11	2.926(6)	Na2–O8	2.866(5)				
Na1B–O2	2.968(6)						
Na1B–O7	2.988(7)						
D–H	d(D–H)	d(H–A)	<DHA	d(D–A)	A		
O9A–H9A	0.978(6)	2.292(5)	122.0(5)	2.916(5)	O3		
O10–H10	0.972(7)	1.509(9)	152.8(11)	2.414(6)	O9A		

twinning. Bearing this in mind, locating H atoms is questionable. We present three H atom locations that we feel are correct. The H positions are from difference-Fourier maps and were refined with soft constraints, an O–H distance of $0.98 \pm .01$ Å, and a fixed isotropic displacement parameter assigned to all H positions. The site occupancy assigned to each H is consistent with its associated O atom. The O–H distance of $0.98 \pm .01$ Å is a proton-proton distance as found in neutron diffraction experiments and is longer than the O–H distance of 0.85 Å found in XRSC experiments. The authors believe the proton-proton distance more accurately represents the atomic structure. The final positional and anisotropic displacement parameters are given in Table 5, and selected bond lengths and angles in Table 6. Tables listing the observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, on the MAC website [document: CM54-5_10.3749/canmin.1600018].

DESCRIPTION OF THE STRUCTURE

There have been several space groups used in the solution of the crystal structures of garronite, the closely related structure of gismondine, and synthetic materials of both species (Table 7). The crystal structure of garronite-Ca, $\text{NaCa}_{2.5}\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 13\text{H}_2\text{O}$, is in tetragonal space group $I4m2$ (Artioli 1992). A Na-free synthetic garronite, $\text{Ca}_{2.83}\text{Al}_{5.66}\text{Si}_{10.34}\text{O}_{32} \cdot 13.9\text{H}_2\text{O}$, was refined in space group $I4_1/a$ by Schröpfer & Joswig (1997) (Table 1). In the present study of the new mineral garronite-Na, $\text{Na}_{5.69}\text{Al}_{6.52}\text{Si}_{9.60}\text{O}_{32} \cdot 7.3\text{H}_2\text{O}$, the structure was solved in space group $I2$.

In the structure of garronite-Na, there are four sites containing Si and Al in tetrahedral coordination. The framework formed by these tetrahedra is known as the “P group” of zeolites (Taylor & Rustum 1964). The Structure Commission of the International Zeolite Association classify this framework as the gismondine-type of structure (*gis*). Gismondine has fully ordered Si and Al sites, but garronite-Ca has disordered tetrahedral sites. As would be expected, attempts at refining the Si/Al ratio at each site were futile and ended in non-convergence. Thus only site occupancy of the *Si* sites could be satisfactorily refined. Garronite-Na has partially ordered tetrahedral sites with the *Si2* site having the highest Si content and the *Si4* site having the highest Al content. In Table 5a, note the average bond lengths for the four Si–O bonds in each tetrahedron. The Si-rich site has a shorter average bond length than the Al-rich site and subsequently a higher bond valence (Table 5a). Partial ordering at the tetrahedral sites lowers the symmetry from $I4_1/amd$ to $I2$. Gottardi & Alberti (1974) discussed this in terms of a domain structure. The framework structure is shown in Figure 2 with its topological equivalent shown in Figure 3. The tetrahedral framework is composed of four- and eight-membered rings that are linked longitudinally in a crankshaft chain configuration (Baerlocher *et al.* 2007). A simpler representation that emphasizes the cage-like units of these channels is shown in Figure 4 in topological format as a single *gis* cage.

The three *Na* sites, with one site split (*Na1*), have a total site occupancy of 6.38 atoms/unit cell, or 70.2 electrons. This agrees very well with the chemical analyses that give an average total of 68.4 electrons at the Na site. *Na1* and *Na2* are both bonded to O atoms

TABLE 7. COMPARISON OF GARRONITE-Na, GARRONITE-Ca, AND SYNTHETIC GARRONITE-Na WITH GISMONDINE

	garronite-Na		garronite-Ca		Syn garronite-Na		Synthetic garronite-Ca		gismondine	
Type locality	Mont Saint Hilaire, Canada	Antrim, Ireland			Synthetic low-Si		Synthetic high-Si		Capo di Bove, Italy	
Formula	$\text{Na}_6(\text{Al}_6\text{Si}_{10}\text{O}_{32}) \cdot 7.3\text{H}_2\text{O}$	$\text{Na}_{1.25}\text{Ca}_{2.50}(\text{Al}_6\text{Si}_{10}\text{O}_{32}) \cdot 14\text{H}_2\text{O}$	$\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{32}) \cdot 15\text{H}_2\text{O}$		$\text{Na}_4(\text{Al}_4\text{Si}_{12}\text{O}_{32}) \cdot 14\text{H}_2\text{O}$		$\text{Ca}_{2.83}(\text{Al}_{5.66}\text{Si}_{10.34}\text{O}_{32}) \cdot 13.9\text{H}_2\text{O}$		$\text{Ca}_4[\text{Al}_8\text{Si}_8\text{O}_{32}] \cdot 16\text{H}_2\text{O}$	
Space group	$I\bar{1}21$ (#5)	$I\bar{4}m2$ (#119)	$C12/c1$ (#15) $\rightarrow I12/a1$		$I4_1/amd$ (#41)		$I4_1/a$ (#88)		$P2_1/c$ (#14)	
<i>a</i>	9.990	9.927	14.239 \rightarrow 10.007		9.999		9.873		10.02	
<i>b</i>	10.032	9.927	9.984 \rightarrow 9.984		9.999		9.873		10.62	
<i>c</i>	10.036	10.303	10.007 \rightarrow 10.205		10.070		10.288		9.84	
α	90	90	90 \rightarrow 90		90		90		90	
β	90.11	90	134.22 \rightarrow 90.43		90		90		92.42	
γ	90	90	90 \rightarrow 90		90		90		90	
<i>V</i>	1005.8	1015.3	1019.5		1006.7		1002.8		1046.2	
<i>D</i> (g/cm ³)	2.07	2.20	2.30		2.13		1.98		2.28	
Optics	α 1.489 β 1.492 γ 1.496	ϵ 1.500 ω 1.502	<i>n</i> (calc) 1.510		<i>n</i> (calc) 1.495		<i>n</i> (calc) 1.440		α 1.525 β 1.531 γ 1.541	
Twin	$m\{011\}$ and $m\{10\bar{1}\}$	Visible optically	SEM visible {111}		Visible		None		None	
Reference	This work	Artoli (1992)	Albert <i>et al.</i> (1998)		Håkansson & Fålhög (1990)		Schröpfer & Joswig (1997)		Fischer (1963)	

GARRONITE-Na

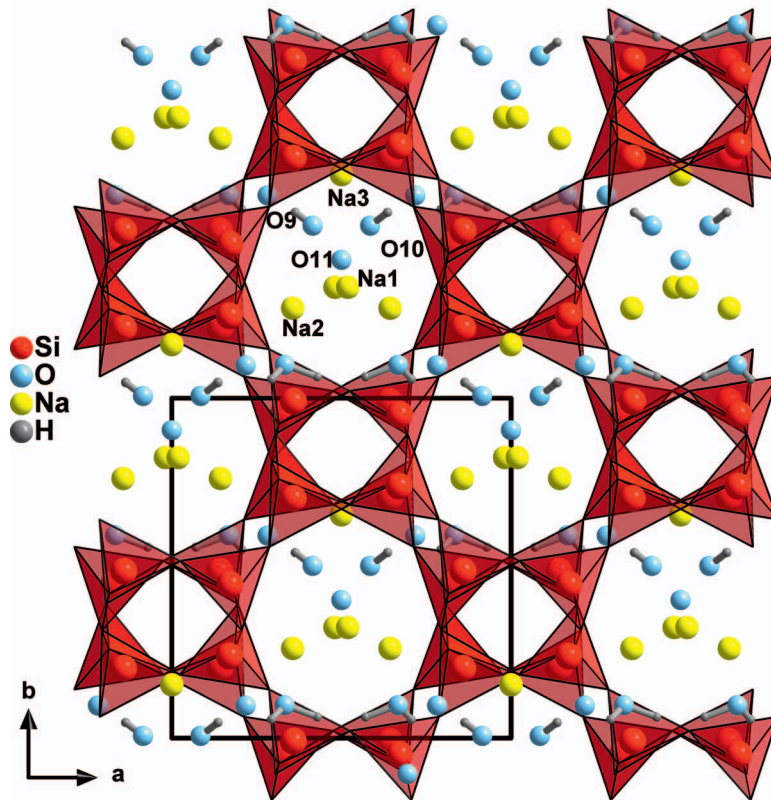


FIG. 2. The framework structure of garronite-Na. It is evident that the framework is topologically nearly tetragonal while the cage contents are strikingly monoclinic.

in the framework, as well as water groups, but *Na3* is only bonded to water groups, giving it much higher anisotropic displacement factors, as it would be rather unstable in the cavity. The closely related crystal structure of gobbinsite, $\text{Na}_6(\text{Al}_8\text{Si}_{10}\text{O}_{32}) \cdot 12\text{H}_2\text{O}$ (Gatta *et al.* 2010), has approximately the same number of Na atoms as garronite-Na, but approximately 50% more water sites. Dehydration of garronite-Na relative to gobbinsite effectively reduces the width of the channels. Taking an average ionic radius for O^{2-} of 1.40 Å, the eight-membered channel diameters (Å) are: garronite-Na, [100] 3.92×4.58 and [001] 4.50×5.58 ; gobbinsite [100] 4.92×6.88 and [010] 3.48×3.96 . The cell dimension transformation matrix for garronite-Na \rightarrow gobbinsite is (010/001/100).

The number of H_2O groups can be determined reasonably well in a structure refinement, but can differ depending on structure refinement methods *i.e.*, the refinement presented here has three groups, split

site *O9*, *O10*, and *O11*, with a total site occupancy of 7.3 *apfu*. If neither displacement factors nor site occupancy are fixed, the number of H_2O groups is slightly lower at 7.0 *apfu*. What is notable (Table 1) is that the number of H_2O groups is considerably less than that of garronite-Ca, gismondine, and similar synthetic phases. The Na atoms and water groups are in the *gis* cages (Fig. 5).

The ratio of Si/Al in the framework cages will determine the possibilities of cation content of the extra-framework cations. Obviously an increase in Si/Al will decrease the number of Ca or Na atoms in the cages. Synthetic high-Si garronite-Na, $\text{Na}_4(\text{Al}_4\text{Si}_{12}\text{O}_{32}) \cdot 14\text{H}_2\text{O}$ (Håkansson & Fälth 1990), has four Na atoms *pfu* while synthetic low-Si garronite-Na, $\text{Na}_8(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 15\text{H}_2\text{O}$ (Albert *et al.* 1998), has eight Na atoms *pfu*. Naturally occurring garronite-Na, $\text{Na}_6(\text{Al}_5\text{Si}_{10}\text{O}_{32}) \cdot 7\text{H}_2\text{O}$, is intermediate with six Na atoms *pfu*. Low-Si garronite-Na was synthesized at

GARRONITE-Na [SiO₄] framework

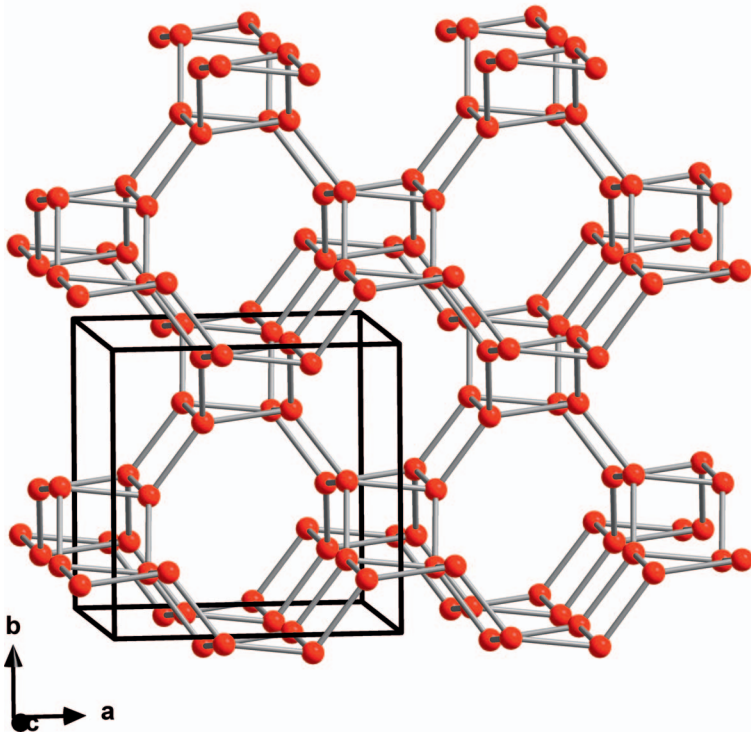


FIG. 3. Topology of the tetrahedral framework of garronite-Na. The [SiO₄] tetrahedra are represented by red circles.

GARRONITE-Na gis UNIT

dcc DOUBLE CRANKSHAFT CHAIN

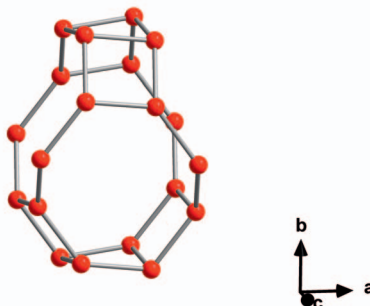


FIG. 4. Topology of the composite building unit in gismondine and garronite-Na. The unit is called a double crankshaft chain (*dcc*). It is made up of secondary building units of eight-fold and four-fold ring nets.

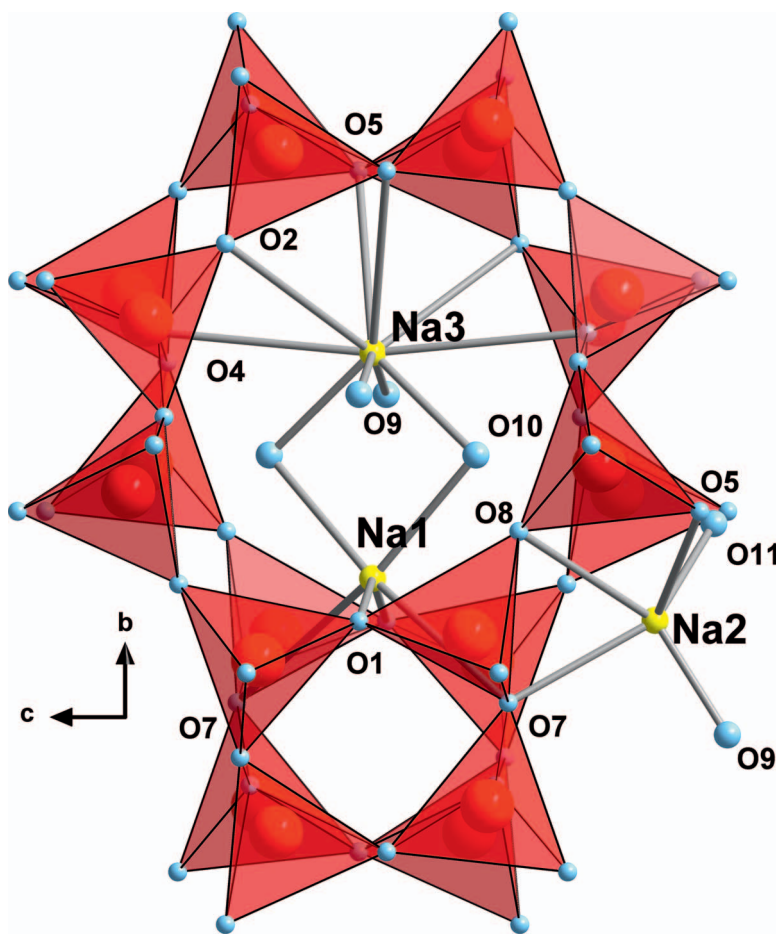


FIG. 5. The *gis* cage in garronite-Na contains the three Na atoms; *Na1*, shown as a single site, *Na2*, and *Na3*, and the three H₂O groups: *O9*, shown as a single site, *O10*, and *O11*.

100 °C while high-Si garronite-Na was synthesized at 200 °C. Barrer *et al.* (1959) synthesized a wide range of Na-hydrated silicates with Si:Al ratios ranging from 12:1 to 1:1. Within the range of the garronite-Na zeolites given above, *i.e.*, 3:1 (high-Si), 2:1 (mineral described here with moderate-Si), and 1:1 (low-Si), there is overlap in their co-existence, but the higher-Si phase is prevalent at higher temperatures of 110–150 °C and the lower-Si phase at lower temperatures of 60–110 °C.

The number of water groups in the cages is not determined by charge balance, but by conditions of formation, with the maximum number determined by the volume of the cage. In Na-P zeolites this maximum has a range of 14 to 16 water groups *pfu*. The much lower value for the MSH garronite-Na, about half the

maximum, may be due to higher temperatures of formation that drive off water.

The role of hydrogen

Only three of the H atoms in this structure could be located and the locations are only approximate. This is due to rather poor intensity data, as explained above. The H-bond lengths are given in Table 6 with only two H bonds showing any linkage to other O atoms, *H9A* bonding the *O9* water group to a framework oxygen *O3* and *H10* bonding the *O10* water group to the *O9* water group.

Related structures

The structure of garronite-Na is closely related to gismondine, CaAl₂Si₂O₈·4H₂O. In the gismondine

framework structure Al and Si are ordered at the tetrahedral sites (Fischer 1963) (Table 1). Ordering these sites lowers the symmetry from space group $I\bar{4}m2$ in garronite-Ca to space group $P2_1/c$ for gismondine. This site ordering and changes in the Si/Al ratio is sufficient for the Subcommittee on Zeolites of the International Mineralogical Association to recognize garronite as a species distinct from gismondine (Coombs *et al.* 1997). Like gismondine, amicite, $K_4Na_4(Al_8Si_8O_{32})\cdot 10H_2O$, has ordered Si and Al in the framework in space group $I2$ (Alberti & Vezzalini 1979). Gobbinsite, $Na_5(Al_5Si_{11}O_{32})\cdot 12H_2O$, has no such ordering at the tetrahedral sites, but differences in the arrangement of extra-framework cations can give rise to small changes in space group $Pmn2_1$ (Artioli & Foy 1994) and $Pmnb$ (Gatta *et al.* 2010).

Two synthetic garronite-Na crystals have been studied: high-Si garronite-Na, $Na_4Al_4Si_{12}O_{32}\cdot 14H_2O$, space group $I4_1/amd$ (Håkansson *et al.* 1990) and low-Si, $Na_8Al_8Si_8O_{32}\cdot 15H_2O$, space group $C2/c$ (Albert *et al.* 1998).

CONCLUSIONS

1. There are now two garronite species: garronite-Ca and garronite-Na.
2. Partial ordering of the Si/Al sites lowers the symmetry of the aluminosilicate framework from tetragonal to monoclinic.
3. The extra-framework cations, Na, and H_2O groups further lower symmetry from monoclinic centrosymmetric to monoclinic non-centrosymmetric.
4. The garronite-Na phase can exist with varying Si:Al ratios within the range 3:1 to 1:1 at least.
5. The Si:Al ratio determines the number of Na cations allowable in the framework cages.
6. The higher Si:Al ratio is favored by higher temperatures of formation.
7. To date, the number of H_2O groups determined in this structure varies from 7 to 15.
8. When garronite-Na is compared to gobbinsite, which is isostructurally equivalent, the channel size increases to accommodate the increase in the number of H_2O groups.
9. The number of H_2O -groups in the framework cage is likely temperature-dependent, but there is no certainty of this at this time.

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