

# Structural refinements of Na-, K-, and Ca-exchanged gmelinites

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Monocationic Ca, Na, and K gmelinite crystals were obtained by cation exchange from three natural samples. Their crystal structures were refined from single crystal XRD data in the  $P6_3/mmc$  space group down to  $R$  values  $< 8\%$ . The structures of the isocationic forms derived from the different natural samples agree within the experimental error, whereas marked differences were found in the different monocationic forms (Na, Ca, K) of each sample. Cation site (C1) in the gmelinite cage is fully occupied in the Na- and K-forms and statistically ( $\approx 50\%$ ) in the Ca-form. Consequently, the tetrahedral framework undergoes deformations involving marked  $c$  lengthening and weak  $a$  shortening in the Ca-Na-K series that are closely correlated to both the occupancy factor and the ionic radius of the cation in the C1 site. The cell parameters of the Ba-form reported in the literature fit this scheme very well.

**Keywords:** Gmelinite; cation exchange; crystal structure

## INTRODUCTION

The chemistry of the zeolite gmelinite is characterized by a nearly constant tetrahedral content [ $Si/(Si + Al) = 0.68 \pm 0.02$ ] and by a common prevalence of Na among the extraframework cations; however, a few samples in which Ca or K are prevalent have also been described.<sup>1-3</sup> The tetrahedral framework<sup>4</sup> is built up by the parallel stacking of double six rings (D6R) in the sequence AABB, with a resulting hexagonal structure characterized by one-dimensional [0001] channels bounded by 12 rings interconnected via two-dimensional channels bounded by 8 rings. Structure refinements carried out on Na-, Ca-, and K-rich natural samples<sup>2,3,5</sup> and on Ba-exchanged crystals<sup>6</sup> have revealed two exchangeable cation sites: C1 in the gmelinite cage just outside the double 6 ring in the [0001] direction and C2 in the large channel near the 8-ring window. The occupancy of the C1 site is complete in Na- and K-rich samples and partial in Ca-rich and Ba-exchanged crystals; the C2 site is always partially occupied with very diverse occupancy factors. As a consequence of the exchangeable cation content, the gmelinite framework undergoes a deformation involving  $c$  lengthening and  $a$  shortening in the Ca-, Na-, and K-rich crystals series which has been

correlated to the radius of the exchangeable cations<sup>2</sup> and to the occupancy and type of the exchangeable cation in the C2 site, i.e., to the strength of the bonds between the C2 cations and the framework oxygens.<sup>3</sup>

Because most of the structure refinements quoted concern polycationic natural crystals, the aim of the present work was to establish the factors responsible for the deformation of the gmelinite framework and the variation in the lattice parameters through structure refinements of Na, K, and Ca monocationic crystals, obtained by cation exchange of three natural gmelinite samples from different occurrences.

## EXPERIMENTAL

### Materials

#### Sample 1

Gmelinite was from Montecchio Maggiore, Vicenza, Italy (sample 1 in Passaglia et al.<sup>1</sup>).  $Si/(Si + Al) = 0.675$ ; there was a large prevalence of divalent compared with monovalent cations [ $(Na + K)/(Ca + Sr) = 0.26$ ]. The crystal structure was reported in Galli et al.<sup>5</sup>

#### Sample 2

Gmelinite was from Queensland, Australia (sample 21 in Passaglia et al.<sup>1</sup>).  $Si/(Si + Al) = 0.690$ ; exchangeable cation content was represented almost exclusively by Na with negligible amounts of Ca and K

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atoms. The crystal structure was described in Galli et al.<sup>5</sup>

### Sample 3

Gmelinite was from San Giorgio Perlana, Fara Vicentina, Vicenza, Italy. The crystal chemistry and structure were given in Vezzalini et al.<sup>3</sup>: Si/(Si + Al) = 0.677; of the exchangeable cations, K prevailed, but noticeable amounts of divalent cations (mainly Ca, but also Sr and Mg) were present.

### Cation exchange and characterization

Natural gmelinite crystals (average size 0.2–0.5 mm) were treated in 1 N solutions of the following exchanging cations: Na, K, and Ca for samples 1 and 3; K and Ca for sample 2. The solutions were prepared with Merck "suprapur" chlorides and deionized water. The treatments were carried out in Teflon tubes slowly oscillating in an oven at 80°C for 1 month with one renewal of the exchanging solutions. At the end of treatment, microprobe point analyses performed on the rim and core of several crystals revealed complete exchanges and chemical homogeneity of the crystals, except for sample 1 Ca-form and sample 3 K-form, henceforth not taken into account because appreciable amounts of Sr and Ca, respectively, were still present.

The electron microprobe analyses were carried out in the wavelength-dispersive mode on an ARL-SEMQ instrument operating at 15 kV and 20 nA beam current and with a defocused beam (spot size  $\approx$  20  $\mu$ m). Natural and synthetic silicates were used as standards and on-line data reduction was based on the Ziebold and Ogilvie method<sup>7</sup> using of Albee and Ray correction factors.<sup>8</sup> To correct for the undetermined loss of zeolitic water under electron bombardment in the vacuum chamber, microprobe data were normalized to 100% by water loss determined on about 5 mg of pure materials using a Du Pont thermal analyzer operated in air at a heating rate of 10°C/min. Unit cell dimensions from X-ray powder patterns were derived by a least-squares refinement of the reflections measured on a Philips diffractometer with Ni-filtered

CuK $\alpha$  radiation and Pb(NO $_3$ ) $_2$  as internal standard. The crystal chemical data of the natural and cation-exchanged gmelinite samples are reported in Table 1; because the microprobe analyses refer to the same crystals as were utilized for X-ray data collection, the chemical composition given in the table ensures that the refined structures are those of practically monocationic gmelinite crystals. Both the framework contents (Si + Al), which are very close to half the oxygen atoms, and the low ( $E < \pm 7\%$ ) balance errors guarantee the reliability of the analyses.

### Structure refinements

Structure refinements were performed on the following exchanged crystals: sample 1, Na- and K-forms; sample 2, K- and Ca-forms; sample 3, Na- and Ca-forms. Data collection was carried out on a CAD4 single-crystal automatic diffractometer (Centro di Strutturistica Diffrattometrica dell'Università di Ferrara) with graphite-monochromatized MoK $\alpha$  radiation in the  $\omega/2\theta$  scan mode. Intensities were corrected for Lorentz and polarization factors and for absorption following the semiempirical method proposed by North et al.<sup>9</sup> Only the reflections with  $I \geq 3\sigma(I)$  were taken as observed and used in the refinements. The lattice parameters obtained by least-squares treatment of 25 reflections along with other crystal data and experimental conditions are summarized in Table 2. The Ca-exchanged crystals are cloudy and milky-white and they exhibit diffuse diffraction spots.

The refinements were carried out in the  $P6_3/mmc$  space group using the SHELX76 computer program.<sup>10</sup> Scattering curves for neutral atoms were taken from International Tables for X-ray Crystallography (Vol. 4). Correction for  $\Delta f'$  and  $\Delta f''$  was taken into account, and no correction was made for secondary extinction. Unit weights were used throughout. The refinements started from the positional parameters of the framework atoms of the natural K-rich gmelinite<sup>3</sup>; after a few cycles with isotropic temperature factors, the positions of C1 and W1 were detected. The refinements were continued with aniso-

**Table 1** Chemical formulas (on the basis of 48 oxygens) and unit-cell parameters of natural (Nat) and cation-exchanged gmelinites

	Sample 1			Sample 2			Sample 3		
	Nat	Na-form	K-form	Nat	K-form	Ca-form	Nat <sup>a</sup>	Na-form	Ca-form
Si	16.21	16.26	16.37	16.49	16.55	16.66	16.32	16.50	16.75
Al	7.82	7.69	7.60	7.41	7.32	7.42	7.79	7.58	7.30
Ca	2.06	0.04	0.07	0.03	tr.	3.52	1.67	0.08	3.53
Sr	1.35	0.02	0.01	tr.	tr.	tr.	0.39	0.07	0.01
Na	0.78	7.75	0.36	7.61	0.63	0.03	0.22	6.87	0.01
K	0.11	0.05	7.24	0.16	7.22	0.01	2.72	0.09	0.01
H $_2$ O	23.23	22.13	19.62	21.51	20.06	23.01	23.52	20.05	22.89
E% <sup>b</sup>	1.43	-2.90	-2.06	-5.36	-6.75	4.80	6.42	4.41	2.82
a(Å) <sup>c</sup>	13.805 (2)	13.772 (2)	13.718 (2)	13.756 (1)	n.d.	13.844 (3)	13.685 (1)	13.765(3)	13.833(2)
c (Å) <sup>c</sup>	9.974 (3)	10.080 (2)	10.293 (4)	10.064 (1)	n.d.	9.811 (3)	10.263 (1)	10.068(3)	9.793(2)
V (Å $^3$ ) <sup>c</sup>	1646.1 (5)	1655.8 (5)	1677.3 (8)	1649.1 (2)	n.d.	1628.4 (7)	1664.9 (2)	1652.1 (7)	1623.0 (5)

<sup>a</sup> Contains also 0.13 atom of Mg.

<sup>b</sup> E% = balance error.<sup>12</sup>

<sup>c</sup> Lattice constants from powder pattern refinements (errors in parentheses).

**Table 2** Crystal and refinement data

	2Ca	3Ca	1Na	3Na	1K	2K
Crystal size (mm)	0.12 × 0.17 × 0.24	0.12 × 0.21 × 0.19	0.21 × 0.31 × 0.40	0.24 × 0.17 × 0.29	0.21 × 0.29 × 0.45	0.24 × 0.24 × 0.19
<i>a</i> (Å)	13.809 (7)	13.807 (4)	13.766 (2)	13.743 (1)	13.700 (2)	13.687 (2)
<i>c</i> (Å)	9.770 (5)	9.792 (3)	10.076 (1)	10.066 (2)	10.272 (1)	10.256 (2)
<i>V</i> (Å <sup>3</sup> )	1613	1617	1654	1646	1670	1664
$\mu$ (cm <sup>-1</sup> )	9.5	id.	id.	id.	id.	id.
Intensity measurement	$\omega/2\theta$ scan	id.	id.	id.	id.	id.
$\theta_{\min}$ – $\theta_{\max}$	2–35°	2–35°	2–45°	2–35°	2–30°	2–35°
Measured reflections	5212	5206	7441	5316	3616	5384
Independent reflections	1369	1365	1936	1393	953	1409
Observed reflections	548	522	1168	929	702	933
<i>R</i> (ani.)	0.0702	0.0720	0.0536	0.0584	0.0561	0.0525

Lattice constants from single crystal refinements (errors in parentheses). id. = idem; *R*(ani.) = *R* in the final anisotropic refinement.

tropic temperature factors for framework and C1 atoms, and the occupancy of the C1 site was refined; the positions of the other water molecules and C2 atoms were then deduced from the difference Fourier map and refined isotropically. The residual peaks with intensities greater than 1  $e/\text{Å}^3$  were assigned to water molecules and the occupancy fixed at a value with an acceptable temperature factor. Because of the very widespread distribution of water molecules, attempts at refining their occupancies and thermal factors alternately failed because both values increase continuously.

In the final cycles, the occupancy factors of exchangeable cation sites (C1 and C2) were refined by fixing the water molecule occupancy factors.

## RESULTS AND DISCUSSION

The unit cell dimensions of the cation-exchanged gmelinites derived from powder pattern (Table 1) and single crystal (Table 2) refinements show that: (a) the values obtained by the two different methods for the same exchanged form normally agree within the bounds of standard deviation; (b) the values of the isocationic forms are very close; and (c) *a* and *c* values decrease and increase, respectively, in the series Ca-Na-K. Point a confirms that all crystals were completely exchanged; points b and c indicate that the cell parameters are strongly correlated to the exchangeable cation content. Because the structural data of the isocationic forms differ within the standard deviations, only the structure refinements of three different monocationic crystals (1Na, 2K, 3Ca) are discussed below.

The atomic coordinates, thermal parameters, and occupancy factors are listed in Table 3, along with the chemical data (number of electrons in extraframework cation sites and number of water molecules) from microprobe analyses and from structure refinements. All the structures are characterized by *R* values <8% (Table 2) and numbers of electrons in extraframework cation sites in good agreement with microprobe data, whereas the number of water molecules is somewhat lower than that found by the

chemical analyses. This latter discrepancy, which is very common in zeolite structure refinements, is due to the random distribution of several water molecules over a large number of sites with occupancy factors that are not statistically significant.

In the structure descriptions, the atoms and sites were coded following the method of Galli et al.<sup>5</sup> The C1 site, located in the gmelinite cage (Figure 1a), is fully occupied in the Na- and K-forms and partially in the Ca-form. In the latter case, the occupancy factor is about 50%, and Ca is statistically distributed in the two equivalent sites (C1 and C1'); thus the symmetry of the crystal remains unchanged. The exchangeable cations lie on the triad axis and are coordinated by three oxygens (O2) of the six ring and by three water molecules statistically distributed in the two equivalent sites (W1 and W1'), which are symmetrical with respect to the (11 $\bar{2}$ 0) mirror plane. The water molecules are on the (0001) mirror plane and in the Na- and K-forms coordinate both cations in the C1 and C1' sites.

The C2 site, localized in the large channel near the 8-ring window (Figure 1b), is always partially occupied with occupancy factors that are very similar (about 30%) in the Na- and K-forms but somewhat lower (12%) in the Ca-form. The cations are coordinated by three oxygen atoms (one O1 and two O4) and by two water molecules distributed in partially occupied sites; W2 is present in all the exchanged forms and lies on the (11 $\bar{2}$ 0) mirror plane, while the other water molecules are W6 in Ca-form, W3 in Na-form, and W4 and W5 in K-form.

Table 4 gives selected interatomic distances and angles. Regarding the tetrahedral framework, we can observe: (a) the T–O distances are regular and very similar in the Na- and K-forms; the distance T–O2 (oxygen coordinated to cations in C1) is significantly longer than the other three in the Na- and, especially, Ca-forms; (b) the O–T–O angles cover a slightly larger range in the Ca-form (105–113°) than in the Na- and K-forms (106–112° and 107–112°, respectively); (c) the T–O–T angles cover a smaller range in the Na-form (136–148°) than in the Ca- and K-forms (136–154° and 140–155°, respectively). In this frame, there is a marked increase and decrease in

**Table 3** Atomic coordinates, equivalent (U<sub>eq</sub>) or isotropic (U) temperature factors (Å<sup>2</sup>) and occupancy factors (Occ.) (%)<sup>a</sup>

		3Ca	1Na	2K
T (24 l) <sup>a</sup>	x	0.4428 (2)	0.4412 (1)	0.4340 (1)
	y	0.1085 (2)	0.1058 (1)	0.0999 (1)
	z	0.0882 (2)	0.0942 (1)	0.0988 (1)
	U <sub>eq</sub>	0.0134 (7)	0.0113 (2)	0.0100 (3)
O1 (12 k)	x	0.425 (1)	0.4171 (3)	0.4279 (4)
	y	0.2126	0.2086	0.2139
	z	0.043 (1)	0.0598 (4)	0.0653 (4)
	U <sub>eq</sub>	0.041 (4)	0.029 (1)	0.027 (1)
O2 (12 k)	x	0.854 (1)	0.8505 (3)	0.8707 (3)
	y	0.4268	0.4253	0.4354
	z	0.045 (1)	0.0607 (3)	0.0726 (4)
	U <sub>eq</sub>	0.035 (4)	0.025 (1)	0.021 (1)
O3 (12 j)	x	0.4211 (8)	0.4110 (3)	0.3949 (3)
	y	0.0795 (9)	0.0658 (4)	0.0564 (4)
	z	1/4	1/4	1/4
	U <sub>eq</sub>	0.035 (5)	0.027 (2)	0.024 (2)
O4 (12 i)	x	0.3547 (8)	0.3557 (3)	0.3453 (3)
	y	0	0	0
	z	0	0	0
	U <sub>eq</sub>	0.032 (3)	0.027 (1)	0.021 (1)
C1 (4 f)	x	1/3	1/3	1/3
	y	2/3	2/3	2/3
	z	0.090 (1)	0.0727 (4)	0.0660 (2)
	U <sub>eq</sub>	0.039 (3)	0.041 (1)	0.0281 (5)
	Occ.	53 (2)	100 (2)	100 (1)
C2 (12 k)	x	0.1057	0.1204	0.1013
	y	0.211 (4)	0.241 (1)	0.203 (1)
	z	0.051 (5)	0.071 (1)	0.077 (1)
	U	0.08 (1)	0.086 (4)	0.129 (4)
	Occ.	12 (2)	34 (2)	31 (2)
W1 (12 j)	x	0.181 (3)	0.1965 (9)	0.162 (1)
	y	0.556 (3)	0.549 (1)	0.550 (1)
	z	1/4	1/4	1/4
	U	0.08 (1)	0.055 (3)	0.077 (5)
	Occ.	50	50	50
W2 (6 h)	x	0.1623	0.1697	0.1787
	y	0.325 (5)	0.339 (2)	0.357 (3)
	z	1/4	1/4	1/4
	U	0.08 (2)	0.088 (5)	0.071 (9)
	Occ.	40	68	34
W3 (12 k)	x		0.163 (2)	
	y		0.0815	
	z		0.117 (2)	
	U		0.069 (5)	
	Occ.		36	
W4 (6 h)	x			0.169 (2)
	y			0.0847
	z			1/4
	U			0.082 (9)
	Occ.			40
W5 (12 k)	x			0.1371
	y			0.274 (3)
	z			0.175 (3)
	U			0.064 (9)
	Occ.			20
W6 (4 e)	x	0		
	y	0		
	z	0.04 (1)		
	U	0.10 (5)		
	Occ.	24		
Number of electrons in extraframework cation sites:				
Chemical analysis		71.3	87.8	144.1

**Table 3** continued

	3Ca	1Na	2K
Structure refinement	71.2	88.9	146.7
Number of water molecules:			
Chemical analysis	22.9	22.1	20.1
Structure refinement	9.4	14.4	12.8

<sup>a</sup> E.s.d.'s on the last significant digit in parentheses.<sup>b</sup> Multiplicity and Wyckoff letter.

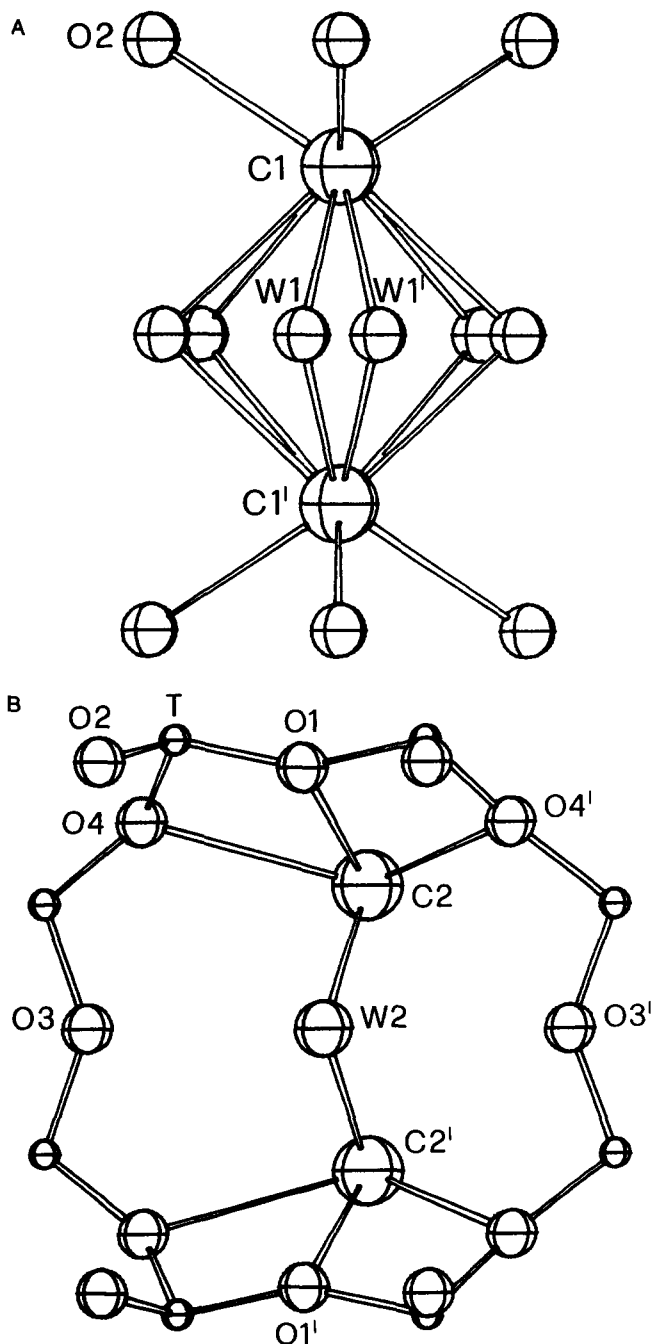
the T–O1–T and T–O3–T angles, respectively, in the series Ca–Na–K. Regarding the extraframework content, we can observe: (a) in the Na- and K-forms, the full occupancy of the C1 site involves C1–C1' cation distance proportional to the ionic radius (K > Na); in the Ca-form, the statistical occupancy of the C1 site allows Ca to approach the (0001) mirror plane and hence the C1–C1' site distance is quite short; (b) the C1–O2 as well as C1–W1 distances are consistent with the cation radii (K > Ca ≈ Na); (c) the O2–C1–O2' angles are very close; (d) with ⟨W1⟩ denoting the mean position of W1 and W1', the ⟨W1⟩–C1–⟨W1⟩ angles increase in the series Na–K–Ca. In the Na- and K-forms, the increase follows from that in the cation radius, whereas in the Ca-form the highest value depends on the reduced C1–C1' site distance; in all cases, the angles adopt values which enable water molecules to remain on the (0001) mirror plane.

In the one-dimensional large channel, the distances of the C2 cation from framework oxygens are comparable in all exchanged forms regarding O4 atoms, but increase in the series Na–Ca–K regarding O1 atoms. The O1–O1' and O3–O3' distances in the 8 ring connecting gmelinite cage and large channel—distances which are decisive for the window dimensions—increase and decrease, respectively, in the series Ca–Na–K. In the same series, the differences between O1–O1' and O3–O3' decrease and, consequently, the ellipsoidal shape of the ring is marked in the Ca-form and weak in the Na- and K-forms. Noteworthy is the fact that in the K-form the O1–O1' distance is anomalously longer than the O3–O3' distance.

## CONCLUSIONS

Owing to the exchangeable cation content, the gmelinite framework undergoes deformations involving merely variations of the lattice parameters in which the *c* parameter varies to a greater extent (about 5%) than the *a* parameter (about 1%). These findings agree with those of other authors,<sup>2,3</sup> but the present monocationic crystal structures reveal that the lattice parameters are related to structural factors not taken into account by the same authors, very likely due to the polycationic state of the crystal utilized in their structural refinements.

The assumption that the  $c$  parameter depends on the exchangeable cation radius<sup>2</sup> is valid for Na and K, but not for Ca. The hypothesis that the  $c$  parameter depends on the bond strengths of the C2 cation<sup>3</sup> is not confirmed in the present study. Indeed, thorough comparison of the structural data of monocationic crystals shows the occupancy and type of the C1 cation to be the main factors influencing the framework geometry and hence the unit cell dimensions. The C1 site is fully occupied only by monovalent cat-



**Figure 1** Projections in the  $ac$  plane of: (a) gmelinite cage showing C1 cation with coordinated oxygen atoms and water molecules; (b) 8-ring window showing C2 cation with coordinated oxygen atoms and W2 water molecules present in all exchanged forms.

**Table 4** Selected interatomic distances (Å) and angle ( $^{\circ}$ )<sup>a</sup>

	3Ca	1Na	2K
T-O1	1.635 (4)	1.643 (3)	1.640 (3)
T-O2	1.658 (7)	1.658 (3)	1.647 (3)
T-O3	1.625 (3)	1.647 (2)	1.652 (2)
T-O4	1.627 (4)	1.641 (2)	1.646 (2)
Average T-O	1.636	1.647	1.646
O1-T-O2	105.6 (7)	108.0 (2)	107.4 (2)
O1-T-O3	113.0 (7)	111.3 (3)	112.2 (3)
O1-T-O4	107.1 (5)	106.2 (2)	107.1 (2)
O2-T-O3	111.2 (6)	111.3 (2)	111.0 (2)
O2-T-O4	110.6 (5)	112.1 (2)	111.3 (3)
O3-T-O4	109.2 (3)	107.8 (1)	107.9 (1)
Average O-T-O	109.4	109.4	109.5
T-O1-T	145.0 (8)	148.2 (3)	155.3 (3)
T-O2-T	136.2 (7)	136.0 (2)	149.0 (3)
T-O3-T	154.4 (6)	144.9 (3)	139.8 (2)
T-O4-T	146.5 (8)	148.3 (3)	142.4 (3)
Average T-O-T	145.5	144.3	146.6
C1-C1'	3.14 (2)	3.573 (6)	3.774 (3)
C1-O2 ( $\times 3$ )	2.60 (1)	2.571 (4)	2.806 (4)
C1-W1 ( $\times 6$ )	2.45 (2)	2.514 (7)	2.80 (1)
C1-<W1> ( $\times 3$ ) <sup>a</sup>	2.40	2.52	2.77
O2-C1-O2' ( $\times 3$ )	96.3 (4)	95.2 (1)	96.6 (1)
<W1>-C1-<W1> ( $\times 3$ )	82.0	71.5	78.7
C2-C2' ( $\times 2$ )	2.72 (4)	3.21 (2)	2.87 (2)
C2-O1	2.72 (5)	2.48 (1)	3.04 (1)
C2-O4 ( $\times 2$ )	3.03 (3)	2.90 (1)	3.01 (1)
C2-W2	2.37 (6)	2.15 (2)	2.55 (3)
C2-W3		2.11 (2)	
C2-W3' ( $\times 2$ )		2.58 (2)	
C2-W4			2.85 (3)
C2-W5			2.68 (4)
C2-W5'			1.31 (4)
C2-W6	2.53 (5)		
C2-W6'	2.69 (7)		
O1-O1' (*) <sup>b</sup>	5.73 (2)	6.243 (6)	6.467 (6)
O3-O3' (*)	6.91 (2)	6.564 (7)	6.177 (8)

<sup>a</sup> E.s.d.'s on the last significant digit in parentheses.

<sup>b</sup> <W1>: mean position of the W1-W1' couple.

<sup>c</sup> (\*) distances in the 8-ring window (see Figure 1b).

ions (Na and K), which are accommodated in the equivalent C1 and C1' sites at a distance proportional to their ionic radius; as the C1-C1' cation distance increases, the gmelinite cage is compelled to elongate in the [0001] direction, with the result that there is a marked increase in  $c$  and a slight decrease in  $a$ . The statistical C1 occupancy by the divalent Ca makes for a marked decrease in the C1-C1' site distance, which causes the shortening of  $c$  and, to a lesser extent, the lengthening of  $a$ . The cell parameters of Ba-exchanged crystals<sup>6</sup> ( $a = 13.793$ ,  $c = 10.021$  Å) agree very well with the proposed scheme. Actually, the C1 site is statistically occupied by Ba in Ba-form as it is by Ca in Ca-form. The resulting  $c$  parameter is consistently longer than that of the Ca-form, markedly shorter than that of the K-form (despite the Ba and K radii being nearly equal), and very similar to that of the Na-form (despite the Ba radius being markedly greater than the Na radius).

The framework deformations induced by the exchangeable cations modify the crystallographic free diameters of the channels, as calculated<sup>11</sup> on the basis

of the atomic coordinates and an oxygen radius of 135 Å. The diameters of the 8 ring window in the respective [0001] and [10 $\bar{1}$ 0] directions are: Ca-form, 3.0 × 4.2 Å; Na-form, 3.5 × 3.9 Å; K-form, 3.8 × 3.5 Å. The diameters of the one-dimensional [0001] channel are: Ca-form, 7.5 × 7.1 Å; Na-form, 7.3 × 7.1 Å; K-form, 7.5 × 6.8 Å.

Finally, the analyses of the tetrahedral frameworks of the monocationic crystals revealed more regularities of T–O distances and T–O–T and O–T–O angles in the case of the Na-form; this fact could be invoked to explain the widespread occurrence of Na-rich gmelinite samples in nature.

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