The partially dehydrated structure of natural heulandite: An in situ high temperature single crystal X-ray diffraction study

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In situ high-temperature crystal structure analysis of natural heulandite with the chemical composition $(\text{Na}_{1.14}\text{K}_{0.40}\text{Ca}_{3.64}\text{Sr}_{0.21})(\text{Al}_{9.21}\text{Si}_{26.88})\text{O}_{72}\cdot 25.2\text{H}_2\text{O}$ from Maharashtra, India was conducted up to 300 °C. The room-temperature and high-temperature X-ray diffraction intensities of a single crystal were measured using an imaging plate detector coupled with a U-shaped high-temperature furnace. At room temperature, the sample was monoclinic, with $C2/m$ symmetry [$a = 17.716(4)$ Å, $b = 17.880(3)$ Å, $c = 7.438(2)$ Å, and $\beta = 116.43(1)^\circ$]. Structural refinement of the data set at room temperature yielded a final R value of $R = 0.049$ and $R_w = 0.115$ for 1663 independent reflections. The crystal structures of the partially dehydrated states at elevated temperatures (100 °C, 150 °C, 200 °C, 250 °C and 300 °C) were refined using $C2/m$ space group. The loss of H_2O and the accompanying migration of cations caused a change in the cell parameters: a - and c -axes and the β angle remained invariant, but the b axis decreased, leading to a reduction of the cell volume. Channels A and B became elongated and compressed, respectively, with increasing degree of dehydration.

Dehydration began with the loss of H_2O coordinated to the Ca1 site in Channel A, defined by 10-membered tetrahedral rings. At 150 °C, the water coordinated to the Ca1 site was expelled radically, and it caused the Ca1 site to migrate to the cavity wall, forming a stronger bond with a tetrahedral framework, whereas the Ca2 site-coordinated water molecules remained in the 8-membered tetrahedral rings with full occupancy. The loss of water at 250 °C from Channel B triggered a structural change: Part of the structure transformed into a heat-collapsed heulandite structure with new T-O-T connections.

Keywords: Heulandite, Dehydration, Heat-collapsed phase B

INTRODUCTION

Heulandite-type zeolites are comprised of heulandite and clinoptilolite having the simplified chemical formulae of $(\text{Na},\text{K})\text{Ca}_4\text{Al}_9\text{Si}_{27}\text{O}_{72}\cdot 24\text{H}_2\text{O}$ and $(\text{Na},\text{K})_6\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot 20\text{H}_2\text{O}$, respectively (Gottardi and Gali, 1985). Both minerals represent naturally occurring zeolites with a high degree of Si and Al disorder (Merkle and Slaughter, 1968; Alberti, 1975). Heulandite series minerals (heulandite-Ca, heulandite-Na, heulandite-K and heulandite-Sr) are isostructural and possess monoclinic symmetry $C2/m$ with lattice constants of $a \approx 17.7$ Å, $b \approx 17.9$ Å, $c \approx 7.4$ Å and $\beta \approx 116.0^\circ$. The structure is characterized by a two-dimensional large channel system composed of 10- and

8-membered tetrahedral rings, commonly named “Channel A” (orientated parallel to the c -axis; 10-membered rings) and “Channel B” (orientated parallel to the c -axis; 8-membered rings) (Stolz et al., 2000). Channels A and B are cross-linked by 8-membered rings of Channel C running parallel to the a -axis and the [102] direction. Cations and water molecules occupy the channels.

Heulandite and clinoptilolite are distinguished based on the Si/Al ratio in the tetrahedral framework (Coombs et al., 1997; Bish and Boak, 2001). Silica-rich crystals ($\text{Si}/\text{Al} \geq 4.0$) are clinoptilolites, and more aluminous crystals with $\text{Si}/\text{Al} < 4.0$ are denoted as heulandite.

The presence of three phases, Phases A, B, and I, has been used by many groups (e.g., Alietti, 1972; Boles, 1972; Alietti et al., 1974). When heulandite is heated in the temperature range 250–500 °C, natural heulandite

(Phase A) transforms into a contracted phase (Phase B), which is stable over a long period of time (Alberti and Vezzalini, 1983). This contracted phase is characterized by a strong distortion of the framework (Alberti, 1973). As a result of the structural collapse, the two-dimensional channels are severely occluded, which renders them almost useless as industrial catalysts and dehydrating agents (Mortier and Pearce, 1981). Dehydration experiments using heulandite with an unmodified cation composition (Alberti and Vezzalini, 1983; Armbruster and Gunter, 1991), and using fully Cd-exchanged heulandite (Döbelin and Armbruster, 2003) showed a collapse of the HEU framework (Gottardi and Gali, 1985) due to the loss of H₂O molecules and the induced movement as well as newly formed bonds of the extra-framework cations. At higher temperatures (360 °C according to Alberti and Vezzalini, 1983; 250 °C according to Döbelin and Armbruster, 2003), the T-O-T bonds break, leading to an altered framework topology known as Phase B.

In previous high-temperature experiments on zeolites, single crystals were quenched (where the sample was dehydrated in a vacuum at a selected temperature and subsequently sealed in glass capillaries). However, the dynamic information at a given temperature cannot be elucidated in this type of experiment, and the true dehydration process is obscured. Therefore, *in situ* high-temperature measurements were carried out in the present study for the following purposes:

1. to understand the dehydration mechanism of natural heulandite as a function of temperature;
2. to monitor the migration of cations within the structural channel system on dehydration;
3. to find any potential phase transitions, as well as the framework topology, for all dehydration states; and
4. to compare the data on the heat-collapsed phase from this study with previous results (Alberti and Vezzalini, 1983; Döbelin and Armbruster, 2003).

EXPERIMENTAL

Heulandite single crystals from Maharashtra, India (hereafter MO-heu) were used in this study. The chemical composition ($\text{Na}_{1.14}\text{K}_{0.40}\text{Ca}_{3.64}\text{Sr}_{0.21}\text{Si}_{26.88}\text{O}_{72} \cdot 26.1\text{H}_2\text{O}$ ($Z = 1$)) was obtained using an electron probe micro analyzer (EPMA: JEOL, JXA-8800M) operating at 15 kV and 15 nA, with 20 μm beam diameter. Thermal analysis (Thermogravimetry and Differential Thermal Analysis) was carried out using a Rigaku Model TG 8120 to determine the H₂O content and dehydration stages. Finely ground samples were heated in static air conditions from room temperature to 900 °C using a heating rate of 10 °C/min.

Data collection and refinement

A suitable single crystal fragment ($240 \times 140 \times 70 \mu\text{m}^3$) that was free from cracks was used for the X-ray diffraction investigations. Single-crystal X-ray diffraction data sets were measured using an imaging plate (IP) X-ray diffractometer (R-Axis IV⁺⁺, Rigaku, Japan) with a rotating anode X-ray source (MoK α radiation, 50 kV, 80 mA). The X-ray intensity data were collected within a ϕ range of 0.0–90.0°. The maximum value of 2θ of the measured reflections used for the refinement was limited to $\leq 50^\circ$ at both room temperature and high temperatures.

The unit cell parameters and intensity data were collected at room temperature and at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C using a U-shaped resistance heater (HUBER: High temperature attachment type 231). The temperature was calibrated using the calibration curve of Komatsu et al., 2003. The sample used for the X-ray diffraction measurements was placed in a boron-silica capillary ($\phi = 300 \mu\text{m}$). The temperature was increased at a rate of 2 °C per minute. The sample was heated for a period of 13 h for centering and stabilizing before data collection, and the total X-ray exposure time was 6 h. After the X-ray diffraction measurements, it took another 1 h and 20 min to finish the process from diffraction to imaging from Rigaku, XRD. No significant changes were observed in the diffraction patterns in each measurement, and the values of R merge were within 5% up to a temperature of 250 °C. The distance from the IP to the sample was 80 mm. Lorentz-polarization effects and background reduction were corrected using the Crystal Clear v.3.1 software package (the operating software of the Rigaku R-Axis IV⁺⁺ XRD). Background reduction for the area detector was conducted using the technique of Amemiya and Ito (2003). Extinction correction was applied (shown in Table 1), and the effect of absorption was ignored, considering the transmittance for lower dimension (70 μm) and higher dimensions (240 μm) of the sample with the absorption coefficient, $\mu = 0.927 \text{ mm}^{-1}$.

The structure was refined on F^2 by the least-squares calculation using SHELXL software package (Sheldrick, 1997). The observed extinction rule suggested the possibility of a $C2/m$, $C2$, Cm or $C\bar{1}$ space group. Therefore, the refinement was performed for $C2/m$, $C2$, Cm and $C\bar{1}$ space groups, but a reasonable model and R factor were achieved for space group $C2/m$. The weight applied was $w = 1/(\sigma^2(F_o^2) + (0.0913p)^2 + 36.4561p)$, where $p = (2F_o^2 + \text{Max}(F_o^2, 0))/3$. Starting from the structural parameters for the framework atoms taken solely from Alberti and Vezzalini (1983), extra-framework atoms were assigned using the difference-Fourier method and the corresponding local structural information, such as bond distances.

Table 1. Data measurement and refinement parameters for natural heulandite

Temperature	RT	100°C	150°C	200°C	250°C	300°C
<i>a</i> /Å	17.716(4)	17.694(5)	17.725(6)	17.716(6)	17.082(6)	17.033(13)
<i>b</i> /Å	17.880(3)	17.801(4)	17.630(4)	17.584(4)	16.685(4)	16.589(13)
<i>c</i> /Å	7.438(2)	7.433(3)	7.459(4)	7.452(3)	7.351(3)	7.330(7)
β (°)	116.43(1)	116.41(2)	116.79(2)	116.70(2)	116.93(2)	117.37(3)
<i>V</i> (Å ³)	2109.8(1)	2097.0(2)	2080.7(2)	2073.9(2)	1867.9(2)	1839.3(36)
No. of H ₂ O	25.20(11)	20.70(18)	15.10(15)	13.30(15)	-	-
Measured reflections $2\theta < 50^\circ$	3432	3214	3330	3155	2962	2680
Unique reflections	1663	1632	1607	1618	1362	1269
Observed reflections, $I_o > 2\sigma I_o$	1594	1587	1489	1484	1179	913
No. of parameters	194	176	165	162	169	169
Extinction co-efficient	0.003	0.006	0.003	0.003	0.032	0.06
R merge	0.021	0.031	0.029	0.025	0.041	0.137
<i>R</i> * (%)	4.97	7.88	7.53	6.37	14.44	16.81
<i>wR</i> † (%)	11.5	20.7	17.1	15.9	37.4	38.4
Goodness-of-fit	1.25	1.10	1.14	1.12	2.91	2.57

RT, room temperature (24 °C)

* $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ † $wR = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (0.0913 p)^2 + 36.4561 p]$, where $p = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$

Structure refinement was performed using neutral atom scattering factors for all the atoms (Si for all tetrahedral sites, labeled “T sites”). At room temperature, individual cation (e.g., Ca, Na, K, and Sr) scattering factors were used. At high temperatures, the Ca atom scattering factor was used for the Ca1 and Ca2 sites. For each assigned cation or water molecule, the occupancy was refined along with the atomic coordinates and an isotropic temperature factor. The occupancy of a cation or water molecule was refined with the occupancies of the remaining cations and water molecules being fixed. In this way, the occupancies of all extra-framework cations and water molecules were refined. Finally, the entire process was repeated for all cations and water molecules.

The total occupancy of the T1 + T1A, T3 + T3A, O9 + O9A, and O9 + 9B sites was fixed at a value of 1 at 250 °C and 300 °C. No hydrogen atom positions were refined. The details of the intensity measurements and structural refinements are given in Table 1.

RESULTS

In the initial stages of the dehydration process, at temperatures up to 250 °C, the *a*- and *c*-axis and β angle of the unit cell parameters remained invariant, while the *b*-axis decreased from 17.880 to 16.685 Å (Table 1). This change induced a unit cell volume decrease of 11.5% at a temperature of 250 °C. At 250 °C, the *a*- and *b*-axes decreased rapidly (Table 1), which is a characteristic of the heat-collapsed structure of heulandite (Alberti, 1973). Although this trend deviates from the results reported by Döbelin and Armbruster (2003) and Armbruster and Gunter (1991), the similarity is that in the heat-collapsed structure, the

a-, *b*-, and *c*-axes decrease and the β angle increases. Our data measurement and refinement parameters are given in Table 1, the atomic parameters in Table 2, and selected bond distances (T-O and M-O) are given in Table 3. The anisotropic displacement parameters at room temperature and at 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C are given in Appendices 1–6.

A continuous weight loss was observed in the thermogravimetric (TG) data (Fig. 1). Based on our structural refinement, the total number of H₂O was found to be 25.2(1) per formula unit (pfu) at room temperature. A 16.7% weight loss was detected in our TG analysis at temperatures between 28 °C and 900 °C, and this value corresponds to 26.5 molecules of water. Hence, the TG and X-ray results are consistent. The DTA data (Fig. 1) showed three endothermic peaks, and all indicated dehydration. The first broad peak was observed at *T* = 155 °C. The weak dehydration stage present in the TG data (254–292 °C) was also reproduced in DTA data. In this temperature range, two sharp peaks were observed at 265 °C and 285 °C, which represents a structural change in heulandite. The examination using standard material (Al₂O₃) and the blank test indicated that the broad peak at 600 °C was the instrumental artifact. The dehydrated structure at 250 °C and 300 °C in our X-ray analysis also showed a structural change. However, this narrow region of dehydration caused a collapse in the heulandite structure.

The structural refinement of natural heulandite dehydrated at temperatures up to 200 °C showed a common HEU framework topology. Heating to 250 °C causes a collapse of this structure with a partially altered topology. This altered topology also maintained at 300 °C. At 250

Table 2. Atomic fractional coordinates, site occupancy factor, and equivalent atomic displacement parameters at several temperatures

Temperature	Atom	x/a	y/b	z/c	sof	$U_{eq}(\text{\AA}^2)$
RT	T1	0.1797(1)	0.1691(1)	0.0968(2)	1	0.0120(4)
100°C		0.1794(1)	0.1683(1)	0.0935(3)	1	0.0203(6)
150°C		0.1800(1)	0.1658(1)	0.0926(3)	1	0.0214(6)
200°C		0.1802(1)	0.1645(1)	0.0931(3)	1	0.0221(5)
250°C		0.1851(2)	0.1474(4)	0.0903(6)	0.785(4)	0.0625(15)
300°C		0.1867(3)	0.1447(6)	0.0935(9)	0.769(4)	0.089(2)
250°C	T1A	0.1713(7)	0.0879(9)	0.0557(19)	0.215(4)	0.046(3)
300°C		0.1725(8)	0.0872(13)	0.050(2)	0.231(4)	0.063(4)
RT	T2	0.2111(1)	0.4099(1)	0.4987(2)	1	0.0121(4)
100°C		0.2100(1)	0.4096(1)	0.4990(3)	1	0.0200(6)
150°C		0.2057(1)	0.4093(1)	0.4955(3)	1	0.0206(6)
200°C		0.2044(1)	0.4096(1)	0.4938(3)	1	0.0228(5)
250°C		0.1770(2)	0.4095(2)	0.4777(5)	1	0.070(14)
300°C		0.1757(3)	0.4090(4)	0.4706(8)	1	0.0949(19)
RT	T3	0.2083(1)	0.1908(1)	0.7171(2)	1	0.0113(4)
100°C		0.2098(1)	0.1905(1)	0.7193(3)	1	0.0195(6)
150°C		0.2137(1)	0.1884(1)	0.7259(3)	1	0.0216(6)
200°C		0.2146(1)	0.1877(1)	0.7279(3)	1	0.0230(5)
250°C		0.2408(3)	0.1773(3)	0.7644(7)	0.785(4)	0.0655(14)
300°C		0.2401(4)	0.1781(5)	0.7681(10)	0.769(4)	0.095(2)
250°C	T3A	0.1814(14)	0.107(2)	0.651(4)	0.215(4)	0.112(9)
300°C		0.1802(12)	0.0989(18)	0.660(3)	0.231(4)	0.108(8)
RT	T4	0.0643(1)	0.2985(1)	0.4106(2)	1	0.0118(4)
100°C		0.0646(1)	0.2975(1)	0.4108(3)	1	0.0202(6)
150°C		0.0655(1)	0.2912(1)	0.4135(3)	1	0.0213(6)
200°C		0.0657(1)	0.2895(1)	0.4146(3)	1	0.0231(5)
250°C		0.0713(2)	0.2570(3)	0.4286(5)	1	0.0675(14)
300°C		0.0715(2)	0.2556(4)	0.4277(7)	1	0.0909(18)
RT	T5	0	0.2119(1)	0	1	0.0130(5)
100°C		0	0.2102(2)	0	1	0.0208(7)
150°C		0	0.2055(2)	0	1	0.0210(8)
200°C		0	0.2040(2)	0	1	0.0224(6)
250°C		0	0.1798(4)	0	1	0.0660(15)
300°C		0	0.1737(5)	0	1	0.0845(19)
RT	O1	0.1961(4)	0.5	0.4498(9)	1	0.0275(13)
100°C		0.1957(5)	0.5	0.4511(12)	1	0.0358(19)
150°C		0.1844(6)	0.5	0.4439(14)	1	0.044(2)
200°C		0.1820(5)	0.5	0.4399(12)	1	0.0462(19)
250°C		0.1302(8)	0.5	0.447(2)	1	0.086(4)
300°C		0.1257(10)	0.5	0.437(3)	1	0.122(7)

Table 2. (Continued-1)

Temperature	Atom	x/a	y/b	z/c	sof	$U_{eq}(\text{\AA}^2)$
RT	O2	0.2305(2)	0.1197(3)	0.6115(6)	1	0.0286(10)
100°C		0.2330(4)	0.1198(4)	0.6130(9)	1	0.0402(16)
150°C		0.2415(5)	0.1182(5)	0.6263(11)	1	0.054(2)
200°C		0.2437(4)	0.1170(4)	0.6312(10)	1	0.0561(17)
250°C		0.2909(7)	0.1058(10)	0.6962(17)	1	0.109(5)
300°C		0.2900(10)	0.1093(16)	0.696(2)	1	0.165(10)
RT	O3	0.1841(3)	0.1535(3)	0.8839(6)	1	0.0285(10)
100°C		0.1834(4)	0.1509(4)	0.8804(8)	1	0.0386(15)
150°C		0.1881(4)	0.1453(4)	0.8853(9)	1	0.0375(16)
200°C		0.1899(3)	0.1439(3)	0.8873(8)	1	0.0396(13)
250°C		0.2092(8)	0.1290(9)	0.9144(18)	1	0.104(4)
300°C		0.2065(10)	0.1296(19)	0.917(3)	1	0.171(9)
RT	O4	0.2397(2)	0.1060(3)	0.2561(6)	1	0.0255(10)
100°C		0.2410(3)	0.1062(4)	0.2560(8)	1	0.0357(14)
150°C		0.2408(4)	0.1048(4)	0.2602(9)	1	0.0376(16)
200°C		0.2402(3)	0.1033(3)	0.2622(8)	1	0.0424(13)
250°C		0.2413(6)	0.0994(8)	0.2972(16)	1	0.100(4)
300°C		0.2419(9)	0.1011(12)	0.303(2)	1	0.146(6)
RT	O5	0	0.3268(4)	0.5	1	0.0295(14)
100°C		0	0.3233(6)	0.5	1	0.043(2)
150°C		0	0.3136(7)	0.5	1	0.052(3)
200°C		0	0.3124(6)	0.5	1	0.061(3)
250°C		0	0.2397(18)	0.5	1	0.181(13)
300°C		0	0.248(3)	0.5	1	0.196(15)
RT	O6	0.0826(2)	0.1569(3)	0.0639(6)	1	0.0238(10)
100°C		0.0822(3)	0.1554(4)	0.0605(8)	1	0.0313(14)
150°C		0.0818(3)	0.1505(4)	0.0513(9)	1	0.0337(16)
200°C		0.0820(3)	0.1494(3)	0.0492(8)	1	0.0373(13)
250°C		0.0811(6)	0.1213(8)	0.0263(16)	1	0.087(3)
300°C		0.0839(6)	0.1199(12)	0.034(2)	1	0.134(6)
RT	O7	0.1269(3)	0.2349(3)	0.5514(7)	1	0.0357(11)
100°C		0.1298(4)	0.2355(5)	0.5528(10)	1	0.0518(19)
150°C		0.1344(5)	0.2293(6)	0.5533(12)	1	0.065(3)
200°C		0.1347(4)	0.2291(4)	0.5557(10)	1	0.0658(19)
250°C		0.1548(8)	0.2034(11)	0.563(3)	1	0.146(7)
300°C		0.1547(10)	0.2030(15)	0.568(3)	1	0.179(10)
RT	O8	0.0087(2)	0.2659(3)	0.1858(6)	1	0.0306(10)
100°C		0.0098(4)	0.2651(4)	0.1864(9)	1	0.0443(17)
150°C		0.0130(4)	0.2605(5)	0.1863(10)	1	0.050(2)
200°C		0.0146(3)	0.2588(4)	0.1888(8)	1	0.0550(17)
250°C		0.0291(8)	0.2361(10)	0.190(2)	1	0.136(6)
300°C		0.0287(10)	0.2374(16)	0.192(2)	1	0.181(10)

Table 2. (Continued-2)

Temperature	Atom	x/a	y/b	z/c	sof	$U_{eq}(\text{\AA}^2)$
RT	O9	0.2105(2)	0.2538(3)	0.1782(6)	1	0.0255(10)
100°C		0.2092(3)	0.2536(4)	0.1693(9)	1	0.0342(14)
150°C		0.2076(4)	0.2526(4)	0.1599(10)	1	0.0346(15)
200°C		0.2080(3)	0.2524(3)	0.1594(8)	1	0.0370(12)
250°C		0.1974(7)	0.2481(7)	0.121(2)	0.785(4)	0.077(3)
300°C		0.1974(9)	0.2465(13)	0.123(3)	0.769(4)	0.119(6)
250°C	O9A	0.177(2)	0	-0.022(5)	0.215(4)	0.044(8)*
300°C		0.183(3)	0	-0.009(7)	0.231(4)	0.067(11)*
250°C	O9B	0.150(4)	0	0.621(10)	0.215(4)	0.098(19)*
300°C		0.148(5)	0	0.670(12)	0.231(4)	0.12(2)*
RT	O10	0.1151(2)	0.3729(3)	0.3954(6)	1	0.0260(10)
100°C		0.1129(3)	0.3739(4)	0.3967(8)	1	0.0361(15)
150°C		0.1101(4)	0.3708(5)	0.4020(11)	1	0.0451(18)
200°C		0.1096(3)	0.3701(4)	0.4041(9)	1	0.0514(16)
250°C		0.0944(8)	0.3534(8)	0.447(2)	1	0.111(4)
300°C		0.0928(10)	0.3524(13)	0.435(3)	1	0.152(7)
RT	Ca1	0.1540(2)	0	0.6680(6)	0.42(1)	0.0541(9)
	Na1	0.1540(2)	0	0.6680(6)	0.28(1)	0.0541(9)
	Sr1	0.1540(2)	0	0.6680(6)	0.052(1)	0.0541(9)
100°C	Ca1	0.1622(6)	0	0.6793(12)	0.62(3)	0.089(2)
150°C		0.1887(6)	0	0.7439(15)	0.42(2)	0.059(2)
200°C		0.1954(5)	0	0.7561(13)	0.38(2)	0.0569(18)
250°C		0.3073(9)	0	0.969(3)	0.48(3)	0.143(6)
300°C		0.3015(15)	0	-0.035(5)	0.36(4)	0.197(14)
RT	Ca2	0.0406(2)	0.5	0.2010(6)	0.48(1)	0.0289(9)
100°C		0.0379(3)	0.5	0.2235(10)	0.46(2)	0.0486(16)
150°C		0.0315(4)	0.5	0.2422(11)	0.42(2)	0.0490(19)
200°C		0.0308(4)	0.5	0.2523(10)	0.40(2)	0.0559(18)
250°C		0	0.4632(11)	0.5	0.34(2)	0.114(5)
300°C		0	0.5302(12)	0.5	0.26(2)	0.106(7)
150°C	Ca3	0.1084(15)	0	0.118(4)	0.08(1)	0.020(6)
200°C		0.1082(11)	0	0.1184(35)	0.10(1)	0.029(4)
250°C	Ca4	0.592(3)	0	-0.158(8)	0.28(5)	0.243(19)*
300°C		0.404(5)	0	0.130(12)	0.09(2)	0.13(2)*
RT	K3	0.715(4)	0	-0.059(7)	0.14(2)	0.10(2)
100°C		0.735(4)	0	0.046(7)	0.16(3)	0.053(9)
150°C		0.696(3)	0	0.052(5)	0.24(3)	0.120(10)
200°C		0.688(3)	0	-0.061(6)	0.20(4)	0.166(13)*
250°C		0.959(3)	0	0.862(7)	0.42(5)	0.29(2)*
300°C		0.945(3)	0	0.834(8)	0.16(3)	0.143(14)*
RT	W1	0.2287(11)	0.5	0.012(3)	0.84(4)	0.040(4)
100°C		0.219(3)	0.5	-0.029(4)	0.76(6)	0.074(11)
150°C		0.2464(16)	0.5	0.066(4)	0.44(5)	0.047(7)*
200°C		0.2466(11)	0	0.060(3)	0.64(6)	0.069(4)*

Table 2. (Continued-3)

Temperature	Atom	x/a	y/b	z/c	sof	$U_{eq}(\text{\AA}^2)$
RT	W2	0.0817(8)	0	0.873(3)	0.82(5)	0.107(5)
100°C		0.075(2)	0	0.864(5)	0.84(6)	0.172(12)*
150°C		0.0789(19)	0	-0.139(5)	0.54(6)	0.104(10)*
200°C		0.0821(18)	0	-0.152(5)	0.44(6)	0.098(9)*
RT	W3	-0.0774(3)	0.5827(4)	0.0314(9)	1	0.0587(15)
100°C		-0.0752(7)	0.5847(9)	0.0306(19)	1	0.112(4)
150°C		-0.090(2)	0.589(3)	0.061(6)	0.59(7)	0.193(14)*
200°C		-0.090(2)	0.586(3)	0.054(6)	0.41(6)	0.174(14)*
150°C	W3'	-0.0384(19)	0.576(3)	0.024(5)	0.56(7)	0.168(14)*
200°C		-0.032(2)	0.578(3)	0.021(5)	0.37(6)	0.138(13)*
RT	W4	0	0.5	0.5	1	0.080(4)
100°C		0	0.5	0.5	1	0.088(6)
150°C		0	0.5	0.5	1	0.109(8)*
200°C		0	0.5	0.5	0.96(9)	0.136(9)*
RT	W5	0.083(3)	0.042(3)	0.371(9)	0.17(3)	0.09(2)
RT	W6	0.0995(9)	0	0.286(3)	0.80(5)	0.092(5)
100°C		0.0924(15)	0	0.2997(60)	0.66(9)	0.146(13)
RT	W7	0.0303(7)	0.0905(11)	0.505(3)	0.50(3)	0.084(5)
100°C		0.029(2)	0.092(3)	0.507(6)	0.22(5)	0.073(12)*

U_{eq} , equivalent isotropic displacement parameter; Sof, site occupancy factor.

* Refined isotropically, site occupancy without standard deviation was fixed.

Details individual occupancy shown at RT as Ca1 site(combination of Ca1,Na1,Sr1), all other cases only shown as total occupancy.

°C, two partially occupied tetrahedra of the T1A and T3A sites appear [occupancy of the central cation is 21.5(4)%]. At the same time, the occupancy of the T1 and T3 tetrahedral sites decreases to 78.5(4)%, which may be interpreted as being a factor contributing to the observed 21.5(4)% in the heat-collapsed structural phase change. The elongation and compression of Channels A and B in natural heulandite at room temperature and at 250 °C with the T1A and T3A sites are compared in Figure 2. The structural refinement of natural heulandite at temperatures from room temperature to 200 °C yielded *R* factors of 4.97–6.37%. The structure at 250 °C was refined using space group *C2/m* to an *R* = 14.44%. It should be noted that the X-ray reflections became weak because of the strong dehydration and cation disorder at 250°C. The overlap of two structural varieties is another reason for the higher value of *R* factor at 250 °C.

DISCUSSION

Structure at room temperature and 100 °C

The heulandite-type framework is built using 10 nodes

and is also known as a 4-4-1-1 unit (Gottardi and Gali, 1985). As shown by Ribbe and Gibbs (1967), the Si/Al ratio in the tetrahedral sites with a high Al content can be estimated from the T-O bond length. Typical bond lengths in tetrahedral coordination are known from the structure of feldspars with an Si-O bond distance of 1.61 Å and an Al-O bond distance of 1.75 Å (Kunz and Armbruster, 1990). From the bond distances in Table 3, the T2 site had the highest Al concentration (from the average T2-O bond distance), while the T4 site had an almost ideal Si-O bond distance (from the average T4-O bond distance). Therefore, it is expected that extra-framework cations preferentially bond to the oxygen atoms of the T2 tetrahedral ligands to compensate for the local charge imbalance caused by the substitution of Al³⁺ ions for Si⁴⁺ ions. Distortions to a framework are commonly described by changes to the angle between corner-sharing tetrahedra. The T-O-T connections are stable in the angle range 135–170° (Gibbs, 1982). In our heulandite sample, all the angles were between 134.5° and 163.7° at room temperature. The Al contents listed in Table 3 are those estimated using the formula $Al/(Al + Si) = 6.58 [(\bar{T}-\bar{O}) - 1.605]$ from Ribbe and Gibbs (1967).

Table 3. Interatomic bond distance (in Å) in Si, Al tetrahedral (T-O) and cation oxygen (M-O) of natural heulandite

	RT	100°C	150°C	200°C	250°C	
					A-Phase	B-Phase
T1 -						T1A -
O9	1.631(4)	1.623(7)	1.617(7)	1.630(6)	1.696(13)	
O4	1.639(4)	1.644(6)	1.633(6)	1.635(5)	1.597(12)	1.64(2)
O6	1.641(3)	1.641(5)	1.646(5)	1.641(4)	1.677(10)	1.56(1)
O3	1.643(4)	1.646(6)	1.656(6)	1.659(5)	1.555(10)	1.61(2)
O9A						1.60(2)
Mean	1.639(4)	1.639(6)	1.638(6)	1.641(5)	1.631(11)	1.60(2)
Al content(%)	22					
T2 -						
O1	1.648(2)	1.644(3)	1.649(3)	1.644(3)	1.676(6)	
O4	1.659(4)	1.657(6)	1.650(7)	1.649(5)	1.618(10)	
O10	1.660(4)	1.665(5)	1.659(6)	1.655(5)	1.622(10)	
O2	1.666(4)	1.652(6)	1.645(6)	1.644(5)	1.624(10)	
Mean	1.658(4)	1.655(5)	1.651(6)	1.648(5)	1.635(9)	
Al content(%)	35					
T3 -						T3A -
O7	1.625(4)	1.618(6)	1.588(7)	1.597(6)	1.603(13)	1.72(4)
O3	1.625(4)	1.627(6)	1.637(6)	1.632(5)	1.642(11)	1.81(3)
O2	1.632(4)	1.632(7)	1.630(8)	1.632(6)	1.671(12)	1.74(2)
O9	1.632(4)	1.636(6)	1.639(7)	1.631(5)	1.603(13)	
O9B						1.85(4)
Mean	1.629(4)	1.628(6)	1.624(7)	1.623(6)	1.630(12)	1.78(3)
Al content(%)	16					
T4 -						
O7	1.608(4)	1.606(7)	1.619(8)	1.603(6)	1.592(12)	
O8	1.625(4)	1.617(6)	1.616(7)	1.604(5)	1.602(13)	
O5	1.634(2)	1.623(4)	1.612(4)	1.609(3)	1.555(6)	
O10	1.638(4)	1.634(6)	1.631(8)	1.635(6)	1.648(13)	
Mean	1.626(4)	1.620(6)	1.620(7)	1.613(5)	1.599(11)	
Al content(%)	14					
T5 -						
O8(×2)	1.637(4)	1.641(6)	1.622(7)	1.627(6)	1.568(12)	
O6(×2)	1.648(4)	1.640(5)	1.640(6)	1.640(5)	1.633(10)	
Mean	1.643(4)	1.641(6)	1.631(7)	1.634(6)	1.605(11)	
Al content(%)	25					
Ca2 -						
W3	2.409(6)×2	2.404(13)×2	2.51(4)×2	2.47(4)×2		
O1	2.545(7)	2.540(9)	2.437(12)	2.401(10)		
W3	2.571(7)×2	2.717(17)×2				
W3'			2.44(4)×2	2.50(5)×2		
W4	2.624(4)	2.429(7)	2.231(8)	2.147(8)		
O10	2.702(5)×2	2.634(7)×2	2.656(9)×2	2.652(7)×2		
Ca2	2.680(8)	2.980 (13)				
Ca1 -						
W1	2.365(19)	2.51(3)				
W2	2.386(18)	2.49(3)	2.47(3)	2.39(3)		
W7	2.555(16)×2	2.69(4)×2				
W6	2.560(17)	2.53(4)				
O2	2.665(5)×2	2.629(8)×2	2.592 (10)×2	2.558(8)×2		
O3			2.773 (8)×2	2.730(7)×2		
K3	2.79(5)	2.04(5)	2.28 (4)	2.28(4)

Figure 1. Thermal analysis of natural heulandite up to 900 °C. Upper figure: Thermogravimetric curve showing continuous weight loss. Lower figure: Differential thermal curve showing dehydration peaks.

Extra-framework sites (cations and H₂O molecules)

Three cation sites (Ca1, Ca2, and K3) were located within the channel system at room temperature and at 100 °C (Table 2 and Fig. 3). According to Bresciani-Pahor et al. (1980), the Ca1 site is in Channel A and is occupied by monovalent and divalent cations, and the Ca2 site is in Channel B and is occupied solely by divalent cations. Using this idea, the cations were assigned by comparing the residual electron densities and the chemical composition.

It was found that the Ca1 site contained Ca, Na, and Sr atoms, but the Ca2 site contained only Ca atoms. The third site was identified by Koyama and Takeuchi (1977), and this was later confirmed for K-exchanged heulandite (Gali et al., 1983).

All the detected cation sites lie on the mirror plane. The Ca1 site in Channel A is sevenfold coordinated by two neighboring oxygen atoms of the tetrahedral framework (O2) and five H₂O molecules (W1, W2, W6, and 2 × W7). The maximum occupancy of the Ca2 site is limited to 50% because of its proximity to Ca2' (i: $-x, -y, -z$). The bond distance between Ca2 and Ca2' is 2.7 Å, which is less than twice the van der Waals radii of 2.0 Å for Ca. In the natural sample, the Ca2 site is eightfold coordinated with three O atoms (2 × O10 and O1) in the tetrahedral framework, and five fully occupied H₂O molecules (4 × W3 and 1 × W4). All the K atoms reside at the K3 site in the center of an 8-membered ring of tetrahedra (Channel C-type).

The total occupancy of the Ca1 site consisting of Ca, Na, and Sr atoms was refined to 75 (1)%. The Ca1 site is bonded to the W1 site, which is 84 (4)% occupied. Because the K3 and W1 sites are very close to each other, (the K3–W1 bond distance is 0.5 Å), these sites were barely resolvable by the room temperature refinement. At 100 °C, the W5 site, which was not coordinated to a cation site, completely disappeared. Other affected sites were the W6 and W7 sites, which lost 19% and 56% occupancy, respectively. The occupancy of the Ca1 site decreased from 75(1)% to 62(3)% because of the effect of dehydration. The decrease in occupancy for the other cations and for the water molecules was not significant.

Partially dehydrated structure at 150 °C and 200 °C

A marked decrease in occupancy of the H₂O site was observed at 150 °C. The cation occupancy of the Ca1 and

Figure 2. Diameter (in Å) of Channels A and B at room temperature and at 250 °C measured from the center of the framework O sites.

Figure 3. Distribution of the framework and extra-framework atoms at room temperature, and at 150 °C and 250 °C. Phase A and Phase B appeared at 250 °C.

Figure 4. Cation coordination at room temperature and at 150 °C projected along the [001] direction. The W4 site is located opposite to the Ca2 site at 150 °C.

Ca2 sites decreased at 150 °C and at 200 °C, while the occupancy of the K3 site increased (Table 2). The reason for the increased occupancy at the K3 site may be cation migration from the Ca1 site to the K3 site, or because of its close association with the disappearance of the W1 site. The W6 and W7 sites coordinated to the Ca1 site disappeared. The Overall H₂O content in Channel A decreased by around 70% compared with the results obtained for the parent structure.

Because of the loss of water, the Ca1 site became spread over different sites, and at the same time bonded to new framework oxygen atoms to compensate the charge imbalance. The Ca1 site was bonded to new framework oxygen atoms (O3) (Ca1–O3 = 2.773 Å). The Ca1 site moved towards the channel wall [Ca1–O2 = 2.67(1) Å and 2.59(1) Å at room temperature and 150 °C, respectively]. The only H₂O molecules bonding to the Ca1 site were the W2 site, and the Ca1 site coordination number decreased to 5 (Fig. 4). Fivefold coordination is unusual, although Armbruster and Gunter (1991) found a decrease in coordination number from 7 to 5 on dehydration at 175 °C. (This was a continuous progression of the dehydration, and data measurement was performed at low

Figure 5. Phase A showing the uninterrupted T1–O9–T3 and T1'–O9'–T3' linkages. The interrupted framework with the new disordered sites (T1A, T3A, O9A, and O9B) is shown in Phase B. The circles inside the framework indicate the original positions in Phase A.

temperatures, -173°C). A new cation site (Ca3) was found near the Ca1 site, and this may be a part of the Ca1 site (Fig. 3). The Ca3 site had a low occupancy 8(1)% and was fourfold coordinated ($2 \times \text{O6}$ and $2 \times \text{O4}$). The W3 site was divided into W3 and W3' sites because of the disorder at high temperature.

In Channel B, the coordination number of the Ca2 site did not decrease like it did for the Ca1 site (Fig. 4). The occupancy of the water molecules coordinated to the Ca2 site also did not decrease according to our refinement data. The Ca2 site maintained its sevenfold coordination number, and therefore no additional bonding with the framework oxygen was observed. The structure at 200°C showed a close similarity to the structure at 150°C . The atomic positions were similar, and the change in occupancy of the cations (also for the W4 site) was not considered to be significant. The W2, W3, and W3' sites decreased in occupancy (18%, 30%, and 34%, respectively), while the W1 site had an increased occupancy (45%) (Table 2), as compared with the result at 150°C .

Partially dehydrated (heat-collapsed) structure at 250°C and the structure at 300°C

The loss of H_2O in this temperature range leads to a distortion of the tetrahedral framework, which causes Channels A and B to compress and elongate (Fig. 2). Part of the structure changes its topology by breaking the T–O–T oxygen bridges [T1–O9–T3 and T1'–O9'–T3' ($i: -x + 1/2, y + 1/2, -z + 1$)] and forming a new framework with new T sites (Fig. 5). The new tetrahedral sites [labeled

T1A and T3A, each with a site occupancy of 21.5(4)%] share three vertices with the previously occupied tetrahedral site. The fourth vertex (O9A and O9B) is on the mirror plane and joins with an adjacent T site (Fig. 5). This suggests that Phase B possesses a particular three-dimensional framework structure with a partial breakdown of the open 10-membered ring common in the heulandite topology. At 250°C , no H_2O molecules were found with our detection limit from the difference Fourier maps (Table 2). The Ca2 moved from $4i$ site (site symmetry $2/m$) to $4h$ site (site symmetry 2) and makes statistical distribution along the b -axis because Ca2–Ca2' distance is only 1.23(4) Å. The Ca1 split into two sites Ca1 and Ca3. The total occupancy of the Ca1 and Ca3 sites is 76.0%, which is equal to the occupancy of the Ca1 site at room temperature. The disordered K3 site was found near the origin (0,0,0) with a high occupancy.

There was a general and continuous increase in the value of U_{eq} with dehydration for the framework atoms up to 200°C , and this feature reflects the possible structural disorder enhanced by the dehydration (Table 2). The temperature factor increased rapidly from 200°C to 250°C . At each temperature, there was a similar value of U_{eq} for the T and O sites. However, at 250°C , some of the atoms had a high value of U_{eq} (the T3A site among the T sites, and the O5, O7, and O8 sites among the O sites), corresponding to the partial breaking of the T–O–T linkages at 250°C . The disorder in the T sites at 300°C was similar to that at 250°C , considering the atomic positions and site occupancy. The occupancy of the Ca1, Ca2, Ca4, and K3 sites decreased. The Ca4 site occupancy decreased from

Figure 6. Change in the T-O-T angles with temperature. A significant change in the T-O-T angles began at 200 °C and became more pronounced at 250 °C.

28(5)% to 9(2)%, and the K3 site occupancy decreased from 42(5)% to 16(3)%.

The distortion of framework occurred at 250°C, which can be well described by the variation of T-O-T angles of T2-O1-T2, T4-O5-T4 and T1-O6-T5 (Fig. 6). The elongation of Channel A causes the T2-O1-T2 and T1-O6-T5 angles to decrease to 128.6° and 127.7°, respectively, from the values of 150.5° and 134.7°, respectively, at 200 °C.

Comparison with the heat-collapsed structure of Alberti and Vezzalini (1983)

Alberti and Vezzalini (1983) studied natural heulandite from Nadap (NB-heu) both before and after 6 h treatment under vacuum at 360 °C. They found that partial breaking of the T-O-T bridges occurred. The T3 site moved to a new site, T3D, with vertices O2, O3, and O7, and a new fourth vertex, O9D. The O9D vertex was positioned on the mirror plane and was either shared with an adjacent unit (Alberti and Vezzalini, 1983) or bonded to a hydrogen atom to form an OH group (Alberti et al., 1985). Migration of the T1 site to form a new tetrahedron was prevented by geometrical constraints. The Ca²⁺ ions in Channel B moved toward the center of the Channel and coordinated by two O1 sites forming the central part of the bow-tie-like connection between Channels A and B. Thus, the O1 site became strongly pulled to the center of Channel B, and the resulting strain was compensated for by the partial breaking of the T1-O9-T3 bridge. The thermal behavior of heulandite is dependent on the cation content of the CS2 site (Ca2 in this study) and the corresponding ionic potential.

NB-heu has a single Ca²⁺ site with an occupancy

of 18% (CS2) in the center of Channel B, whereas in the case of MO-heu, Phase B contains two Ca²⁺ sites, each with an occupancy of 34%. Therefore, the attraction of the framework oxygen, O1, towards the center of Channel B is stronger in MO-heu than in NB-heu.

According to Alberti and Vezzalini, (1983), the value of the *b*-axis is a function of the degree of breaking of the T-O-T bridge. The higher the number of T-O-T bridges that are broken, the greater the decrease in the *b*-axis. The decrease in the *b*-axis in the heat-collapsed phase of MO-heu is 6.7% (17.880 Å to 16.685 Å), and this value is smaller than that in NB-heu. However, the degree of T-O-T bridge breaking is enhanced more in the case of MO-heu (from T1 to T1A and T3 to T3A) than in the case of NB-heu (from T3 to T3D).

Gali et al. (1983) found a lower contraction of the unit cell parameters in a dehydration study on K-exchanged heulandite compared with Ca-heulandite. The higher K content of NB-heu than MO-heu did not influence much the cell contraction. The cell parameters showed a contraction in the *b*-axis of 9.1%, the *a*-axis of 4.3%, and the *c*-axis of 2.4% in NB-heu, whereas in this study, the respective contractions were 6.7%, 3.6%, and 1.2%. On the other hand, a less-disordered structure of NB-heu than MO-heu would follow the results of Koyama and Takéuchi (1977), i.e., the higher K content and the position at the center of channels would retard structural collapse.

Comparison with the heat-collapsed structure of Döbelin and Armbruster (2003)

There were similarities in the tetrahedral site disorder and T-O-T bridge breaking between a study by Döbelin and Armbruster (2003) and this study. Döbelin and Armbruster (2003) used a Cd-exchanged heulandite in stepwise dehydration experiments. At 250 °C, part of the structure changed its topology by breaking the T-O-T oxygen bridges to form a new tetrahedral configuration, with new T sites (T1A and T3A) and O sites (O9A and O9B) on the mirror plane. At 250 °C, the highly occupied Cd site, Cd1, (occupancy = 26.5%) in Channel B is within bonding distance of the O1 site of the tetrahedral framework. The disorder from T3 site to T3A is probably related to the higher ionic potential of Cd²⁺ than Ca²⁺ and the presence of significantly occupied Cd sites in Channel A.

According to the Döbelin and Armbruster (2003) study, at 250 °C, the strong elongation of Channel A is caused by six Cd sites (Cd2, Cd3, and Cd4) with an occupancy between 12.2% and 19.5%, while in the case of MO-heu, the elongation is accompanied by four cation

sites (Ca1 and Ca4) with high occupancies of 48.0% and 28.0%, respectively.

CONCLUSIONS

The dehydration sequence of MO-heu can be specified by the in situ single-crystal X-ray diffraction. The observed distribution of water molecules as a function of temperature reflects the structural roles of the Ca1 and Ca2 sites. The Ca1 site position was changed by the dehydration, and some cations located at the Ca1 site migrated towards the K3 site center of the 8-membered rings. A partial breaking of the framework structure was detected in the MO-heu sample, and this structural change is strongly dependent on the cations residing at the Ca2 site.

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Appendix 1. Anisotropic displacement parameters at room temperature

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca2	0.0128(15)	0.029(2)	0.034(2)	0	0.0007(14)	0
Ca1	0.068(2)	0.047(2)	0.050(2)	0	0.0287(17)	0
Na1	0.068(2)	0.047(2)	0.050(2)	0	0.0287(17)	0
Sr1	0.068(2)	0.047(2)	0.050(2)	0	0.0287(17)	0
K3	0.10(2)	0.16(5)	0.04(2)	0	0.024(17)	0
T1	0.0074(6)	0.0164(8)	0.0119(7)	0.0019(5)	0.0041(5)	-0.0007(5)
T2	0.0111(6)	0.0126(8)	0.0131(7)	-0.0001(5)	0.0057(5)	0.0010(5)
T3	0.0110(6)	0.0131(8)	0.0109(7)	0.0003(5)	0.0059(5)	0.0010(5)
T4	0.0085(6)	0.0152(8)	0.0115(8)	0.0006(5)	0.0042(5)	-0.0005(5)
T5	0.0077(8)	0.0167(12)	0.0129(10)	0	0.0031(7)	0
O1	0.041(3)	0.015(3)	0.022(3)	0	0.009(3)	0
O2	0.028(2)	0.036(3)	0.028(2)	-0.0087(19)	0.0179(17)	0.0026(18)
O3	0.037(2)	0.034(3)	0.023(2)	0.0011(18)	0.0206(18)	-0.0055(18)
O4	0.0246(19)	0.030(3)	0.017(2)	0.0050(17)	0.0055(16)	0.0099(17)
O5	0.030(3)	0.033(4)	0.037(4)	0	0.025(3)	0
O6	0.0116(17)	0.026(3)	0.032(2)	0.0031(18)	0.0083(15)	0.0003(15)
O7	0.030(2)	0.036(3)	0.031(3)	0.012(2)	0.0048(18)	0.0112(19)
O8	0.023(2)	0.040(3)	0.027(2)	-0.015(2)	0.0097(17)	-0.0028(18)
O9	0.0204(19)	0.022(3)	0.035(2)	-0.0076(18)	0.0127(17)	-0.0068(16)
O10	0.0188(18)	0.030(3)	0.027(2)	0.0012(18)	0.0075(16)	-0.0064(16)
W1	0.069(9)	0.021(5)	0.055(12)	0	0.049(9)	0
W2	0.065(8)	0.076(12)	0.150(14)	0	0.019(8)	0
W3	0.048(3)	0.055(4)	0.058(4)	0.006(3)	0.011(3)	-0.004(3)
W4	0.064(8)	0.061(10)	0.116(12)	0	0.041(8)	0
W5	0.07(3)	0.05(3)	0.17(5)	0.02(3)	0.08(3)	0.01(2)
W6	0.078(9)	0.100(15)	0.103(12)	0	0.045(9)	0
W7	0.051(7)	0.062(13)	0.122(13)	-0.020(9)	0.022(9)	-0.007(5)

Appendix 2. Anisotropic displacement parameters at 100 °C

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca2	0.019(2)	0.057(4)	0.047(4)	0	-0.007(2)	0
Ca1	0.124(6)	0.080(6)	0.083(5)	0	0.062(5)	0
K3	0.10(2)	0.033(13)	0.05(3)	0	0.06(2)	0
T1	0.0098(9)	0.0395(13)	0.0113(11)	0.0024(7)	0.0046(7)	-0.0007(7)
T2	0.0140(9)	0.0333(12)	0.0121(10)	0.0004(7)	0.0053(7)	0.0014(7)
T3	0.0138(9)	0.0358(12)	0.011(1)	0.0008(7)	0.0073(7)	0.0014(7)
T4	0.0100(9)	0.0382(13)	0.0124(11)	-0.0009(7)	0.0050(7)	-0.0008(7)
T5	0.0103(12)	0.0392(18)	0.0105(14)	0	0.0025(9)	0
O1	0.047(5)	0.029(5)	0.023(4)	0	0.008(3)	0
O2	0.035(3)	0.062(5)	0.031(3)	-0.010(3)	0.021(3)	0.000(3)
O3	0.045(3)	0.058(4)	0.020(3)	-0.006(3)	0.021(3)	-0.013(3)
O4	0.028(3)	0.056(4)	0.019(3)	0.002(3)	0.006(2)	0.006(3)
O5	0.037(4)	0.070(7)	0.040(5)	0	0.032(4)	0
O6	0.015(3)	0.046(4)	0.034(3)	0.001(3)	0.011(2)	0.002(2)
O7	0.039(3)	0.071(5)	0.036(4)	0.017(3)	0.008(3)	0.014(3)
O8	0.032(3)	0.070(5)	0.028(3)	-0.017(3)	0.011(2)	-0.001(3)
O9	0.027(3)	0.039(4)	0.038(3)	-0.004(3)	0.016(2)	-0.005(2)
O10	0.022(3)	0.060(4)	0.023(3)	0.002(3)	0.007(2)	-0.010(3)
W1	0.10(2)	0.086(17)	0.06(2)	0	0.063(19)	0
W3	0.087(7)	0.119(11)	0.085(8)	0.019(7)	-0.002(6)	-0.005(7)
W4	0.088(13)	0.073(14)	0.130(18)	0	0.072(13)	0
W6	0.060(14)	0.16(4)	0.21(3)	0	0.051(17)	0

Appendix 3. Anisotropic displacement parameters at 150 °C

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca2	0.030(3)	0.064(6)	0.036(4)	0	-0.001(3)	0
Ca1	0.067(5)	0.049(6)	0.072(6)	0	0.040(5)	0
Ca3	0.014(12)	0.010(13)	0.022(14)	0	-0.003(10)	0
K3	0.23(4)	0.035(13)	0.13(2)	0	0.11(3)	0
T1	0.0124(10)	0.0351(14)	0.0162(12)	0.0026(9)	0.0061(8)	-0.0012(8)
T2	0.0219(11)	0.0213(13)	0.0197(12)	-0.0009(8)	0.0103(9)	0.0003(8)
T3	0.0193(10)	0.0308(14)	0.0171(12)	-0.0007(9)	0.0102(8)	-0.0003(8)
T4	0.0154(10)	0.0321(14)	0.0166(12)	-0.0015(9)	0.0073(8)	-0.0018(8)
T5	0.0142(13)	0.0301(19)	0.0165(16)	0	0.0051(11)	0
O1	0.062(6)	0.022(6)	0.032(5)	0	0.009(4)	0
O2	0.057(4)	0.071(6)	0.051(5)	-0.012(4)	0.039(4)	0.004(4)
O3	0.044(4)	0.049(5)	0.024(3)	0.001(3)	0.020(3)	-0.010(3)
O4	0.035(3)	0.044(4)	0.028(4)	0.006(3)	0.009(3)	0.011(3)
O5	0.064(6)	0.052(7)	0.070(8)	0	0.057(6)	0
O6	0.019(3)	0.039(4)	0.044(4)	0.009(3)	0.016(3)	-0.002(2)
O7	0.047(4)	0.080(7)	0.047(5)	0.020(4)	0.004(3)	0.020(4)
O8	0.044(4)	0.069(6)	0.026(4)	-0.021(3)	0.007(3)	0.004(3)
O9	0.030(3)	0.031(4)	0.044(4)	-0.001(3)	0.018(3)	-0.002(2)
O10	0.034(3)	0.050(5)	0.046(4)	0.000(3)	0.013(3)	-0.013(3)

Appendix 4. Anisotropic displacement parameters at 200 °C

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca2	0.037(3)	0.066(5)	0.047(4)	0	0.003(3)	0
Ca1	0.068(4)	0.031(4)	0.084(5)	0	0.044(4)	0
Ca3	0.022(9)	0.012(9)	0.051(13)	0	0.016(9)	0
T1	0.0148(8)	0.0315(11)	0.0206(10)	0.0031(7)	0.0086(6)	-0.0009(6)
T2	0.0248(9)	0.0206(10)	0.0253(10)	-0.0006(7)	0.0134(7)	-0.0001(6)
T3	0.0225(9)	0.0272(10)	0.0224(10)	-0.0001(7)	0.0130(7)	0.0001(6)
T4	0.0189(8)	0.0313(11)	0.0202(10)	-0.0016(7)	0.0097(7)	-0.0031(6)
T5	0.0170(11)	0.0289(15)	0.0196(13)	0	0.0068(9)	0
O1	0.064(5)	0.020(4)	0.040(5)	0	0.011(4)	0
O2	0.065(4)	0.060(5)	0.065(4)	-0.017(3)	0.048(3)	-0.000(3)
O3	0.049(3)	0.048(4)	0.031(3)	-0.006(2)	0.025(2)	-0.014(2)
O4	0.041(3)	0.050(4)	0.028(3)	0.006(2)	0.008(2)	0.010(2)
O5	0.067(5)	0.079(8)	0.066(6)	0	0.057(5)	0
O6	0.022(2)	0.039(3)	0.055(3)	0.000(2)	0.021(2)	-0.0005(19)
O7	0.055(4)	0.067(5)	0.054(4)	0.020(3)	0.005(3)	0.020(3)
O8	0.050(3)	0.072(5)	0.033(3)	-0.022(3)	0.010(2)	0.005(3)
O9	0.033(2)	0.032(3)	0.050(3)	-0.005(2)	0.022(2)	-0.009(2)
O10	0.039(3)	0.053(4)	0.058(4)	0.003(3)	0.018(3)	-0.014(3)

Appendix 5. Anisotropic displacement parameters at 250 °C

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca2	0.071(6)	0.121(13)	0.167(14)	0	0.069(8)	0
Ca1	0.114(8)	0.113(13)	0.172(13)	0	0.037(8)	0
T1	0.050(2)	0.071(4)	0.067(3)	0.006(2)	0.0275(17)	0.0008(17)
T1A	0.041(6)	0.031(8)	0.059(7)	0.017(5)	0.017(5)	0.067(4)
T2	0.072(2)	0.060(3)	0.083(2)	0.0001(16)	0.0379(17)	-0.0009(13)
T3	0.062(2)	0.071(3)	0.068(2)	0.0063(19)	0.0331(18)	-0.001(2)
T3A	0.084(12)	0.17(3)	0.085(12)	0.007(14)	0.041(10)	0.032(14)
T4	0.0567(19)	0.078(3)	0.071(2)	-0.0087(15)	0.0312(15)	-0.0103(13)
T5	0.055(2)	0.080(4)	0.063(3)	0	0.0271(18)	0
O1	0.070(7)	0.109(13)	0.075(8)	0	0.030(6)	0
O2	0.106(7)	0.155(14)	0.099(7)	0.021(7)	0.075(6)	0.042(7)
O3	0.129(8)	0.107(11)	0.112(8)	-0.014(7)	0.087(7)	-0.011(7)
O4	0.096(7)	0.082(9)	0.086(7)	-0.014(6)	0.008(5)	0.005(5)
O5	0.163(18)	0.17(3)	0.31(4)	0	0.19(2)	0
O6	0.072(5)	0.089(8)	0.118(8)	0.026(6)	0.058(5)	0.024(4)
O7	0.085(7)	0.148(16)	0.161(13)	-0.016(11)	0.016(7)	0.045(8)
O8	0.129(10)	0.130(14)	0.118(10)	-0.070(10)	0.029(8)	-0.019(8)
O9	0.081(6)	0.049(7)	0.103(8)	0.016(6)	0.042(6)	0.004(4)
O10	0.117(8)	0.079(10)	0.136(9)	-0.041(8)	0.057(7)	-0.045(6)

Appendix 6. Anisotropic displacement parameters at 300 °C

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca2	0.083(8)	0.107(18)	0.165(15)	0	0.089(10)	0
Ca1	0.144(16)	0.17(4)	0.19(2)	0	0.002(15)	0
T1	0.070(3)	0.110(7)	0.096(4)	0.005(3)	0.045(3)	0.001(3)
T1A	0.042(6)	0.064(12)	0.080(8)	0.005(7)	0.025(5)	0.015(6)
T2	0.097(3)	0.076(4)	0.114(4)	0.003(2)	0.051(2)	-0.003(2)
T3	0.086(3)	0.087(5)	0.116(4)	0.012(3)	0.050(3)	-0.011(3)
T3A	0.093(11)	0.16(3)	0.102(12)	0.006(12)	0.069(10)	-0.014(11)
T4	0.083(3)	0.095(4)	0.100(3)	-0.008(2)	0.047(2)	-0.011(2)
T5	0.074(3)	0.087(5)	0.092(4)	0	0.037(2)	0
O1	0.110(11)	0.14(2)	0.117(12)	0	0.049(9)	0
O2	0.155(11)	0.25(3)	0.125(10)	0.013(11)	0.090(9)	0.057(13)
O3	0.155(11)	0.25(3)	0.145(12)	0.035(13)	0.100(10)	-0.006(12)
O4	0.155(11)	0.106(16)	0.107(9)	-0.003(8)	0.0001(69)	-0.026(9)
O5	0.21(2)	0.20(5)	0.25(3)	0	0.17(3)	0
O6	0.071(6)	0.152(17)	0.185(14)	0.034(10)	0.064(7)	0.024(6)
O7	0.114(10)	0.20(3)	0.173(15)	0.063(16)	0.026(9)	0.014(11)
O8	0.158(12)	0.26(3)	0.089(9)	-0.059(12)	0.030(7)	-0.030(13)
O9	0.111(10)	0.085(17)	0.149(13)	0.024(10)	0.049(9)	0.006(8)
O10	0.156(11)	0.109(19)	0.175(13)	-0.012(11)	0.062(10)	-0.065(11)