

The temperature-dependent $P2_1/c$ – $C2/c$ phase transition in the clinopyroxene kanoite $MnMg[Si_2O_6]$: a single-crystal X-ray and optical study

THILO ARLT* and THOMAS ARMBRUSTER**

*Mineralogisch-Petrographisches Institut, Universität Bern,
Baltzerstr. 1, CH-3012 Bern, Switzerland

**Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern,
Freiestr. 3, CH-3012 Bern, Switzerland

Abstract: The crystal structures and optical properties of kanoite, $MnMg[Si_2O_6]$, from Bani Hamid (United Arab Emirates) were investigated as a function of temperature. Kanoite was found to undergo a phase transition from space group $P2_1/c$ to $C2/c$ at approx. 240°C. The temperature dependence of the cell dimensions shows considerable deviations from linearity at the phase transition. The $h+k = \text{odd}$ X-ray reflections of the $P2_1/c$ phase remain sharp but decrease in intensity with increasing temperature and disappear at the phase transition. Single-crystal X-ray structure refinements were performed at 200°C (space group $P2_1/c$, $a = 9.758(3)$, $b = 8.897(1)$, $c = 5.283(1)$ Å, $\beta = 108.74(2)^\circ$, $V = 434.3$ Å³) and at 270°C (space group $C2/c$, $a = 9.796(5)$, $b = 8.880(8)$, $c = 5.315(3)$ Å, $\beta = 109.26(4)^\circ$, $V = 436.5$ Å³). The structures of low ($P2_1/c$) and high ($C2/c$) kanoite are isotypic with the low-Ca clinopyroxenes ($P2_1/c$) and their high-temperature $C2/c$ modifications, respectively. The two symmetry-independent $[Si_2O_6]^{4-}$ chains of the $P2_1/c$ phase become equivalent in the $C2/c$ phase. The M2 site (enriched in Mn) of the low-temperature phase is irregularly seven-fold coordinated (5+2), whereas it is six-fold coordinated (4+2) in the high-temperature phase.

Temperature-dependent optical properties of kanoite were calculated on the basis of the point dipole model, leading to non-linear birefringence at the phase transition. A non-linear change of retardation due to the phase transition was monitored with a polarising microscope equipped with a heating stage. A two-phase field, related to chemical inhomogeneity, was found over a temperature range of approximately 30°C.

Key-words: kanoite, clinopyroxenes, crystal structure, phase transition, optical properties, electronic polarisabilities.

Introduction

Kanoite, ideally $MnMg[Si_2O_6]$, was first reported as a $P2_1/c$ clinopyroxene by Kobayashi (1977) from the Tatehira mine, Oshima Peninsula in Hokkaido, Japan. Other occurrences, all from Mn-rich amphibolite-facies metamorphic belts, have also been described: Balmat in New York state, U.S.A. (Brown *et al.*, 1980; Petersen *et al.*, 1984), Buritirama, Brazil (Peters *et al.*, 1977; Schultz-Güttler *et al.*, 1986) and Bani Hamid area, United Arab Emirates (Gnos *et al.*, 1996). The Wabush Iron formation in SW-Labrador (Klein, 1966) is prob-

ably the fifth locality (Huebner, 1986). Recently Woermann (1996, pers. comm.) reported kanoite from the Mn-deposit Otjosondou, Namibia.

The first structure refinement on a synthetic kanoite with the composition $Mn_{0.9}Mg_{1.1}[Si_2O_6]$ was presented by Ghose *et al.* (1975), but only published in abstract form. Gordon *et al.* (1981) report a structure refinement of $P2_1/c$ kanoite coherently intergrown with a $C2/c$ pyroxene (Mn-rich diopside). Ordering of Mg on M1 and Mn on M2 was confirmed by a single-crystal X-ray study of kanoite from the United Arab Emirates (Gnos *et al.*, 1996). The sample of Gnos *et al.* (1996)

was also used for the high-temperature investigation presented in this study.

The $P2_1/c$ – $C2/c$ transition in kanoite at $330 \pm 20^\circ\text{C}$ was observed by Gordon *et al.* (1981) with *in situ* heating experiments using the TEM. In their exsolved $P2_1/c$ clinopyroxene, the authors observed antiphase boundaries to be unchanged before and after heating, indicating their stabilisation by some defects (e.g. Ca) at the domain boundaries.

Polymorphism with space group $P2_1/c$ at low and $C2/c$ at high temperatures is well known for low-Ca clinopyroxenes such as pigeonite (Mg, Fe, Ca)(Mg,Fe)[Si₂O₆] (Brown *et al.*, 1972), clinoferrisilite (Fe,Mg)₂[Si₂O₆] (Smyth, 1974; Sueno *et al.*, 1984) and clinoenstatite (Shimobayashi & Kitamura, 1991). The phase transition, originally suggested by Morimoto & Tokonami (1969), was subsequently confirmed by Smith (1969). The transition from $P2_1/c$ to $C2/c$ and *vice versa* is non-quenchable, rapid and displacive, and therefore extensively investigated by high-temperature X-ray techniques (Smyth, 1969, 1974; Prewitt *et al.*, 1971; and others). Thermodynamically, it is a first order transition. Based on high-temperature transmission electron microscopy (HTTEM), Shimobayashi & Kitamura (1991) recently suggested a thermoelastic type of a martensitic transformation mechanism.

The goal of this study is threefold: (1) to investigate the structures of low and high kanoite and the accompanying structural changes due to the $P2_1/c$ – $C2/c$ transition by means of single-crystal X-ray data collected as a function of temperature; (2) to model observed room temperature optical properties from crystal structure data and to extend the modelling to high-temperature kanoite structures; (3) to determine optical retardation values as a function of temperature in order to track the phase transition.

Experimental procedure

Single-crystal structure refinement

The kanoite crystal, approximately $0.05 \times 0.13 \times 0.2$ mm in size, employed for the structure refinement was selected from sample 6005 described by Gnos *et al.* (1996). Data were collected with an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer using graphite monochromated MoK α X-radiation. During the high-temperature measurements between 25 and $315(5)^\circ\text{C}$ the crystal

Table 1. Crystal data and refinement parameters for $P2_1/c$ kanoite (200°C) and $C2/c$ kanoite (270°C).

T	200°C	270°C
a (Å)	9.758(3)	9.796(5)
b (Å)	8.897(1)	8.880(8)
c (Å)	5.283(1)	5.315(3)
β (°)	108.74(2)	109.26(4)
V (Å ³)	434.3	436.5
Space group	$P2_1/c$	$C2/c$
No. refls.	1648	1405
No. unique refls.	1107	630
No. obs.	733	494
	$I > 2\sigma(I)$	$I > 3\sigma(I)$
No. parameters	93	50
R _{int} (%)	1.7	3.3
R (%)	2.7	3.0
R _w (%)	2.6	3.0
R _g (%)	3.3	3.8
Goof	1.56	1.90

$$R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum F_{\text{obs}}$$

$$R_w = (\sum w(|F_{\text{obs}} - F_{\text{calc}}|)^2 / \sum w F_{\text{obs}}^2)^{1/2}$$

$$R_g = wR = (\sum (w(|F_{\text{obs}} - F_{\text{calc}}|)^2 / \sum (w F_{\text{obs}}^2))^{1/2}$$

$$\text{Goof} = (\sum w(|F_{\text{obs}} - F_{\text{calc}}|)^2 / (N_{\text{ref}} - N_{\text{param}}))^{1/2}$$

was heated by a regulated ($\pm 5^\circ\text{C}$) hot-air blower. The exact temperature was checked after each experiment by using a specially designed goniometer head with a micro-thermocouple mounted at the crystal position.

Cell dimensions were determined from the angular settings of 10 reflections with $\theta < 18^\circ$. To determine the temperature dependence of the cell constants, the temperature was changed in steps of approx. 20°C . Intensities of selected P lattice characteristic reflections were measured at each temperature step.

Diffraction data with an ω -scan of $1.5^\circ + 0.35 \tan\theta$ were collected up to $\theta = 30^\circ$ yielding 1648 unique reflections for low kanoite at 200°C of which 733 had $I > 2\sigma(I)$, and 1405 unique reflections for high kanoite at 270°C of which 494 had $I > 3\sigma(I)$ (Table 1). Intensity data were empirically corrected for absorption effects by using psi-scans. Data reduction, including background and Lorentz-polarisation corrections, was carried out with the SDP program system (Enraf-Nonius, 1983). The structure was refined with the program SHELXTL (Siemens, 1990) using as initial values the structural parameters determined by Gnos *et al.* (1996), neutral atom scattering factors (International Tables for Crystallography, 1992), and a weighting scheme of $1/(\sigma^2(F) + 0.0001F^2)$. According to the electron microprobe analyses of Gnos *et*

al. (1996), 0.07 Ca p.f.u. was assigned to the M2 position, and the Mg/Mn ratio was allowed to vary on M1 and M2. Both M1 and M2 were assumed to be fully occupied. Because of the similarity of Mn, Fe and Mg, Al, Na scattering factors, the small iron concentrations in kanoite are represented by Mn and the low Al, Na concentrations by Mg. All atoms were refined with anisotropic displacement parameters, converging at $R = 2.7\%$ and $R = 3.0\%$ for low and high kanoite, respectively.

Optical investigations

The optical properties of synthetic end-member kanoite (sample R8020) were determined using the oil immersion technique. Synthetic idiomorphic kanoite crystals, approx. $0.01 \times 0.01 \times 0.05$ mm in size, were synthesized at 750°C and 0.2 GPa in hydrothermal autoclaves from oxide mixtures in sealed Au capsules. The certified refractive index liquids (series M, R.P. Cargille Laboratories Inc., USA) were calibrated with an oriented smithsonite refractometer crystal (Medenbach, 1985). Refractive indices were measured by the λ -variation method using a Leitz narrow-band interference filter (Jena^{er} Glas, SCHOTT, Mainz). The calculation of oil Cauchy constants and the fitting of crystal dispersion data to the Cauchy equation was done using the software-package described by Gunter *et al.* (1989).

The program "opt40" (Abbott, 1996) was used to optimise the electronic polarisabilities (α) with crystal structure, refractive indices and optical orientation as observables. Individual polarisabilities of Mn, Mg, Si, O_b (bridging) and O_{nb} (non-bridging) atoms were refined on the basis of the atomic coordinates described by Gnos *et al.* (1996) and optical properties known for kanoite at room temperature (Kobayashi, 1977, and measurements from this study). The optimised polarisabilities were used to calculate (Abbott, 1993, 1994) the refractive indices and the orientation of the optical indicatrix of low kanoite ($T = 200^\circ\text{C}$) and high kanoite ($T = 270^\circ\text{C}$) based on the respective structure refinements.

A polished section of approximately 80 μm thickness was chosen to measure the retardation vs. temperature (25–500 $^\circ\text{C}$) with a Leitz polarising microscope equipped with a LINKAM THMSG 600 heating and cooling stage (accuracy $\pm 1^\circ\text{C}$) and a Leitz Tilting Compensator. Kanoite

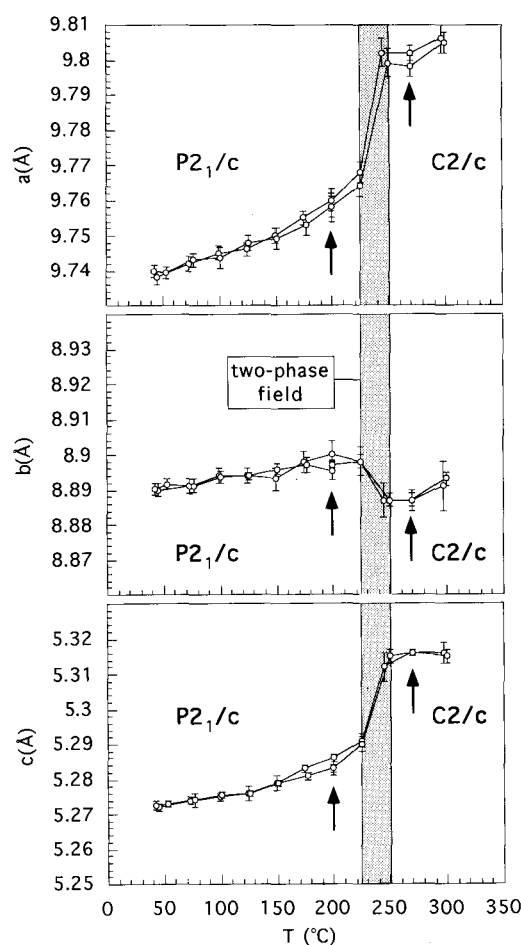


Fig. 1. Cell parameter vs. temperature in kanoite. Arrows indicate the temperatures where X-ray intensity data for structure refinements were collected.

grains in the thick section were adjusted to show maximum interference colours under crossed polarisers (45° position). Using the tilting compensator, the exact phase difference of two rays with different polarisation directions (retardation) was determined at each temperature.

The chemical composition of the kanoite used to measure retardation as a function of temperature was determined with a CAMECA SX50 electron microprobe (15 keV accelerating voltage/20 nA beam current). Synthetic and natural silicates were used as standards and ZAF-PAP corrections were applied for the quantitative analysis.

Results

Non-linear changes of lattice constants and intensities of $h+k = \text{odd}$ reflections

The variation of all cell dimensions (a , b , c , β and V) with temperature (25–300°C) is shown in Fig. 1 and 2. The temperature dependence of all unit-cell parameters exhibits considerable deviations from linearity in the vicinity of the phase transition. Between 225 and 250°C, a , c , β and V increase strongly while b decreases slightly, representing the $P2_1/c$ – $C2/c$ transition.

The transition temperatures were also determined by monitoring the intensities of the $h+k = \text{odd}$ reflections (forbidden in $C2/c$) over the temperature range from 25 to 300°C (Fig. 3). Heating the crystal, the critical reflections decrease gradually in intensity but remain sharp and go to zero at 245°C. After two days heating at 270°C (data collection) and short equilibration at 300°C the crystal was cooled down and the $h+k = \text{odd}$ reflections appeared at slightly higher temperature. These reflections were already observed at 250°C whereas the cell parameters still showed the characteristics of the $C2/c$ unit cell. At 225(10)°C a unit cell characteristic of the $P2_1/c$ phase was refined.

Optical investigations

Because no set of electronic polarisabilities could be found to reproduce the optical properties of kanoite determined by Kobayashi (1977), point dipole calculations were repeated with the optical measurements of synthetic crystals made in this study (Table 3). The results are in good agreement with calculated polarisabilities of other clinopyroxenes (Abbott, 1996). The optimised values are: $\alpha(\text{Mg}) = 0.48 \text{ \AA}^3$, $\alpha(\text{Mn}) = 0.37 \text{ \AA}^3$, $\alpha(\text{Si}) = 0.19 \text{ \AA}^3$, $\alpha(\text{O}_{\text{nb}}) = 1.40 \text{ \AA}^3$, $\alpha(\text{O}_b) = 1.43 \text{ \AA}^3$ ($R = 0.0041$).

These individual polarisabilities determined for kanoite at room temperature were used to model the optical properties of the high-temperature kanoite structures (Table 3). With rising temperature, the birefringence Δ_{calc} increases from 0.0247 at 25°C to 0.0264 at 200°C. If the birefringence of the 25°C and 200°C data is extrapolated to 270°C, a value of $\Delta = 0.0271$ is obtained which is lower than the calculated value of 0.0276 for the $C2/c$ phase at the same temperature. Thus, the phase transition is indicated by a weak non-linear

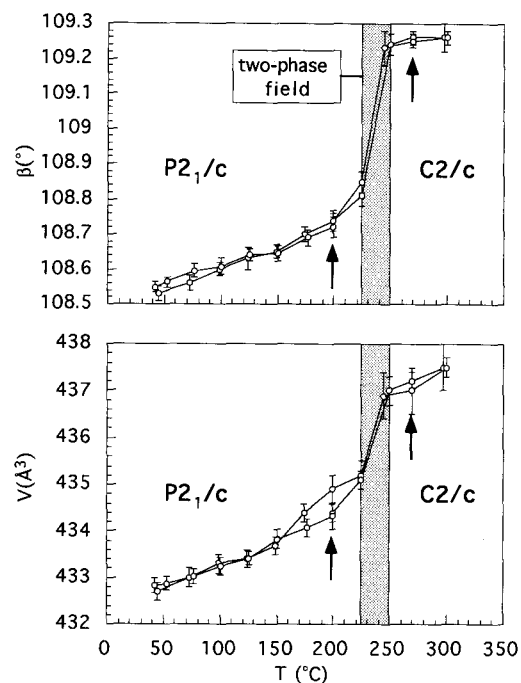


Fig. 2. Cell angle β and cell volume V vs. temperature in kanoite. Arrows indicate temperatures where X-ray intensity data for structure refinements were collected.

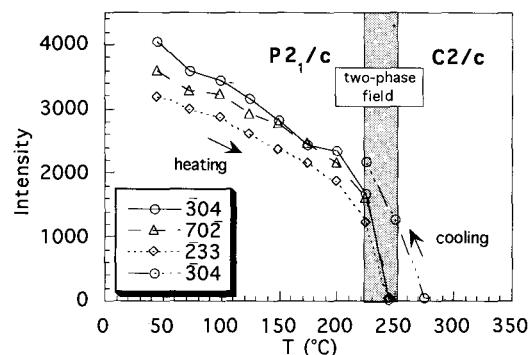


Fig. 3. $h+k = \text{odd}$ reflections vs. temperature in kanoite.

earity of birefringence. In other words, the non-linear increase of the interference colours with temperature due to the phase transition should be visible with the polarising microscope and crossed polarisers.

The temperature dependence of the birefringence was tested experimentally on a thick section

Table 2. Chemical composition (wt%) of synthetic kanoite R8020, natural kanoite 6005 used in the single-crystal X-ray study (Gnos *et al.*, 1996) and natural kanoite grain investigated optically.

kanoite (wt%)	R8020 synthetic	sample 6005 grain 83 (optical study)	sample 6005 Gnos <i>et al.</i> , (single crystal)
MnO	30.61	26.42	26.22
MgO	18.17	16.74	17.79
CaO	-	2.81	1.7
SiO ₂	51.71	52.07	52.42
FeO	-	0.97	0.65
Na ₂ O	-	0.36	0.25
K ₂ O	-	0.0	0.0
Al ₂ O ₃	-	0.47	0.38
Cr ₂ O ₃	-	-	0.03
TiO ₂	-	-	0.02
Total	100.49	99.84	99.46

(80 μ m) of sample 6005 (Fig. 4). The chemical composition of the investigated grain was found to be homogeneous by means of electron microprobe analyses (Table 2). Starting at room temperature the retardation of the $P2_1/c$ phase increases slightly up to the beginning of the $P2_1/c$ – $C2/c$ transition at approx. 205°C (Fig. 5a). With continued heating an abrupt change of interference colours is observable corresponding to an increase of retardation. The area of higher retardation ($C2/c$ phase) grows within the crystal grain when heated. The $P2_1/c$ – $C2/c$ phase boundary moves conspicuously like a coloured curtain that changes the transmitted light. At 215°C the grain

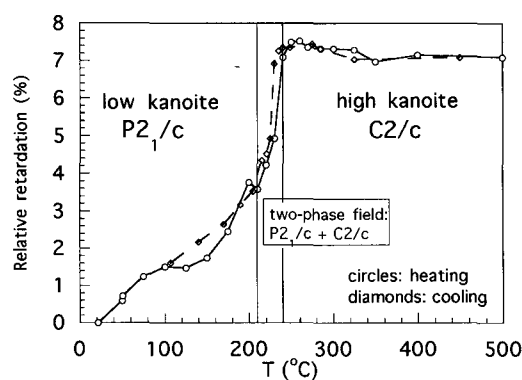


Fig. 4. Relative retardation vs. temperature of kanoite grain 83 in sample 6005.

is divided into a $C2/c$ and a $P2_1/c$ phase field (Fig. 5b). The position of the boundary is reproducibly correlated with temperature. At approx. 240°C the kanoite grain changes completely to the high kanoite form. A $P2_1/c$ – $C2/c$ two-phases field extends over approximately 30°C (Fig. 4).

Structural details

In $P2_1/c$ clinopyroxenes two symmetry-independent tetrahedral chains are distinguished. The more extended chain is termed the A chain and the more kinked one is referred to as the B chain (Cameron & Papike, 1980). The rotational aspect of the chains is described by the O or S notation.

Table 3. Observed and calculated optical properties of synthetic and natural low and high kanoite.

optical properties	observed data		calculated data		
	low-kanoite 25°C, $P2_1/c$ own data, Cauchy fit	low-kanoite 25°C, $P2_1/c$ Kobayashi (1977)	low-kanoite 25°C $P2_1/c$	low-kanoite 200°C $P2_1/c$	high-kanoite 270°C $C2/c$
$n(\alpha)$	1.699 ± 0.001	1.715 ± 0.002	1.699	1.694	1.692
$n(\beta) \parallel b$	1.702 ± 0.001	1.717 ± 0.002	1.702	1.696	1.694
$n(\gamma)$	1.724 ± 0.005	1.728 ± 0.002	1.724	1.720	1.719
$c \wedge Z$	40°	42°	39°	40°	34°
$2V_{Z, \text{exp}}$	54.5°	40–42°			
$2V_{Z, \text{calc}}$	39.7	46.2	40.5°	32.2°	31.6°
$\Delta\gamma - \alpha, \text{calc}$	0.025	0.013	0.0247	0.0264	0.0276

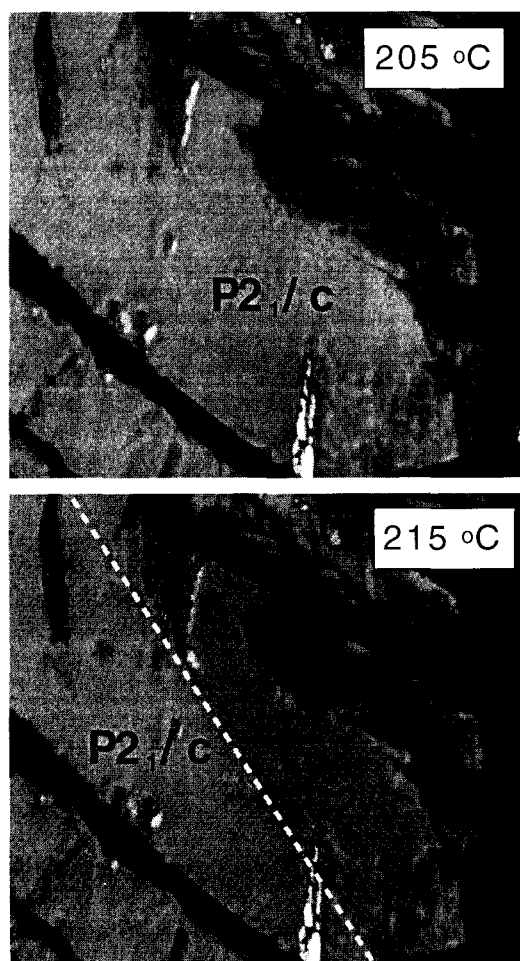


Fig. 5. Microscopic image of a kanoite grain in sample 6005 (edge length approx. 0.1 mm). a: low kanoite at 205°C, just below the phase transition. b: low kanoite ($P2_1/c$) and high kanoite ($C2/c$) at 215°C. – The colours of the photograph were intensified and transformed to grayscale by image processing. Light gray ($P2_1/c$) represents second-order red interference colours; dark gray colours ($C2/c$) represent third-order blue.

In an O-rotation, the basal triangular faces of the tetrahedra (O2-O3-O3'-plane) have an orientation opposite to the triangular faces of the octahedral strip to which they are linked through apical O1 oxygen atoms. In an S-rotation, the triangular faces of the octahedra and tetrahedra that are joined through O1 have the same orientation.

The atomic coordinates, populations and displacement parameters are given in Tables 4 and 5,

Table 4. Atomic coordinates and isotropic displacement parameters for low kanoite ($P2_1/c$) at 200°C and high kanoite ($C2/c$) at 270°C.

200 °C	x/a	y/b	z/c	B _{eq} (Å ³)
M1	0.2506(2)	0.6539(1)	0.2367(3)	0.48(2)
M2	0.2531(1)	0.02387(7)	0.2353(2)	0.95(1)
SiA	0.0420(1)	0.3410(2)	0.2693(2)	0.56(2)
SiB	0.5462(1)	0.8391(2)	0.2426(2)	0.58(2)
O1A	0.8670(3)	0.3376(4)	0.1629(5)	0.69(5)
O1B	0.3712(3)	0.8377(4)	0.1370(6)	0.72(5)
O2A	0.1182(3)	0.5021(4)	0.3265(6)	0.89(5)
O2B	0.6239(4)	0.9942(4)	0.3571(6)	1.13(5)
O3A	0.1043(3)	0.2586(3)	0.5661(6)	0.99(5)
O3B	0.6046(3)	0.7199(4)	0.4984(6)	1.03(5)

270 °C	x/a	y/b	z/c	B _{eq} (Å ³)
M1	0	0.9041	1/4	0.65(3)
M2	0	0.2740	1/4	1.20(2)
Si	0.2935	0.0905	0.2592	0.71(2)
O1	0.1190	0.0882	0.1510	0.92(4)
O2	0.3699	0.2502	0.3402	1.29(4)
O3	0.3538	0.0060	0.0420	1.64(4)

* kanoite at 25 °C (Gnos *et al.*, 1996)

M1(200 °C): 0.969(5) Mg and 0.031(5) Mn

M2(200 °C): 0.07 Ca, 0.790(6) Mn, and 0.140(6) Mg

M1(270 °C): 0.979(8) Mg and 0.021(8) Mn

M2(270 °C): 0.07 Ca, 0.786(9) Mn, and 0.144(9) Mg

Note: $B_{eq} = 8/3\pi^2 \sum_i (U_{ij} a_i^* a_j^* a_i a_j)$

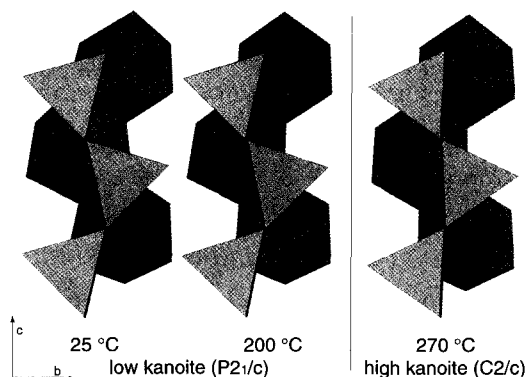


Fig. 6. B chain of SiO_4 -tetrahedra in low kanoite ($P2_1/c$) at 25°C and at 200°C compared with high kanoite ($C2/c$) at 270°C.

while selected interatomic distances are summarised in Table 6. The B silicate chain in low kanoite extends with increasing temperature until it becomes equivalent to the A chain at the transition temperature (Fig. 6). This chain extension is accompanied by a shift of O3B out of the coordination sphere of M2 and the movement of O3B' into it, where O3 is the chain-bridging oxygen (O_b).

Table 5. Anisotropic displacement parameters with standard deviations in parentheses, for low kanoite ($P2_1/c$) at 200°C and high kanoite ($C2/c$) at 270°C.

	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
200 °C						
M1	0.0063(5)	0.0064(5)	0.0057(6)	0.001(1)	0.0019(4)	0.0006(8)
M2	0.0128(3)	0.0126(3)	0.0093(3)	0.0017(5)	0.0014(2)	0.0010(4)
SiA	0.0059(6)	0.0073(6)	0.0080(5)	-0.0005(6)	0.0023(4)	-0.0007(5)
SiB	0.0070(6)	0.0078(6)	0.0079(5)	-0.0012(6)	0.0031(4)	-0.0009(5)
O1A	0.006(1)	0.012(2)	0.009(1)	0.000(2)	0.003(1)	0.000(1)
O1B	0.005(1)	0.011(2)	0.010(1)	-0.001(2)	0.002(1)	0.000(1)
O2A	0.012(2)	0.008(2)	0.014(1)	-0.004(1)	0.005(1)	-0.002(1)
O2B	0.015(2)	0.013(2)	0.015(1)	0.004(1)	0.004(1)	0.010(1)
O3A	0.007(1)	0.015(2)	0.015(1)	0.004(1)	0.004(1)	0.010(1)
O3B	0.011(2)	0.018(2)	0.012(1)	0.000(1)	0.006(1)	0.006(1)
270 °C						
M1	0.0169(4)	0.0144(4)	0.0118(4)	0	0.0013(3)	0
M2	0.0084(7)	0.0075(7)	0.0078(7)	0	0.0017(5)	0
Si	0.0080(4)	0.0088(4)	0.0099(4)	-0.0010(3)	0.0028(3)	-0.0008(3)
O1	0.0077(9)	0.013(1)	0.014(1)	-0.0001(7)	0.0031(8)	-0.0010(8)
O2	0.017(1)	0.012(1)	0.020(1)	-0.0047(8)	0.0068(9)	-0.0031(9)
O3	0.011(1)	0.030(1)	0.020(1)	0.0003(9)	0.0031(9)	-0.015(1)

Note: displacement parameters are of the form:

$$\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

In low kanoite, A and B chains are kinked with different O3-O3'-O3'' angles. The A chain is slightly S-rotated but almost fully extended. The O3A-O3A'-O3A'' angle is 188.3(2)° at 25°C (calculated from Gnos *et al.*, 1996) and 186.7(3)° at 200°C. The O-rotated B chain is relatively kinked (O3B-O3B'-O3B'' = 154.0(2)° at 25°C (Gnos *et al.*, 1996) and 157.2(3)° at 200°C). In high kanoite both chains are equivalent (O3-O3'-O3'' = 175.4(2)° at 270°C) and O-rotated (Fig. 8). The extension of the chains corresponds to an increase of the *c* axis where the relative change of *c* is more pronounced than that of *a* and *b*.

In kanoite Mn is strongly enriched on M2 while Mg favours M1. Bond valence calculations of kanoite at 25°C were reported by Gnos *et al.* (1996). The M2 position of low kanoite is coordinated by seven O atoms (5+2). The four M2-O_{nb} (non-bridging oxygen) distances range from 2.10 to 2.20 Å and are relatively temperature-independent. The bridging oxygen O3A bonds to M2 within 2.412 Å at 200°C (2.391 Å at 25°C, Gnos *et al.*, 1996) and the remaining two O_b have M2-O_b distances of 2.757 and 2.801 Å at 200°C and are strongly temperature-dependent (2.682 and 2.846 Å at 25°C, Gnos *et al.*, 1996).

In high kanoite the M2 position is six-coordinated (4+2) with M2-O_{nb} distances of 2× 2.182 and 2× 2.141 Å whereas O3 and O3' bond within 2.544 Å (Table 6).

In low kanoite the average of the six shortest M-O lengths expands to 0.16%/100°C in M1

Table 6. Selected interatomic distances and angles in low and high kanoite.

	200°C ($P2_1/c$)		270°C ($C2/c$)
	A chain	B chain	
Si-O2	1.598(4)	1.596(4)	1.595(3)
Si-O1	1.616(3)	1.617(3)	1.614(3)
Si-O3'	1.652(4)	1.655(4)	1.642(4)
Si-O3	1.659(3)	1.667(3)	1.660(3)
ave(4)	1.631(4)	1.634(4)	1.628(3)
ave (A+B)		1.633(4)	1.628(3)
M1-O1	2.056(3)	2.176(4)	2x 2.171(4)
M1-O1'	2.158(4)	2.065(3)	2x 2.066(3)
M1-O2	2.028(4)	2.039(4)	2x 2.031(3)
ave(6)		2.087(4)	2.089(3)
M2-O1	2.195(4)	2.174(4)	2x 2.182(3)
M2-O2	2.150(3)	2.108(3)	2x 2.141(3)
M2-O3	2.412(3)	2.757(4)	2x 2.544(4)
M2-O3'		2.801(3)	
ave(6)		2.299(3)	2.289(3)
ave(7)		2.371(3)	
OAV(M2)		291.6	520.2
BLD(M2)		8.268	7.427
Si-O3-Si	138.7(2)	136.1(2)	140.3(2)
O3-O3-O3	186.7(3)	157.2(3)	175.4(2)

OAV = octahedral angle variance (Robinson *et al.*, 1971)

BLD = bond length distortion (Renner & Lehmann, 1986)

O3A-O3A'-O3A (25 °C, Gnos *et al.*, 1996) = 188.3(2)

O3B-O3B'-O3B (25 °C, Gnos *et al.*, 1996) = 154.0(2)

whereas the expansion of the M2O₆ (or M2O₇) polyhedron (0.48 or 0.41%/100°C) is more pronounced due to the shifts of the O3B oxygens. The expansion in M1O₆ does not change during the $P2_1/c$ - $C2/c$ transition, but the average of the six shortest M2-O lengths decreases slightly. The

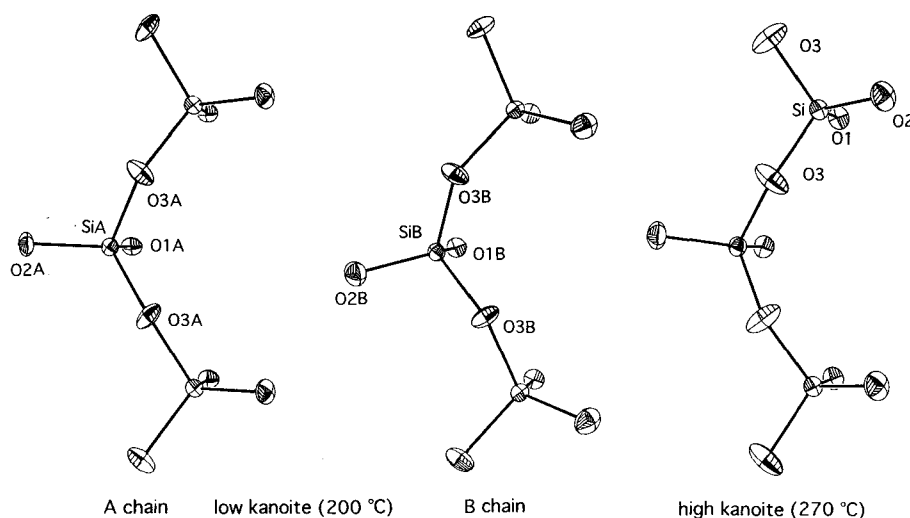


Fig. 7. Pyroxene characteristic "Zweier-Einfachketten" displayed with anisotropic displacement parameters (80% probability). O3 shows anisotropic motion perpendicular to the Si-O3-Si vector indicating dynamic disorder of the O3-O3-O3 angle in low kanoite at 200°C (A and B chain) and in high kanoite at 270°C.

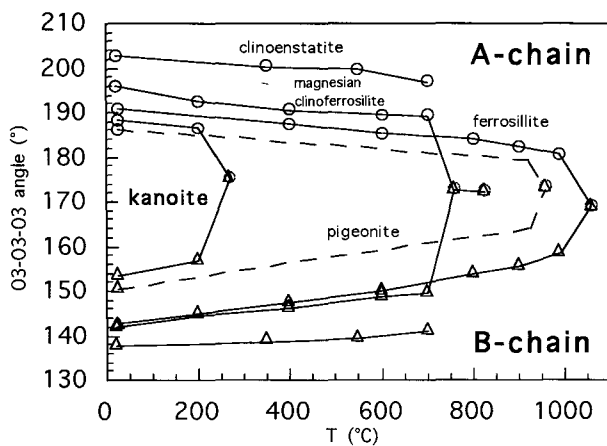


Fig. 8. O3-O3-O3 angles of $P2_1/c$ clinopyroxenes and orthoferrosilite vs. temperature (clinoenstatite: Pannhorst, 1984; magnesian clinoferrosilite: Smyth, 1974; pigeonite: Brown *et al.*, 1972; clinoferrosilite: Sueno *et al.*, 1984; kanoite: this study); dashed line: speculative slope of O3-O3-O3 angles in pigeonite.

expansion of the M2 polyhedron up to 200°C and the slight contraction above the phase transition (Table 6) is reflected in the b cell dimension. These expansion trends are in agreement with data presented for pigeonite (Brown *et al.*, 1972).

During the $P2_1/c - C2/c$ inversion the most significant change of atomic displacement parameters (ADP's) is observed for the bridging O3 positions. O3 strongly vibrates perpendicular to the Si-O-Si direction, corresponding to a highly variable O3-O3-O3 angle in high kanoite (Fig. 7).

Discussion

Crystal optics and electronic polarisabilities of clinopyroxenes

One of the new approaches of this study is the direct observation of the $P2_1/c - C2/c$ transition in a clinopyroxene with the polarising microscope equipped with a heating stage. Furthermore, the increase in birefringence at the $P2_1/c - C2/c$ inversion was predicted by point dipole calculations.

Such semi-quantitative predictions can be made, only if the *P* structure is refined at two different temperatures and a refinement of the *C* structure close to the inversion temperature is available. Fundamental for such calculations is the knowledge of the electronic polarisabilities which are refined on the basis of the room temperature optical properties.

The refractive indices and the derived birefringence $n(\gamma) - n(\alpha) = \Delta = 0.026$ determined in this study for synthetic kanoite are significantly different to those reported by Kobayashi (1977, $\Delta = 0.013$) for a natural sample with similar composition. However, the newly determined birefringence (Table 3) is much closer to the known values for clinopyroxenes (diopside-hedenbergite: $\Delta = 0.029\text{--}0.031$; pigeonite $\Delta = 0.023\text{--}0.029$) (Tröger, 1982). In addition, the failed attempt to calculate polarisabilities with the optical data of Kobayashi (1977) suggests that the refractive indices of Kobayashi (1977) are inaccurate.

Reinterpreting the data of Abbott (1996), the ratios of polarisabilities $\alpha(M1)/\alpha(M2)$ were found to be linearly correlated with the ratios of the ionic radii $r(M1)/r(M2)$ (Fig. 9). Ionic radii are those for octahedral coordination by Shannon (1976). The $\alpha(M1)/\alpha(M2)$ ratio obtained from calculations with the optical properties of our synthetic kanoite follows this trend. In alkali-free pyroxenes the ratios increase in the order diopside-hedenbergite-johannsenite-kanoite, whereas in sodium pyroxenes the ratios increase in the order jadeite-kosmochlor-aegirine. The equations derived from linear regression (Fig. 9) provide the possibility to estimate the $\alpha(M1)/\alpha(M2)$ ratio and allow a further check of correlation between optical and structural data.

The $P_{21/c}$ – $C2/c$ phase transition in kanoite

Two different crystals from the same sample were used for the single-crystal X-ray experiment and for the temperature-dependent optical study. The observed phase transition occurs over a temperature range (210–240°C) rather than at a unique point. The two-phase field could be observed directly by optical means. The high-temperature precision obtained on the heating stage ($\pm 1^\circ\text{C}$) excludes the possibility that this two-phase range is due to temperature fluctuations. In addition, we assume that the two-phase range is not caused by transition kinetics because at a stable temperature

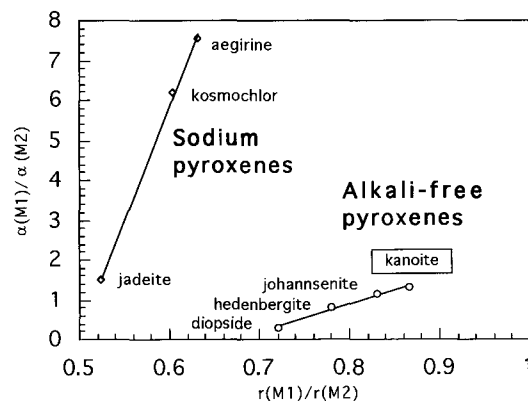


Fig. 9. Ratio of electronic polarisabilities vs. ratio of ionic radii $M1/M2$ in clinopyroxenes (data from Abbott, 1996, kanoite: this study). Ionic radii are from Shannon (1976). Linear regression: $\alpha(M1)/\alpha(M2) = 7.0 * r(M1)/r(M2) - 4.7$ (alkali-free pyroxenes); $\alpha(M1)/\alpha(M2) = 57.1 * r(M1)/r(M2) - 28.4$ (sodium pyroxenes).

the *P* and *C* phases coexist with a straight boundary and neither of the phases grows at the expense of the other. The position of the phase boundary is highly reproducible during heating and cooling.

The transition of the crystal studied by X-ray diffraction revealed various peculiarities. Disappearance of $h+k = \text{odd}$ reflections and non-linear increase of the unit-cell volume indicate transformation to the $C2/c$ phase between 225 and 250°C. Thus the inversion occurs at a slightly higher temperature than observed in the optical experiment (210–240°C).

The variation of the transition temperature and the existence of the two-phase field is most probably caused by minor chemical zonation. It has also been observed in the course of this study that other grains in the same microscopic section show even more pronounced differences in the transition temperature depending on the Na and Ca concentrations. In this context it is interesting to note that Gordon *et al.* (1981) determined the $P_{21/c}$ – $C2/c$ transition for a kanoite of the composition $\text{Ca}_{0.12}\text{Mn}_{1.02}\text{Mg}_{0.86}[\text{Si}_2\text{O}_6]$ at $330 \pm 20^\circ\text{C}$, and Pre-witt *et al.* (1971) report inversion temperatures for pigeonites from at least 1000°C for Mg-rich compositions down to 500°C for Fe-rich compositions.

The increase of the *c*-axis during the $P_{21/c}$ – $C2/c$ transition is easily explained by stretching the silicate chains aligned parallel to this direction. In low kanoite ($P_{21/c}$) the chains are kinked

within the (100) plane and therefore stretching leads to a decrease of b and to an extension of the octahedral layer parallel to a . The increase of a and c is much stronger compared with the decrease of b and increase of β , resulting in a significant increase of the cell volume.

The unit-cell volume of $C2/c$ kanoite is significantly larger than that of the $P2_1/c$ phase (Fig. 2b) at a similar temperature. For this reason it must be expected that with increasing pressure the phase transition shifts to higher temperatures. Kanoite from the Bani Hamid area (Gnos *et al.*, 1996; this study) formed under amphibolite facies with metamorphic peak conditions at 800–850°C and 0.65–0.9 GPa (Gnos & Kurz, 1994). Gordon *et al.* (1981) showed that their kanoites (Balmat, New York), which formed in regionally metamorphosed rocks with peak conditions at $625 \pm 25^\circ\text{C}$ and 0.65 ± 0.05 GPa, display antiphase domains (APD's) characteristic of a C – P transition. Thus kanoite crystallised in the C lattice and upon cooling transformed to the P lattice. By analogy the same assumption is made for the Bani Hamid sample.

In pigeonites the size of APD's correspond to the diffuseness of $h+k = \text{odd}$ reflections and were used as a rough guide to cooling rates (Buseck *et al.*, 1980, and references therein). In low kanoite the $h+k = \text{odd}$ peaks remained sharp until they disappeared at the $P2_1/c$ – $C2/c$ transition, indicating a large domain size. This is in agreement with a slow cooling rate due to its metamorphic origin and with the TEM observations of Gordon *et al.* (1981) who measured the APD's in kanoite to lie between 40 and 350 nm. Similar observations were made in the course of high-temperature X-ray experiments by Smyth (1974, magnesian clinoferrosilite) and Brown *et al.* (1972, pigeonite) where peak half widths also remained constant up to the transition point.

Related phase transitions in other pyroxenes

The results of this study show that the structures of low ($P2_1/c$) and high ($C2/c$) kanoite are isotypic with the corresponding high-temperature modifications found in pigeonite (Brown *et al.*, 1972), magnesian clinoferrosilite (Smyth & Burnham, 1972; Smyth, 1974) and ferrosilite phases (Sueno *et al.*, 1984). In clinoenstatite a $P2_1/c$ – $C2/c$ transition above 1000°C has been observed with HTTEM (Shimobayashi & Kitamura, 1991) but

no crystallographic data are available of high-temperature $C2/c$ clinoenstatite.

Thus one may ask whether, using data relating structure to temperature, a criterion can be defined which predicts the existence and temperature of such displacive phase transformations. There are two common principles of the phase transition: (a) stretching of the tetrahedral chain as analysed in terms of the O3–O3–O3 angle (b) a change from six- or seven-fold coordination for M2 in the P phase with strong bond-lengths distortion, to a more regular six-fold coordination (4+2) in the C phase. Both principles are correlated because the M2–O3 distances are also the longest and most irregular M2–O distances within the M2 coordination polyhedra.

In Fig. 8 the O3–O3–O3 angle for kanoite (this study, Gnos *et al.*, 1996) and other clinopyroxenes (Brown *et al.*, 1972; Smyth, 1974; Pannhorst, 1984; Sueno *et al.*, 1976, 1984) are compared. In the low phases both tetrahedral chains expand more or less linearly with temperature until the transition temperature is reached. Although no structural data are available for the structure of pigeonite just below the transition point, the $P2_1/c$ – $C2/c$ transition of pigeonite seems to be smoother. This is apparent in the variation of the O3–O3–O3 angle compared with the relatively strong changes in the low-Ca pyroxenes (kanoite, magnesian clinoferrosilite) and in ferrosilites (ortho– $C2/c$ transition). Although the O3–O3–O3 angles in kanoite are similar to those in pigeonite (Brown *et al.*, 1972) at ambient temperature, the difference of the transition temperature is about 700°C.

In all investigated pyroxenes with a $P2_1/c$ – $C2/c$ transition, M2 in the P phase is strongly shifted out of the centre of the distorted oxygen coordination polyhedron. However, this out-of-centre distortion remains preserved in the C phase. The high bond-length distortion (BLD) of M2 in the P phase, analysed in terms of BLD according to Renner & Lehmann (1986), is reduced in the C phase but the angular distortion (OAV according to Robinson *et al.*, 1971) behaves oppositely. There is also no significant variation of the M2 bond valence due to the $P2_1/c$ – $C2/c$ transformation. Thus, based on the coordination of M2 no general rule can be detected which may be responsible for the phase transition.

The $P2_1/c$ – $C2/c$ transition temperature between 210 and 240°C (optical data) in kanoite is the lowest observed in natural clinopyroxenes and confirms a very low activation energy barrier.

The $C2/m$ to $P2_1/m$ inversion in cummingtonite at -30°C reported by Yang & Smyth (1996) suggests that the $P2_1/c$ – $C2/c$ transition is not kinetically inhibited below ambient temperatures. Since the transition temperature of about 200°C is easily accessible experimentally, kanoite is of potential interest as an analogue to other $P2_1/c$ pyroxenes in further studies.

The high-temperature $C2/c$ clinopyroxene structures discussed above are generally different to the high-pressure $C2/c$ polymorphs of clinoenstatite (Angel *et al.*, 1992) and clinoferrosilite (Hugh-Jones *et al.*, 1994). Compression causes the $P2_1/c$ clinopyroxenes to decrease in volume resulting in $C2/c$ structures with extremely kinked tetrahedral chains. The decrease of the $\text{O3-O3}'\text{-O3}''$ angle (133.4° in MgSiO_3 ; 138.4° in FeSiO_3) is correlated with a strong decrease of the monoclinic β angle (101.50° in MgSiO_3 ; 103.01° in FeSiO_3). In contrast to this behaviour, the high-temperature phase transitions from $P2_1/c$ to $C2/c$ lead to stretching of the B chain (*e.g.* $\text{O3-O3}'\text{-O3}'' = 175.4^\circ$ in kanoite, this study) and of the monoclinic β angle ($>109^\circ$ in high-temperature $C2/c$ polymorphs). The cell volume increases 0.5% ($\Delta V = 0.14\text{ cm}^3\text{mol}^{-1}$ in $\text{Mn}_{0.5}\text{Mg}_{0.5}\text{SiO}_3$) during the high-temperature $P2_1/c$ – $C2/c$ transition, whereas the volume decreases approx. 3% during the high-pressure transition ($\Delta V = -0.80\text{ cm}^3\text{mol}^{-1}$ in MgSiO_3 , Angel *et al.*, 1992). Recently Hugh-Jones *et al.* (1996) observed with the TEM that the normally non-quenchable transformation of high-p $C2/c$ to $P2_1/c$ clinoferrosilite can be inhibited by defects.

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