

The crystal structure of low melanophlogite

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ABSTRACT

The crystal structure of the low temperature form of natural melanophlogite, $46\text{SiO}_2 \cdot 6\text{M}^{14} \cdot 2\text{M}^{12}$ ($\text{M}^{14} = \text{N}_2, \text{CO}_2$; $\text{M}^{12} = \text{CH}_4, \text{N}_2$), was determined using single-crystal X-ray diffraction data at room temperature. The structure is tetragonal with space group $P4_2/nbc$ and unit cell $a = 26.818(2)$ and $c = 13.365(1)$ Å, which is the $(2 \times 2 \times 1)$ superstructure of high-temperature cubic melanophlogite and includes four formula units. The structure with 335 variable parameters including anisotropic temperature factors (or atomic displacement factors) was refined to $R = 0.0288$ for 2706 observed reflections. The main silica framework consists of nearly regular SiO_4 tetrahedra forming large internal voids represented by distorted tetrakaidecahedra and pentagondodecahedra, which accommodate CO_2 or N_2 and CH_4 or N_2 guest molecules, respectively.

This low temperature form is a displacive variant of the cubic high-temperature form. The mean bond length is 1.588(4) Å for Si-O, and the bond angles for Si-O-Si are distributed over a large range from about 145 to 171° with a mean value of 159.4(3)°. The thermal vibrations of Si are nearly isotropic with amplitudes approximately equal to the average mean square displacement of 0.0119(4) Å². The thermal vibrations of the O atoms are highly anisotropic with a wide range of mean square displacements. There is a positive correlation between the Si-O-Si bond angles and the mean-square displacements of the O atoms.

INTRODUCTION

Melanophlogite is a very rare mineral, known from only five localities in nature. Its chemical composition is mainly silica, but includes some guest molecules like CH_4 , CO_2 , and N_2 . The mineral is known to crystallize in a clathrate structure, isotypic with gas hydrate I (v. Stackelberg and Müller 1954). One of the characteristic features common to the natural and synthetic clathrasil structures is the existence of the large voids inside the framework of SiO_4 units. The volumes of the cages range from 97 Å³ for the pentagondodecahedra to 356 Å³ for the eicosahedra, if we ignore the O atoms and connect all the Si atoms (Gies 1983; Gerke and Gies 1984). The large void spaces in melanophlogite are represented by pentagondodecahedral (denoted as $[5^{12}]$) or tetrakaidecahedral ($[5^{12}6^2]$) cages. The cubic unit cell of the structure of melanophlogite includes two $[5^{12}]$ voids and six $[5^{12}6^2]$ voids; the former is occupied mainly by CH_4 molecules and the latter by N_2 and CO_2 (Gies et al. 1982; Gies 1983).

According to Žák (1972) and Gies (1983), natural melanophlogite is tetragonal at room temperature with transformation-twinning of microdomains having the tetragonal c axis statistically oriented parallel to the edges of the crystal cubes. Gies (1983) studied crystals from Mt. Hamilton, California, using mainly X-ray single-crystal techniques and differential scanning calorimetry (DSC). Single-crystal diffraction patterns obtained at 80 °C indicated that the tetragonal low-temperature phase had changed to a cubic high-temperature

phase. The DSC experiments proved that a phase transition takes place at 65 °C with a transition energy of 41 J/mol. From observations of double refraction using a microscope with a heating stage, Gies (1983) found that the transition temperature differed with locality. Hereafter we refer to the tetragonal form of melanophlogite as α -melanophlogite and to the cubic form as β -melanophlogite.

A detailed structural study of β -melanophlogite was reported by Gies (1983). The composition of the sample was $46\text{SiO}_2 \cdot 6\text{M}^{14} \cdot 2\text{M}^{12}$, where M^{12} is CH_4 and N_2 in the $[5^{12}]$ cage, and M^{14} is CO_2 and N_2 in the $[5^{12}6^2]$ cage. The space group is $Pm\bar{3}n$, and the unit cell with $a = 13.436(3)$ Å at 200 °C has one formula unit. The mean value of 1.576 Å for the Si-O bond in β -melanophlogite is considerably smaller than the overall mean of 1.608 Å for silica frameworks reported by Brown and Gibbs (1969). The four independent Si-O-Si angles in β -melanophlogite are 148, 168, 179, and 180° with a mean value of 168.8°, which is considerably higher than the overall mean of 144° reported by Tossel and Gibbs (1978).

As already noted, microscopic observation or X-ray single-crystal diffraction patterns show that natural melanophlogite is usually twinned (Žák 1972). The crystals sometimes show fine growth zoning parallel to the cube faces (Skinner and Appleman 1963; Žák 1972). Žák (1972) obtained tetragonal diffraction patterns from the central parts of cubic crystals from Chvaletice, Bohemia, and measured nearly singly oriented unit cells with space group $P4_2/nbc$ and $a = 26.82$ and $c = 13.37$ Å. Micro-scale twinning in three orientations is thought to be inevitable in any natural crystalline specimen if it crystallized in

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the cubic structure at a temperature higher than the high-low transition temperature, and then cooled down to the tetragonal phase. The twinning is likely why a detailed structure study of α -melanophlogite has not previously been reported.

For this study, transparent cubic crystals with single domains were found in specimens collected from Mt. Hamilton, California, by Rogers Mineral (no. 1230), Ontario. X-ray single-crystal photographs taken with both oscillation and Weissenberg methods were firstly employed to determine the crystal symmetry and space group, and then X-ray integrated intensities were obtained for crystal structure determination and further refinement. All the measurements were carried out at room temperature. The refined structure was compared with that of β -melanophlogite.

DETERMINATION OF SPACE GROUP AND INTENSITY MEASUREMENTS

A clear cubic crystal was chosen and cut into cubes of ca. $0.3 \times 0.3 \times 0.3$ mm. Thin fragments showed clear extinction under a microscope. Weissenberg and oscillation photographs were taken with Ni-filtered $\text{CuK}\alpha$ radiation. An oscillation photograph showed layer lines as a symmetrical arrangement of reflections about the zero-layer line, and gave a repeat unit similar to the cubic c axis of α -melanophlogite, ca 13.4 Å. Weissenberg photographs taken for the first to the second layer showed clear reflections corresponding to a unit cell with $a = 26.8$ Å and a plane symmetry of $4mm$. The diffraction symmetry was thus determined to be $4/mmm$. All observed reflections were indexed with the tetragonal cell ($2 \times 2 \times 1$ superstructure) of β -melanophlogite, and the systematic absences, $h + k \neq 2n$ for $hk0$, $h \neq 2n$ for $h0l$ and $l \neq 2n$ for hhl , lead uniquely to space group $P4_2/nbc$, which was previously reported by Žák (1972).

X-ray diffraction intensities and cell constants were measured with a four-circle diffractometer (Rigaku AFC7s), using the $\omega/2\theta$ scan method with a scanning speed of $\omega = 4$ °/min. Monochromatized $\text{MoK}\alpha$ radiation was used for these measurements. An automatic search and indexing procedure successfully assigned a tetragonal primitive cell with lattice parameters $a = 26.818(3)$ and $c = 13.365(1)$ Å [$V = 9612(2)$ Å³] using 16 reflections in the 2θ range 25 to 30°. The X-ray integrated intensities of 17965 reflections from $2\theta = 0$ to 50° were collected through a quarter of the sphere ($h, k, l \geq 0$ and the Friedel pairs), and converted to structure factors after correction for Lorentz and polarization factors. All reflections satisfying $|F| \geq 3\sigma(F_o)$ were assumed to be observed. An absorption correction was applied for each reflection ($\mu R = 0.106$ for $\text{MoK}\alpha$ radiation) by assuming a spherical shape for the crystal. Symmetry-equivalent reflections were averaged and the standard deviations were estimated from the counting statistics. An isotropic extinction parameter was refined throughout the refinement. The details of the data collection and refinement procedure are given in Table 1.

STRUCTURE DETERMINATION AND REFINEMENT

The crystal structure of α -melanophlogite was not known prior to the present study. The structure determination was begun by assigning atoms to positions equivalent to those in the structure of β -melanophlogite (Gies 1983). The assumption was

that the structure of the α form may result from the β form by slight displacements of atoms, without breaking Si-O bonds. The atomic coordinates of the cubic basic cell of Gies (1983), which are mostly on special positions, were transformed to those in the new tetragonal superstructure cell. Consequently all 184 Si atoms, 368 O atoms, 24 guest molecules (M^{14}) in the $[5^{12}6^2]$ cages and 8 guest molecules (M^{12}) in the $[5^{12}]$ cages in the tetragonal superstructure cell were assigned to 13, 25, 3, and 1 groups of different equipoints of $P4_2/nbc$, respectively, as tabulated in Table 2, where the three kinds of the M^{14} sites are denoted as G1, G2, and G3, and the M^{12} site as G4. The origin of $P4_2/nbc$ was placed at the special position 222 at $-1/4, -1/4, 0$ to facilitate comparison with the structure of β -melanophlogite.

The $[5^{12}]$ and $[5^{12}6^2]$ cages were all assumed to be partially occupied by CH_4 and CO_2 molecules, respectively. Taking the structural model of the β form of Gies (1983) and also our preliminary molecular dynamics simulation into consideration, the guest molecules in this mineral are thought to move around or rotate via potential minima inside the cages, even at room temperature. Following Gies (1983), the present structure determination proceeded with dummy atoms (F and Mg) which the author chose to give the effective numbers of electrons, i.e., 8 and 12, of the partially occupied cages. The atomic scattering factors for neutral atoms were taken from the *International Tables for X-ray crystallography IV* (Ibers and Hamilton 1974).

After some initial difficulties, the least squares refinement converged at $R = 0.0296$ ($R_w = 0.0430$) for 2706 reflections with 335 parameters including anisotropic displacement factors. The difference Fourier synthesis at this stage showed large negatives at the centers of the G4 cages. The atomic scattering factors for G4 were then changed to those for carbon. The final model resulted in $R = 0.0288$ ($R_w = 0.0427$), and no significant peak was left in the difference Fourier synthesis. The F_o - F_c table is available on request to the primary author. The positional and atomic displacement parameters are listed in Table 3, where the former are compared with the initial coordinates transformed from those of Gies (1983). The absolute displacements of atoms from the initial positions of the high symmetry β phase are also shown in Table 3. The Si-O lengths and Si-O-Si angles are listed in Table 4 and Table 5, respectively.

TABLE 1. Details of data collection

Formula	$46\text{SiO}_2 \cdot 6\text{M}^{14} \cdot 2\text{M}^{12} (\text{M}^{14} = \text{CO}_2, \text{N}_2; \text{M}^{12} = \text{CH}_4, \text{N}_2)$
Space group	$P4_2/nbc$
Z	4
$F(000)$	6240
μ (cm ⁻¹)	7.09
Diffractometer	Rigaku AFC7s
Temperature (K)	297 K
h, k, l ranges	0 to 43, 0 to 43, 0 to 21 (and the Friedel pairs)
Total reflections measured	17965
Independent reflections	4750
$F_o \geq 3\sigma(F_o)$	2707
R, R_w	$R = 0.0288, R_w = 0.0427$
No. of refined parameters	335
Goof	1.8945

STRUCTURE AND MEAN SQUARE DISPLACEMENTS OF ATOMS

The present tetragonal superstructure is a displacive low-temperature variant of β -melanophlogite with the gas hydrate

type I structure. The unit cell with $a = 26.818(3)$ and $c = 13.365(1)$ Å is basically $2 \times 2 \times 1$ times of that of the cubic β -form with $a = 13.436(3)$ Å at 200 °C, and the $a/2c$ ratio, 1.0033, is only slightly greater than 1.0. The structure may possibly

TABLE 2. Equivalent sites between α - and β -melanophlogites

β -melanophlogite <i>Pm</i> $\bar{3}n$ $a = 13.436(3)$ Å at 200 °C (Gies 1983)				α -melanophlogite <i>PA</i> $_2/nbc^*$ $a = 26.818(2)$, $c = 13.365(1)$ Å at room temperature (this study)					Atomic sites
Atomic sites	Number of positions, Wyckoff ns ation, and site symmetry			Number of atoms in the cell	Number of positions, Wyckoff notation, and site symmetry			Atomic sites	
Si1	24	<i>k</i>	<i>m.</i>	96	16	<i>k</i>	1	$\times 6$	Si1 to Si6
Si2	16	<i>i</i>	$\bar{3}$.	64	16	<i>k</i>	1	$\times 4$	Si7 to Si10
Si3	6	<i>c</i>	$4m.2$	24	8	<i>i</i>	.2	$\times 2$	Si11, Si12
					8	<i>j</i>	..2	$\times 1$	Si13
O1	48	<i>l</i>	1	192	16	<i>k</i>	1	$\times 12$	O1 to O12
O2	24	<i>k</i>	<i>m.</i>	96	16	<i>k</i>	1	$\times 6$	O13 to O18
O3	12	<i>f</i>	$mm2..$	48	8	<i>h</i>	.2	$\times 2$	O19, O 20
					16	<i>k</i>	1	$\times 2$	O21, O22
O4	8	<i>e</i>	.32	32	16	<i>k</i>	1	$\times 1$	O23
					8	<i>j</i>	..2	$\times 2$	O24, O25
M ¹⁴ [5 ¹²⁶]	6	<i>d</i>	$\bar{4}m.2$	24	4	<i>c</i>	$\bar{2}22$	$\times 1$	G1
					4	<i>d</i>	4..	$\times 1$	G2
					16	<i>k</i>	1	$\times 1$	G3
M ¹² [5 ¹²]	2	<i>a</i>	<i>m</i> $\bar{3}$.	8	8	<i>h</i>	.2	$\times 1$	G4

Note: * The origin is on special position 222 at $-1/4, -1/4, 0$ for $\bar{1}$, being displaced from that appeared in the *International Tables for Crystallography* (Hahn 1987).

TABLE 3. Fractional coordinates and temperature factors of atoms in tetragonal α -melanophlogite

Atom	x	(x initial)	y	(y initial)	z	(z initial)	d (Å)	B_{eq} (Å ²)
(a) fractional coordinates and equivalent displacement factors								
Si1	0.19275(5)	[0.1927]	0.00847(5)	[0]	0.30894(8)	[0.3098]	0.2275(6)	1.16(3)
Si2	0.30728(5)	[0.3073]	0.00588(4)	[0]	0.31027(8)	[0.3098]	0.1578(4)	1.12(3)
Si3	0.09507(5)	[0.0951]	0.05733(5)	[0.0573]	-0.00311(8)	[0]	0.0416(2)	1.20(3)
Si4	0.40568(5)	[0.4049]	0.05722(5)	[0.0573]	-0.00631(8)	[0]	0.0869(3)	1.20(3)
Si5	0.25299(5)	[0.25]	0.15934(4)	[0.1549]	0.09941(7)	[0.1146]	0.2487(5)	1.05(2)
Si6	0.24701(5)	[0.25]	0.15235(4)	[0.1549]	0.87135(7)	[0.8854]	0.2154(6)	1.07(2)
Si7	0.16017(5)	[0.1587]	0.09715(4)	[0.0914]	0.17183(8)	[0.1827]	0.2155(5)	1.14(2)
Si8	0.15674(5)	[0.1587]	0.08642(4)	[0.0914]	0.80804(8)	[0.8173]	0.1895(5)	1.16(3)
Si9	0.34199(5)	[0.3413]	0.09456(4)	[0.0914]	0.17469(8)	[0.1827]	0.1377(4)	1.07(2)
Si10	0.34046(5)	[0.3413]	0.08852(5)	[0.0914]	0.81046(8)	[0.8173]	0.1219(5)	1.13(2)
Si11	0.12470(7)	[0.125]	0	[0]	1/2	[1/2]	0.0081(2)	0.95(4)
Si12	0.37501(7)	[0.375]	0	[0]	1/2	[1/2]	0.0004(1)	1.07(4)
Si13	0.25162(4)	[0.25]	=1/2-x	[0.25]	1/4	[1/4]	0.0616(2)	0.95(3)
O1	0.0381(1)	[0.0483]	0.1801(1)	[0.1819]	0.2594(3)	[0.2533]	0.290(2)	3.70(10)
O2	0.0590(1)	[0.0483]	0.1833(1)	[0.1819]	0.7485(2)	[0.7467]	0.290(2)	3.28(9)
O3	0.0702(1)	[0.0682]	0.1163(1)	[0.1267]	0.3889(2)	[0.4035]	0.345(2)	3.14(9)
O4	0.0676(1)	[0.0682]	0.1362(1)	[0.1267]	0.5800(2)	[0.5965]	0.338(2)	2.65(8)
O5	0.1171(1)	[0.1234]	0.1997(1)	[0.2017]	0.3616(2)	[0.3637]	0.180(2)	3.38(9)
O6	0.1329(1)	[0.1234]	0.2031(1)	[0.2017]	0.6322(2)	[0.6363]	0.263(2)	3.26(9)
O7	0.3175(1)	[0.3182]	0.0499(1)	[0.0483]	0.2331(3)	[0.2467]	0.187(2)	3.67(10)
O8	0.3197(1)	[0.3182]	0.0464(1)	[0.0483]	0.7393(3)	[0.7533]	0.198(2)	3.58(9)
O9	0.3816(1)	[0.3734]	0.0735(1)	[0.0682]	0.0976(2)	[0.0965]	0.262(2)	3.14(9)
O10	0.3667(1)	[0.3734]	0.0638(1)	[0.0682]	0.9050(2)	[0.9035]	0.216(2)	2.94(9)
O11	0.2995(1)	[0.2983]	0.1234(1)	[0.1234]	0.1151(2)	[0.1363]	0.285(2)	2.78(8)
O12	0.2957(1)	[0.2983]	0.1220(2)	[0.1234]	0.8472(2)	[0.8637]	0.234(2)	4.28(11)
O13	0.1590(2)	[0.1596]	0.0093(1)	[0]	0.4056(3)	[0.4051]	0.249(2)	3.29(10)
O14	0.3407(1)	[0.3405]	0.0142(1)	[0]	0.4069(2)	[0.4051]	0.381(2)	2.60(8)
O15	0.0469(1)	[0.0475]	0.0903(1)	[0.0905]	0.0196(3)	[0]	0.262(2)	2.81(9)
O16	0.4538(1)	[0.4526]	0.0906(1)	[0.0905]	-0.0285(2)	[0]	0.382(2)	2.29(8)
O17	0.2604(1)	[0.25]	0.2094(1)	[0.2025]	0.1619(2)	[0.1809]	0.420(2)	2.12(7)
O18	0.2412(1)	[0.25]	0.1970(1)	[0.2025]	0.7945(2)	[0.8191]	0.431(2)	2.74(8)
O19	0.0791(2)	[0.0781]	0	[0]	0	[0]	0.026(1)	2.14(14)
O20	0.4225(2)	[0.4220]	0	[0]	0	[0]	0.013(1)	1.92(13)
O21	0.2499(1)	[0.2500]	0.1737(1)	[0.1720]	-0.0170(2)	[0]	0.231(1)	1.76(7)
O22	-0.0068(1)	[0]	0.2501(2)	[0.25]	0.1575(2)	[0.1561]	0.182(1)	2.20(7)
O23	0.1185(1)	[0.1250]	0.1305(1)	[0.125]	0.2241(2)	[0.25]	0.414(2)	3.21(9)
O24	0.3687(1)	[0.3750]	=1/2-x	[0.1250]	1/4	[1/4]	0.240(1)	3.55(9)
O25	0.1208(2)	[0.1250]	=1/2-x	[0.3750]	1/4	[1/4]	0.159(1)	4.17(11)
G1	0	[0]	0	[0]	1/4	[1/4]	0	37.7(12)
G2	0	[0]	1/2	[1/2]	1/4	[1/4]	0	41.6(14)
G3	0.2503(8)	[0.25]	0.1243(3)	[0.125]	0.5117(7)	[0.5]	0.158(4)	30.7(6)
G4	0.2506(6)	[0.25]	0	[0]	0	[0]	0.016(2)	6.1(3)

Continued next page

TABLE 3. —Continued

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(b) anisotropic displacement factors (U_{ij})[*]						
Si1	0.0130(7)	0.0167(6)	0.0146(6)	-0.0021(5)	0.0014(5)	0.0011(4)
Si2	0.0124(7)	0.0150(7)	0.0150(6)	0.0007(4)	-0.0005(5)	0.0008(4)
Si3	0.0131(8)	0.0153(8)	0.0173(6)	0.0010(5)	-0.0009(4)	-0.0005(4)
Si4	0.0138(8)	0.0145(8)	0.0174(6)	0.0011(5)	-0.0004(4)	-0.0001(4)
Si5	0.0144(6)	0.0132(5)	0.0124(5)	-0.0005(5)	-0.0010(4)	-0.0006(4)
Si6	0.0172(6)	0.0111(5)	0.0122(5)	0.0011(5)	-0.0008(5)	-0.0008(4)
Si7	0.0137(7)	0.0155(7)	0.0140(5)	-0.0019(5)	0.0015(4)	0.0006(4)
Si8	0.0171(7)	0.0132(6)	0.0138(6)	-0.0006(5)	-0.0013(5)	-0.0002(4)
Si9	0.0136(7)	0.0137(6)	0.0132(5)	0.0011(5)	-0.0009(4)	0.0000(4)
Si10	0.0137(7)	0.0144(7)	0.0147(6)	0.0001(5)	0.0010(4)	-0.0016(4)
Si11	0.0086(10)	0.0140(10)	0.0136(8)	0	0	-0.0003(6)
Si12	0.0091(10)	0.0164(11)	0.0153(8)	0	0	-0.0009(6)
Si13	0.0140(5)	= U_{11}	0.0082(6)	-0.0011(9)	-0.0007(4)	= U_{13}
O1	0.038(2)	0.048(3)	0.054(2)	0.018(2)	-0.022(2)	-0.002(2)
O2	0.037(2)	0.048(2)	0.040(2)	0.002(2)	0.017(2)	-0.015(2)
O3	0.057(3)	0.037(2)	0.024(2)	-0.014(2)	0.009(2)	0.008(1)
O4	0.039(2)	0.026(2)	0.036(2)	0.005(2)	-0.015(2)	-0.014(1)
O5	0.045(2)	0.050(3)	0.034(2)	-0.030(2)	0.000(2)	-0.011(2)
O6	0.046(2)	0.032(2)	0.045(2)	-0.020(2)	0.006(2)	0.010(2)
O7	0.041(2)	0.050(2)	0.048(2)	-0.012(2)	0.001(2)	0.031(2)
O8	0.055(3)	0.037(2)	0.044(2)	-0.010(2)	-0.010(2)	-0.020(2)
O9	0.040(2)	0.048(2)	0.032(2)	0.015(2)	0.014(2)	-0.006(2)
O10	0.033(2)	0.042(2)	0.037(2)	-0.003(2)	-0.019(2)	0.010(2)
O11	0.037(2)	0.036(2)	0.033(2)	0.018(2)	-0.012(1)	0.000(1)
O12	0.052(3)	0.069(3)	0.041(2)	0.040(2)	0.005(2)	-0.011(2)
O13	0.031(2)	0.063(3)	0.031(2)	-0.006(2)	0.019(2)	0.003(2)
O14	0.029(2)	0.040(2)	0.030(2)	0.009(2)	-0.017(2)	-0.005(2)
O15	0.024(2)	0.034(2)	0.049(2)	0.016(2)	0.000(2)	0.003(2)
O16	0.026(2)	0.027(2)	0.034(2)	-0.012(2)	0.001(1)	-0.004(1)
O17	0.037(2)	0.026(2)	0.018(1)	-0.002(1)	0.002(1)	-0.009(1)
O18	0.063(3)	0.020(2)	0.022(1)	-0.003(2)	-0.005(2)	0.005(1)
O19	0.033(4)	0.013(3)	0.035(3)	0	0	0.001(2)
O20	0.027(3)	0.014(3)	0.032(3)	0	0	0.000(2)
O21	0.031(2)	0.025(2)	0.011(1)	0.003(2)	-0.004(1)	-0.002(1)
O22	0.038(2)	0.013(1)	0.033(2)	-0.001(1)	0.002(1)	0.000(2)
O23	0.041(2)	0.051(2)	0.030(2)	0.013(2)	0.012(2)	-0.009(2)
O24	0.046(2)	= U_{11}	0.042(3)	-0.005(3)	-0.019(2)	= U_{13}
O25	0.057(3)	= U_{11}	0.045(3)	-0.029(3)	0.014(2)	= U_{13}
G1	0.56(4)	= U_{11}	0.31(2)	0	0	0
G2	0.65(5)	= U_{11}	0.27(2)	0.07(3)	0	0
G3	0.47(2)	0.25(1)	0.45(1)	-0.00(2)	0.04(1)	-0.016(8)
G4	0.086(8)	0.086(8)	0.060(6)	0	0	-0.001(5)

Notes: Initial coordinates deduced from cubic β -melanophlogite and final displacements d in Å are also listed.

TABLE 4. The interatomic distances (Å) of Si-O in a-melanophlogite

Si1-O1	1.584(4)	Si7-O2	1.576(4)
O2	1.598(4)	O4	1.595(3)
O13	1.577(4)	O6	1.588(4)
O22	1.602(4)	O23	1.592(4)
mean	1.590(4)	mean	1.588(4)
Si2-O7	1.590(4)	Si8-O1	1.579(4)
O8	1.586(4)	O3	1.591(4)
O14	1.589(3)	O5	1.586(4)
O22	1.593(4)	O23	1.580(4)
mean	1.589(4)	mean	1.584(4)
Si3-O3	1.590(3)	Si9-O7	1.574(4)
O4	1.590(3)	O9	1.583(4)
O15	1.595(4)	O11	1.592(4)
O19	1.597(2)	O24	1.580(3)
mean	1.593(3)	mean	1.582(3)
Si4-O9	1.593(3)	Si10-O8	1.578(4)
O10	1.590(4)	O10	1.591(4)
O16	1.598(4)	O12	1.578(4)
O20	1.601(2)	O25	1.575(3)
mean	1.596(3)	mean	1.581(4)
Si5-O6	1.577(4)	Si11-O13 ^{x2}	1.581(4)
O11	1.589(4)	O15 ^{x2}	1.581(4)
O17	1.594(3)	mean	1.581(4)
O21	1.604(3)	Si12-O14 ^{x2}	1.593(3)
mean	1.591(3)	O16 ^{x2}	1.591(3)
Si6-O5	1.588(4)	mean	1.592(3)
O12	1.572(4)	Si13-O17 ^{x2}	1.591(3)
O18	1.584(3)	O18 ^{x2}	1.594(3)
O21	1.601(3)	mean	1.593(3)
mean	1.586(3)		

TABLE 5. Bond angles (°) Si-O-Si, in melanophlogite

α -melanophlogite (this study)		β -melanophlogite (Gies 1983)	
Si1-O1-Si8	165.7(3)	Si2-O1-Si1	166.9(2)
Si1-O2-Si7	160.4(3)		
Si3-O3-Si8	156.9(2)		
Si3-O4-Si7	154.6(2)		
Si6-O5-Si8	157.8(2)		
Si5-O6-Si7	168.2(3)		
Si2-O7-Si9	163.4(3)		
Si2-O8-Si10	163.4(3)		
Si4-O9-Si9	159.6(3)		
Si4-O10-Si10	158.3(3)		
Si5-O11-Si9	157.3(2)		
Si6-O12-Si10	172.1(3)		
Si1-O13-Si11	170.1(3)	Si3-O2-Si1	179.0(2)
Si2-O14-Si12	158.1(3)		
Si3-O15-Si11	159.5(2)		
Si4-O16-Si12	155.4(2)		
Si5-O17-Si13	157.3(2)		
Si6-O18-Si13	157.6(2)		
Si3-O19-Si3	148.9(4)	Si1-O3-Si1	148.3(3)
Si4-O20-Si4	147.3(4)		
Si5-O21-Si6	145.1(2)		
Si1-O22-Si2	148.1(2)		
Si7-O23-Si8	160.8(2)	Si2-O4-Si2	180.0(1)
Si9-O24-Si9	166.1(2)		
Si10-O25-Si10	171.1(2)		
grand mean	159.4(3)		168.8

distort in Brillouin zone-boundary modes in the \mathbf{a}^* and \mathbf{b}^* directions of the cubic P lattice, resulting in slightly larger shrinking along the \mathbf{c} axis. The cell volume divided by four is about 1% smaller than that of the β form of Gies (1983) at 200 °C. The $[5^{12}]$ and $[5^{12}6^2]$ cages are slightly distorted in complying with the distortion of the lattice. However, the thirteen symmetrically independent SiO_4 units all retain the regular tetrahedral lengths and angles: the average Si-O distance is 1.588(4) Å and O-Si-O angle 109.5(2)°, compared to 1.576 Å and 109.45° obtained for the α form of Gies (1983) at 200 °C. The average Si-O-Si angle is 159.4(3)°, which is much smaller than that of the β form, 168.8°. The inverse relationship between the Si-O lengths in the α and β forms appears to be comparable with that observed in other framework structures. However, in recent studies of silica or other framework structures, the inverse relation of atomic distances with temperature is not necessarily as it appears in the usual harmonic structure refinements. According to Kihara (1990), Downs et al. (1992), Dove et al. (1997), Kihara (2001), and others, the Si-O bonds in some framework structures evidently expand with increasing temperature. As shown later, the displacement factors of the O atoms are strongly anisotropic with large amplitudes in the longest principal axes of thermal ellipsoids. The displacement parameters obtained in the present study suggest that large librational motions are responsible for the reduction in Si-O distances.

A projection of the structure along the \mathbf{c} axis is shown in Figure 1. The $[5^{12}6^2]$ cages are connected by sharing distorted hexagons of Si-Si joins to form columns of cages parallel with the three crystallographic axes. The G1 and G2 cages are both in $[001]$, and the G3 cages in $[100]$ and $[010]$. The six Si-Si vectors form an interfacial hexagon with four long and two

short lengths. The interfaces between any non-equivalent pairs for G1, G2, G3, and G4 are the distorted pentagons of three kinds of Si-Si joins, each having two, two, and one joins with different lengths.

The G1 cage consists of Si1, Si3, Si7, Si8, Si11, O1, O2, O3, O4, O13, O15, O19, and O23 atoms (Figure 2a). Six Si, four Si3, and two Si11 atoms form the hexagonal rims with six O atoms (consisting of four O15 and two O19 atoms) located away from the Si-Si vectors. Any adjacent two G1 cages are connected by sharing this atomic ring. The displacements of the atoms in the ring from the cubic positions are relatively small in comparison with those for the remaining atoms of the cage (Table 3). The G2 cage involving Si2, Si4, Si9, Si10, Si12, O7, O8, O9, O10, O14, O16, O20, O24, and O25 atoms (Fig. 2b) is not equivalent with the G1 cage, but its distortion pattern appears similar to that for the G1 cage. The displacements of the Si4, Si12, O16, and O20 atoms, which form a ring shared by two G2 cages, from the cubic positions are also small as observed for G1. The G3 site is on a general position, and the atoms involved in this cage are Si1 to Si13, O1 to O18, and O21 to O25 (Fig. 2c); all of the atoms except those shared by the G1 and G2 cages are on general positions. This cage is distorted more than the G1 and G2 cages. The G4 cage involving Si atoms from Si1 to Si10, O atoms from O1 to O12, and from O19 to O22 (Fig. 2d), is also slightly distorted.

The mean-square displacements (abbreviated as msd) or B_{eq} values (Table 3) for Si atoms are about equal, and the msd matrices are almost isotropic. The mean obtained from averaging over the three principal directions for all Si atoms is 0.0119(4) Å². On the contrary, the msds for O atoms are highly anisotropic (Fig. 2) and show a wider distribution than the Si atoms. The mean msd obtained by averaging over all the principal axis directions for all O atoms is 0.038(1) Å². The msds for the shortest axes are distributed over a narrow range from 0.012 to 0.017 Å², which is about equal to that for Si atoms. The directions of the largest msd values for O atom ellipsoids are nearly perpendicular to the Si-O-Si planes (Fig. 2), suggesting the librational motions of the Si-O-Si planes around the Si-Si axes. The α form of this mineral appears to be similar to ordinary framework silica compounds with small unit cells. However, we are aware of large msds in the longest principal axes of the thermal ellipsoids of some O atoms in comparison with the room temperature values for more common silica minerals like quartz and tridymite.

Figure 3 shows the relationship between Si-O-Si angles and the average msd for O atoms. We see that the msds for the shortest principal axes stay level or are only slightly positive, while the values for the longest and the second longest axes have strong positive correlations with the Si-O-Si angles. That is to say, larger msd values are associated with larger angles. This positive correlation between the Si-O-Si angles and the msd values of O atoms is not well known in silica compounds. It may be a characteristic feature since more than two or three different configurations are necessary to link the corners of tetrahedra in clathrasil structures. Alpha-melanophlogite with low symmetry and the superstructure cell consists of many independent O atoms, which form a large variety of Si-O-Si bonds scattered over a wide range. In the β form, four independent O

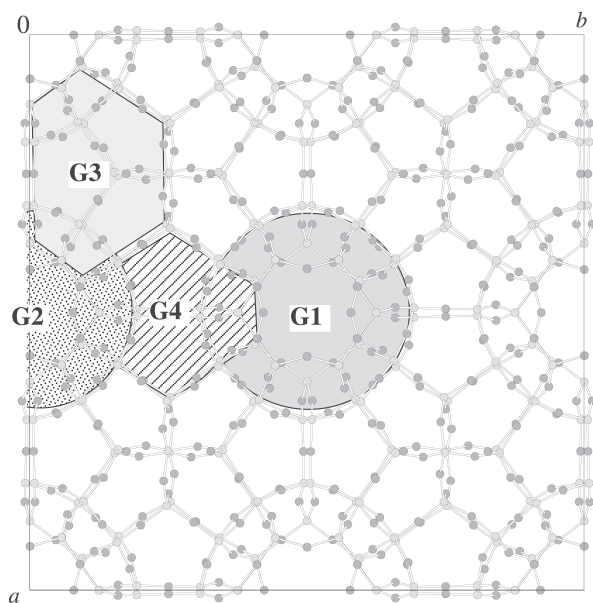


FIGURE 1. The structure of tetragonal α -melanophlogite projected along the \mathbf{c} axis. Three symmetrically different tetrakaidecahedra are indicated with dots. A pentagondodecahedron is also shown with a striped pattern.

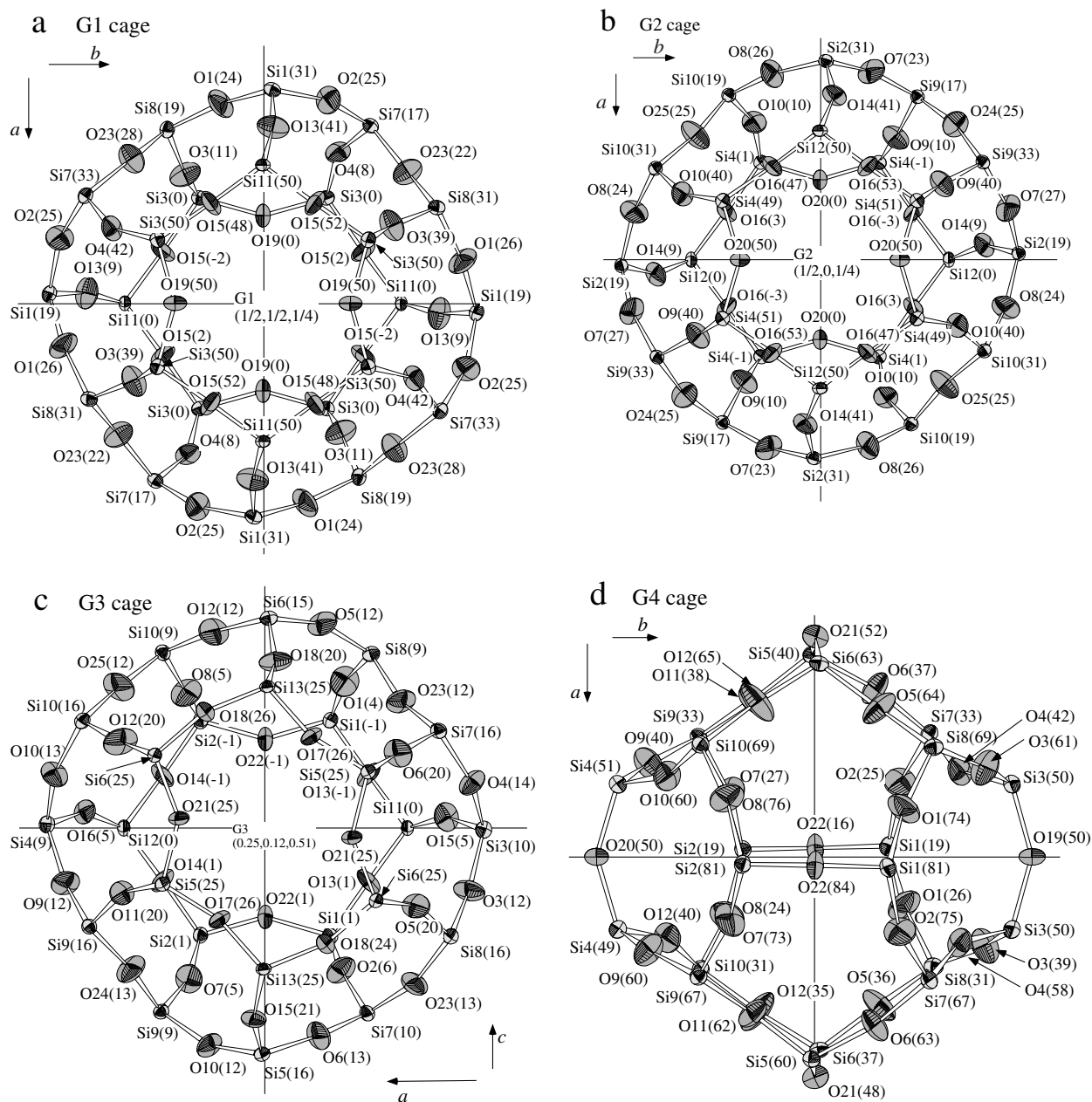


FIGURE 2. Thermal ellipsoid drawings of atoms (50% probability). (a) G1 cage, (b) G2 cage, (c) G3 cage, and (d) G4 cage. Numbers in parentheses show the z fractional coordinates of atoms in percentages.

atoms form Si-O-Si angles with different values, 148, 168, 179, and 180°, but these can be seen to belong to three different groups. In the present case, such groupings of O atoms is not clear-cut, but it may be possible to divide them into two groups, one a minor group with smaller angles about 147° and the other a major group of larger but widely scattered values from about 155 to 172°. The msd values for the longest axes of the thermal ellipsoids of O atoms forming the interfacial atomic ring connecting G1 and G1, G2 and G2, and G3 and G3 are smaller than those for other O atoms. The O19, O20, O21, and O22

atoms, all corresponding to O3 in the β form and attending the interfaces connecting the cages, belong to the group of the smallest angle of the Si-O-Si bonds, about 147° in the common planes. O atoms at other parts of cages show larger and widely scattered angles, and they have larger msd values.

The displacement factors for the G1, G2, and G3 sites are unusually large (Table 3), which indicate randomly moving guest molecules, weakly trapped in the large space cage of the silica framework. In our preliminary molecular dynamics simulation, the guest molecules, CO₂ in the [5¹²6²] cage and CH₄ in

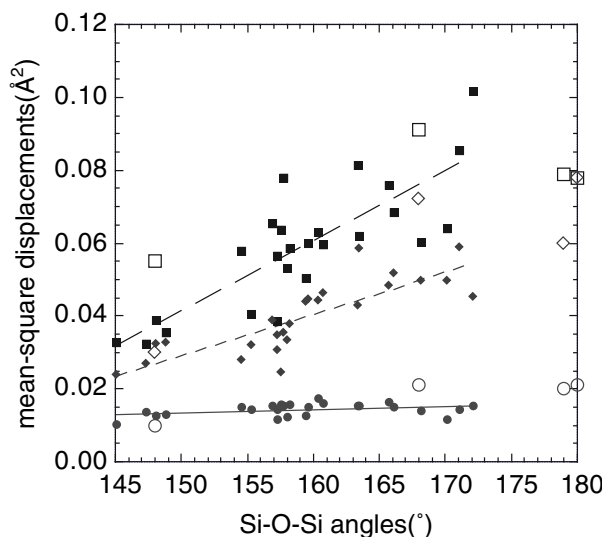


FIGURE 3. The relationship between Si-O-Si bond angles and the mean square displacements of O atoms relative to the principal axes. The values for the shortest, intermediate and longest principal axes of the thermal ellipsoids for the O atoms are marked with solid circles, solid diamonds and solid squares, respectively. The open marks represent values for cubic β -melanophlogite.

the $[5^{12}]$ cage, move randomly inside the cages. In particular, the linear CO_2 molecules move around in the large $[5^{12}6^2]$ cage, in almost arbitrary directions. There was no clear indication of multiple potential energy minima inside the cages in the Fourier difference syntheses. The displacement factor of the G4 molecule is also large, but remains at a value only slightly larger than expected, suggesting that the tetrahedral CH_4 molecule fits well in the G4 cage and is well approximated by the carbon atomic form factors. Some parts of the large displacement factors for the cage sites are certainly superficial, arising from the substitution of single atoms for the non-spherical, tetrahedral or linear molecules.

The characteristic structural features described here are all consistent with an SiO_4 rigid body model of correlated Si and O vibrations. According to a preliminary calculation by R. Downs (private communication), the average of Si-O distances

corrected by a rigid-body analysis (Downs et al. 1990) is 1.612 Å in good agreement with those known for ordinary silicas, e.g., 1.610 Å for quartz (Kihara 1990).

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