

Studies on clathrasils. III.*

Crystal structure of melanophlogite, a natural clathrate compound of silica**

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Abstract. The high temperature form of melanophlogite, $46 \text{ SiO}_2 \cdot 6\text{M}^{14} \cdot 2\text{M}^{12}$ ($\text{M}^{12} = \text{CH}_4, \text{N}_2$; $\text{M}^{14} = \text{CO}_2, \text{N}_2$), is cubic with space group $Pm\bar{3}n$ and $a = 13.436(3) \text{ \AA}$ at 200°C . The mineral is isostructural with the cubic gas hydrates of type I. Structure refinement with 667 independent reflections led to a weighted $R_w = 0.040$. Corner-sharing $[\text{SiO}_4]$ tetrahedra form a 3-dimensional framework which contains two types of cages: 2 pentagondodecahedra ($V \sim 97 \text{ \AA}^3$) and 6 tetrakaidecahedra ($V \sim 136 \text{ \AA}^3$) per unit cell. From difference Fourier syntheses it is concluded that the guest molecules M^{12} and M^{14} within the dodecahedral and tetrakaidecahedral cages are oriented in such a way that the van der Waals contacts between the guest molecules and the SiO_2 framework are optimized. The mean value of the Si–O–Si angles (168.8°) is considerably higher and that of the Si–O distances (1.576 \AA) is considerably lower than corresponding angles and distances in the known silica polymorphs.

Introduction

Melanophlogite is a very rare mineral reported as a silica polymorph which contains up to 8 % C, H, O, N and S (Skinner and Appleman, 1963). The role of these additional elements was not understood until Kamb (1965) concluded from X-ray powder data that melanophlogite is isostructural with the cubic gas hydrates of type I (v. Stackelberg and Müller, 1954).

* Gies et al. (1982a) and Gies et al. (1982b) are considered to be part I and part II of this series "Studies on Clathrasils" respectively.

** Parts of these studies have been presented at the XIV. International Conference on Crystallography, Ottawa (Gies and Liebau, 1981).

Melanophlogite then is a clathrate compound which consists of a 3-dimensional host framework of $[\text{SiO}_4]$ tetrahedra with small guest molecules entrapped within the cages of the host structure. The guest molecules have been indentified as CH_4 , N_2 and CO_2 by mass spectroscopic techniques (Gies et al., 1982a). According to Žák (1972) natural melanophlogite is tetragonal at room temperature with transformation-twinned crystals. In contrast to the natural material, synthetic crystals with $\text{CH}_4 + \text{CO}_2 + \text{N}_2$ or with $\text{Kr} + \text{N}_2$ as guest molecules are cubic at room temperature (Gies et al., 1982a). The present study was undertaken on the high temperature form of the natural mineral in order to determine the exact structure of the SiO_2 framework and the distribution and behaviour of the clathrated molecules.

Experimental

For single crystal studies by the Weissenberg technique at elevated temperature a heating device of F. Huber, Rimsting, was used. A Dupont 1090 was used for differential scanning calorimetric (DSC) investigations. For X-ray intensity measurements on an automatic four circle diffractometer Philips PW 1100, a crystal cube measuring $0.2 \times 0.2 \times 0.2$ mm of natural melanophlogite from Mt. Hamilton, California, was mounted in a temperature-regulated air stream. With $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) the intensities of 3491 reflections with $\theta \leq 30^\circ$ were collected using $\omega - 2\theta$ scan while the crystal was held at 200°C . 3409 reflections had recorded intensities > 0 . By averaging symmetry equivalent reflections a set of 667 unique reflections was obtained

$$\left(R = \frac{\sqrt{\sum N(\sum(\bar{F} - F)^2 w)}}{\sum(N-1) \cdot \sum w F^2} = 0.040 \right)$$
. No correction for absorption seemed to be necessary ($\mu = 6.31 \text{ cm}^{-1}$). The calculations were performed with the SHELX-76 system (Sheldrick, 1976) using all 667 reflections, including 34 reflections with $|F_0| < 3\sigma(|F_0|)$. Refined cell parameters were determined with the program LAT (Hornstra and Vossier, 1973/74).

Results

Polymorphism

At room temperature melanophlogite is tetragonal and microtwinned. The tetragonal *c*-axis is statistically oriented parallel to the edges of the crystal cubes. Weissenberg photographs taken at 80°C from such a crystal clearly indicate that the tetragonal low temperature phase has changed to a cubic high temperature phase yielding a single crystal. In addition, DSC experiments with melanophlogite from Mt. Hamilton (California) proved that a displacive phase transformation takes place at 65°C with a transformation

energy of 41 J/mol SiO₂. The transformation temperature was determined using a hot-stage microscope to measure the temperature at which double refraction vanishes; it varies from locality to locality (Fortullino, Italy: 55 °C, Mt. Hamilton, California: 65 °C) and for a given locality from crystal to crystal ($\Delta T = 4$ °C). The mean value for crystals from Mt. Hamilton of 65 °C is in good agreement with the transformation temperature measured by DSC method. For melanophlogite from Sicily and from Chvaletice no phase transformation below 150 °C could be observed.

Results of structure refinement

Systematic extinction (hkl no condition, $hhl: l = 2n + 1$) led to space groups $Pm\bar{3}n$ and $P43n$. The structure was refined in space group $Pm\bar{3}n$ with a refined cell parameter $a = 13.436(3)$ Å and started with a set of fractional coordinates for Si and O obtained from the cubic gas hydrate I (Kamb, 1965). Anisotropic refinement of the SiO₂ host framework converged at $R = 0.082$

and $R_w = 0.080$ $\left(R_w = \sqrt{\frac{\sum(w)(|F_o| - |F_c|)^2}{\sum w F_o^2}} \right)$. Taking into account the guest molecules within the cages as described later improved the structure refinement and led to final residuals $R = 0.061$ and $R_w = 0.040$. Final results of the refinement, atomic parameters and Si–O distances and Si–O–Si angles are listed in Tables 2 and 3. A list of observed and calculated structure factors can be obtained from the authors.

Description of the structure

Host framework. [SiO₄] tetrahedra in melanophlogite are corner linked to build a 3-dimensional 4-connected net isotypic with the [OH₄] framework of the cubic gas hydrates I (Fig. 1). The framework contains two types of cages per unit cell: two pentagondodecahedra, [5¹²] cages, and six tetrakaidecahedra, [5¹²6²] cages. The SiO₂ framework can completely be constructed from [5¹²6²] cages which therefore may be considered as the fundamental cages of melanophlogite. These form columns parallel [100], [010], and [001] by sharing the hexagon-faces (Fig. 2). Eight out of twelve pentagons of each [5¹²6²] cage take part in the linkage between the columns. The voids between the [5¹²6²] cages are the [5¹²] cages. In Fig. 2 two [5¹²6²] cages are emphasized by stippling, one [5¹²] cage by hatching.

Si–O distances as well as Si–O–Si angles calculated from the final coordinates of Table 2 differ significantly from those of the common silica phases. The mean value 1.576 Å of the Si–O distances in melanophlogite is considerably lower (0.032 Å) than the grand mean value 1.608 Å reported by Brown and Gibbs (1969) for silica frameworks. Si–O–Si angles in melanophlogite vary between 148.3° and 180° with a mean value of 168.8°.

Table 1. Atomic parameters and thermal parameters $U_{ij}[\text{\AA}^2]$ with standard deviation (temperature factor of the form $\exp[-2\pi^2(U_{11} \cdot h^2 \cdot a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$; $B_{\text{eq}} = 8\pi^2 \left[\frac{U_{11} + U_{22} + U_{33}}{3} \right]$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Si(1)	0	0.3098(1)	0.1142(1)	0.0259(5)	0.0193(5)	0.0198(5)	-0.0020(4)	0	0	1.711
Si(2)	0.1826(1)	0.1826(1)	0.1826(1)	0.0218(3)	0.0218(3)	0.0218(3)	-0.0002(3)	-0.0002(3)	-0.0002(3)	1.721
Si(3)	0.25	0	0.5	0.0127(9)	0.0208(6)	0.0208(6)	0	0	0	1.429
O(1)	0.0963(2)	0.2465(2)	0.1360(2)	0.0536(15)	0.0673(17)	0.0646(16)	0.0107(13)	-0.0125(13)	0.0322(13)	4.882
O(2)	0	0.4056(2)	0.1813(2)	0.1022(27)	0.0368(18)	0.0426(19)	-0.0256(16)	0	0	4.780
O(3)	0.3423(3)	0	0	0.0383(24)	0.0164(17)	0.0502(24)	0	0	0	2.761
O(4)	0.25	0.25	0.25	0.0736(20)	0.0736(20)	0.0736(20)	-0.0269(18)	-0.0269(18)	-0.0269(18)	5.811
[5 ¹² 6 ²]	0.25	0.5	0	0.243(19)	1.010(111)	0.243(19)	0	0	0	
[5 ¹²]	0	0	0	0.174(15)	0.174(15)	0.174(15)	0	0	0	

Table 2. Interatomic distances in Å and angles in degrees with standard deviation in melanophlogite from Mt. Hamilton

Si(1)–O(1)	1.577(2)	2 ×	O(1)–Si(1)–O(1)	110.3(2)	O(1)–O(1)	2.589(5)
Si(1)–O(2)	1.571(2)		O(2)–Si(1)–O(1)	109.6(1)	O(1)–O(2)	2.572(3)
Si(1)–O(3)	1.595(2)		O(3)–Si(1)–O(1)	109.0(1)	O(1)–O(3)	2.583(3)
average	1.580		O(3)–Si(1)–O(2)	109.1(2)	O(2)–O(3)	2.580(3)
			average	109.4	average	2.575
Si(2)–O(1)	1.572(3)	3 ×	O(1)–Si(2)–O(1)	109.0(1)	O(1)–O(1)	2.560(4)
Si(2)–O(4)	1.569(3)		O(1)–Si(2)–O(4)	109.9(1)	O(4)–O(1)	2.571(2)
average	1.571		average	109.5	average	2.566
Si(3)–O(2)	1.569(3)	4 ×	O(2)–Si(3)–O(2)	110.3(1)	O(2)–O(2)	2.575(5)
average	1.569		O(2)–Si(3)–O(2)	107.9(2)	O(2)–O(2)	2.538(6)
grand mean value	1.576		average	109.5	average	2.563
			grand mean value	109.45	grand mean value	2.572
Si(2)–O(1)–Si(1)	166.9(2)	48 ×	Si(1)–Si(1)	3.069(2)		
Si(3)–O(2)–Si(1)	179.0(2)	24 ×	Si(1)–Si(2)	3.128(3)		
Si(1)–O(3)–Si(1)	148.3(3)	12 ×	Si(1)–Si(3)	3.140(1)		
Si(2)–O(4)–Si(2)	180.0(1)	8 ×	Si(2)–Si(2)	3.137(5)		
average	168.8		average	3.119		

Table 3. Guest molecule distribution and population densities for melanophlogite. Results were obtained by combination of mass spectroscopic analyses and refinement of site occupation factors and temperature factors of guest molecules

Cage type	Guest-molecule	Guest molecule distribution for every cage [%]	Electrons per cage calculated for 100 % population density	Electrons per cage experimental	Population density [%]
[5 ¹²]	CH ₄	100	10	9	90
[5 ¹² 6 ²]	N ₂	78	14	12	59
	CO ₂	22	22		17

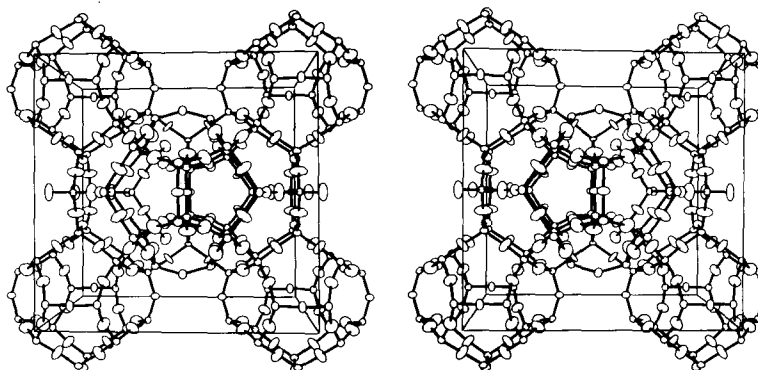


Fig. 1. Stereo view of melanophlogite parallel [100]. The $[5^{12}]$ cages and part of the $[5^{12}6^2]$ cages are shown

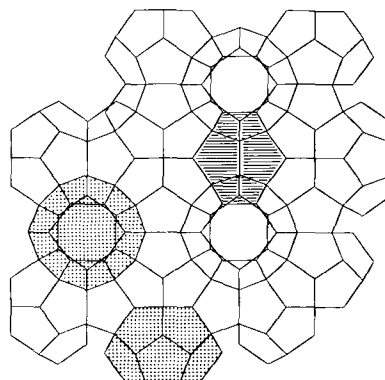


Fig. 2. Projection of the structure of melanophlogite parallel [100]. One $[5^{12}]$ cage is emphasized by hatching, two $[5^{12}6^2]$ cage by stippling

which is considerably higher (24.8°) than the grand mean value 144° reported by Tossel and Gibbs (1978). In agreement with the correlation reported by Hill and Gibbs (1979) between Si—O distance and Si—O—Si angle in SiO_2 polymorphs the very high mean value $\langle \angle \text{Si—O—Si} \rangle$ found in melanophlogite involves a very low $\langle d(\text{Si—O}) \rangle$ value. In addition, the rather high temperature factors of the oxygen atoms in melanophlogite perpendicular to the direction of the Si—O bonds can be interpreted as considerable static or dynamic disorder of the oxygen atoms.

Guest molecules. By mass spectroscopic analysis the guest molecules in melanophlogite from Mt. Hamilton were found to be molecular methane, carbon dioxide, and nitrogen with a molar ratio of $\text{CO}_2 : \text{N}_2 : \text{CH}_4$ near to

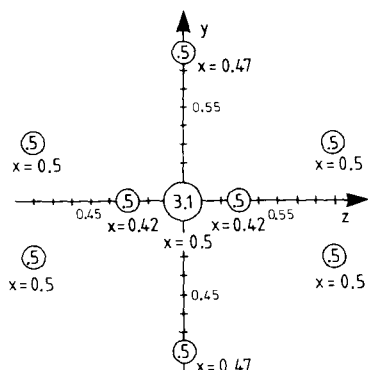


Fig. 3a. Schematic representation of the distribution of the residual electron density maxima within the $[5^{12}]$ cage shown as projection parallel $[100]$. x coordinates of centers of the maxima and relative heights of the residual electron density maxima are given

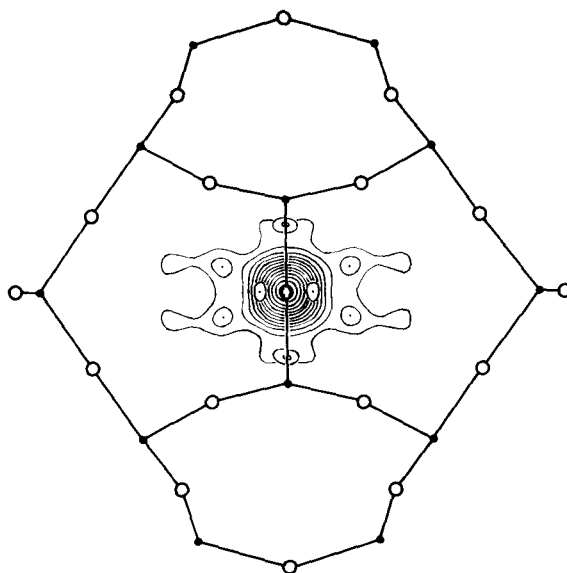


Fig. 3b. Projection of the $[5^{12}]$ cage parallel $[100]$ including the section $\rho(Oyz)$ of the electron density distribution of the guest molecule. In addition the secondary maxima on the mirror planes perpendicular to the plane of the projection are inserted

1:3.6:1.8. From molecular size and geometric aspects it has been suggested (Gies et al., 1982a) that CH_4 and N_2 are located in the $[5^{12}]$ cages and CO_2 and N_2 in the $[5^{12}6^2]$ cages. This suggestion is strongly supported by sections through the cage centres from difference Fourier maps $\rho_{\text{obs}} - \rho_{\text{calc. (Si, O)}}$ shown in Figure 3b and 4b. The free space within the smaller $[5^{12}]$ cage can be

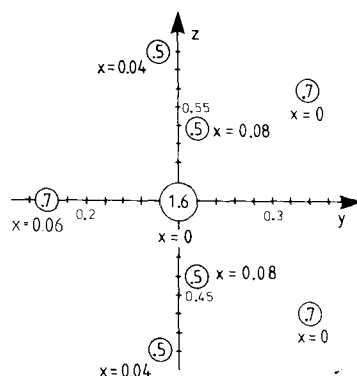


Fig. 4a. Schematic representation of the distribution of the residual electron density maxima within the $[5^{12}6^2]$ cage shown as projection parallel $[100]$. x coordinates of the centers of the maxima and relative heights of the residual electron density maxima are given

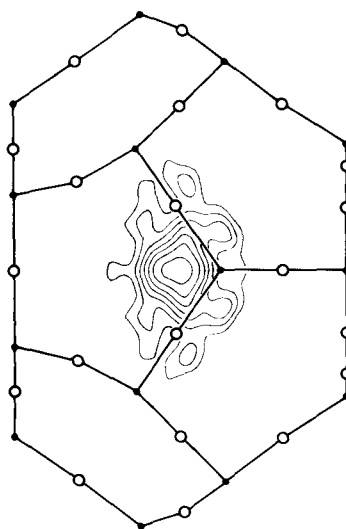


Fig. 4b. Projection of the $[5^{12}6^2]$ cage parallel $[100]$ including the section $\rho(Oyz)$ of the electron density distribution of the guest molecules

described by a sphere-like void with a diameter $d \sim 5.7 \text{ \AA}$ and a volume $V \sim 97 \text{ \AA}^3$. The free space within the $[5^{12}6^2]$ cage is an ellipsoid with $d_1 \sim d_2 \sim 5.8 \text{ \AA}$, $d_3 \sim 7.7 \text{ \AA}$ and $V \sim 136 \text{ \AA}^3$.

In addition to a central maximum M_c in the middle of each cage there are 12 smaller secondary maxima M_s between the midpoints of the pentagons and

the cage centres (Fig. 3a and 4a). The positions of the difference Fourier maxima within the cages of the silica framework (Fig. 3 and 4) reveal that the guest molecules are not fully disordered but rather incorporated with preferential orientations.

In the $[5^{12}]$ cage (site symmetry of cage centre: $m\bar{3}$) the distance $d(M_c - M_s)$ is about 1.1 Å and can be interpreted as C–H bond length (1.091 Å) (Kennard, 1968). The twelve secondary maxima between the midpoints of the pentagons and the cage centre (Fig. 3b) represent 30 equivalent orientations of CH₄ molecules. If the carbon atom and the hydrogen atoms are assumed to be located at the centres of the central and the secondary maxima, respectively, the bond angles H–C–H of the methane molecule would be $109^\circ(3 \times)$, 139° and $71^\circ(2 \times)$. The large deviation of two of these six angles from the tetrahedral angle of an undistorted CH₄ molecule can readily be explained by slight displacement of the carbon atoms from the centres of the $[5^{12}]$ cage and corresponding displacements of the hydrogen atoms from the centres of the secondary maxima. Such displacement of the methane carbon atom increases the number of positions in this special site in space group $Pm\bar{3}n$ from 2 to 48. In each cage then 24 different carbon positions with 96 hydrogen positions have to be considered. Then each of the twelve secondary maxima in the difference map is a superposition of 8 split hydrogen positions. Such displacement of the methane molecule from the special position of space group $Pm\bar{3}n$ is in agreement with the rule formulated by Jewess (1982) for structures with orientational disorder that only coincidence of like symmetry elements of the disordered molecule and pointgroup symmetry is significant for the specific kind of disorder, while coincidence of unlike symmetry elements is not itself significant.

The distances $d(M_c - M_s)$ in the $[5^{12}6^2]$ cage (site symmetry of cage centre: $\bar{4}2m$) are found to be 1.21 Å ($8 \times$) and 1.24 Å ($4 \times$). The molecular dimensions of CO₂ ($d(C-O) = 1.155$ Å) (Simons and Peters, 1980) and N₂ ($d(N-N) = 1.098$ Å) (Ondik and Smith, 1968) do not fit very well with the distances $d(M_c - M_s)$ in the $[5^{12}6^2]$ cage. There are 12 secondary maxima (Fig. 4a) between the midpoints of the pentagon and the cage centre but not between the hexagons and the cage centre. If one assigns the centre of the maximum M_c to the carbon atom and the centres of two of the maxima M_s to oxygen atoms of a CO₂ guest molecule then the most suitable bond angle O–C–O for 12 selected molecule orientations would be $167^\circ(4 \times)$, $131^\circ(4 \times)$ and $125^\circ(4 \times)$ while corresponding O...O distances would be 2.40 Å ($4 \times$), 2.23 Å ($4 \times$), and 2.20 Å ($4 \times$). The strong deviations from the angle of 180° can be removed by slight displacement of the carbon atom from the centre of the $[5^{12}6^2]$ cage while the oxygen atoms nearly coincide with the positions of the secondary maxima. The distances $d(M_s - M_s)$ for these 12 different orientations are close to the O...O distance 2.310 Å reported by Simons and Peters (1980) for the CO₂ molecule and statistical distribution of the molecules between these

12 possible equivalent orientations is in agreement with the very broad central maximum for the carbon atom.

In addition to CO₂ the N₂ molecules are predominantly located within the [5¹²6²] cages. Orientations of the diatomic molecule are such that one nitrogen atom nearly coincides with one secondary maximum to attain van der Waals contacts with the SiO₂ framework. The second atom coincides with the central maximum of the cage.

The discrepancies between the N . . N distance 1.098 Å in N₂ reported by Ondik and Smith (1968) and the O . . O distance 2.310 Å in CO₂ reported by Simons and Peters (1980) on the one hand and the distances $d(M_c - M_s)$ and $d(M_s - M_s)$ respectively on the other hand may be due to the statistical character of the N₂/CO₂ distribution within the [5¹²6²] cages of these crystals.

For structure refinement in each cage a spherical scatterer was assumed with a scattering factor of one carbon atom. Refinement of site occupation factors and anisotropic temperature factors improved the residuals as described above.

The refined site occupation factors were used to calculate the residual electron density within each cage. If one considers the mass spectroscopic results for melanophlogite from Mt. Hamilton and supposes that the [5¹²] cage is occupied only by methane and the other cage only by N₂ + CO₂ it is possible to estimate the numbers of guests which populate the different cages. The results of this procedure are summarized in Table 4. The result of the crystallographic analysis of orientations and distribution of the guest molecules in the cages has only semiquantitative character and is valid only for the crystal investigated. Structure refinements of other crystals of melanophlogite from Mt. Hamilton are in general in agreement with the results; more conscientious analyses, however, show small variations. A more detailed study of cage contents in natural melanophlogite and in melanophlogites synthesized with different guest species is in progress.

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