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Single-crystal X-ray and Raman investigation on melanophlogite from Varano Marchesi (Parma, Italy)

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ABSTRACT

The results of a new single-crystal structure refinement and of a Raman spectroscopy investigation on melanophlogite, a clathrate structure of SiO_2, are reported. The studied sample comes from a new finding at Varano Marchesi (Parma, Italy), and occurs in small veins and pockets along fractures in a siliceous marl from a chaotic complex. Melanophlogite is invariably separated from the host rock by a thin crust of opal-CT.

Raman spectroscopy was done to investigate the guest molecules that are hosted in the cages of the structure. In the Varano Marchesi melanophlogite, only CH_4 is present in the clathrate structure. During a comparative investigation of melanophlogite from different geological setting (Racalmuto, Sicily, Italy), H_2S also was found, together with CH_4, in the cavities of the structure.

A single-crystal X-ray refinement of the Varano Marchesi sample was done using the $Pm\overline{3}n$ symmetry of β-melanophlogite [$a = 13.399(2)$, $R_{4\sigma} = 4.7\%$]. According to the site refinement from X-ray diffraction results, CH_4 occupies 71 and 91% of the 5^{12} and $5^{12}6^2$ site cavities, respectively.

The Varano Marchesi melanophlogite formed as a result of low-temperature hydrothermal activity. The mineral growth occurred at the expense of opal, in connection with CH_4 flux through the porous material.

Keywords: Melanophlogite, single-crystal X-ray diffraction, Raman spectroscopy, phase transition, CH_4

INTRODUCTION

Melanophlogite is a clathrate phase of silica. It is a tectosilicate belonging to the clathrasil series of phases structurally related to zeolite, with a framework consisting of interconnected SiO_4 tetrahedra with small isolated cages in between (Liebau 1988). In these cages, guest molecules, like CH_4, N_2, and CO_2, can be present (Gies 1983; Kolesov and Geiger 2003).

There is recent and growing interest in melanophlogite as a possible host for greenhouse gases (Navrotsky et al. 2003), although in nature melanophlogite is a rare mineral. In fact, melanophlogite is found at only a few localities, related to low-temperature hydrothermal processes in connection with gaseous activity. The enthalpy of formation of melanophlogite is very close to that of amorphous silica (Navrotsky et al. 2003) and its crystallization is likely due to the templating action of the guest gaseous phases, which enables the nucleation of melanophlogite (Gies et al. 1982; Navrotsky et al. 2003).

X-ray structural analysis (Gies 1983; Nakagawa et al. 2001, 2005; Nakagawa and Kihara 2006) has shown that a tetragonal → cubic ($P4_2/nbc \rightarrow Pm\overline{3}n$) phase transition occurs between α- and the β-melanophlogite at 63 °C in the case of the material from Mt. Hamilton (Nakagawa et al. 2005). Due to the phase transition, a cell doubling along the **a** and **b** axes, and a distortion from cubic symmetry, are observed. The transition temperature is apparently related to the nature of the guest molecules: and it was found to vary between 30 and 60 °C (Gies 1983). The nature of the interactions of the guest molecules with the silica framework was studied using Raman spectroscopy by Kolesov and Geiger (2003). They found that Raman-active modes of the enclathrated gaseous molecules occurred at significantly lower wavenumber than in the case of the free-gaseous molecules. Moreover, at least for CH_4, two symmetric stretching modes were present. This result is consistent with the occurrence of molecules in two cavities: the larger $5^{12}6^2$ (136 Å^3) and the relatively small 5^{12} (97 Å^3) cavity (Gies 1983). Those previously reported structural and Raman studies were done on melanophlogite from Mt. Hamilton (California, U.S.A.), which has N_2, CH_4, and CO_2 guest molecules. A combined Raman and single-crystal analysis was not performed in samples from other locations, and the effect of different gaseous species on the structure of the mineral has not yet been investigated.

This paper reports a combined single-crystal X-ray diffraction and microRaman investigation on natural melanophlogite, from

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the recently discovered locality of Varano Marchesi (Parma, Italy). The study aims to determine the structural changes related to different gaseous species enclathrated in melanophlogite. Specifically, in the sample studied in the present work, the Raman spectroscopic finding that CH_4 is the only type of guest molecule makes possible a simplified discussion of the melanophlogite-guest molecule interactions. In addition, new Raman data are reported on melanophlogite from other locations, and a genetic model for the Varano Marchesi melanophlogite is proposed.

EXPERIMENTS AND RESULTS

Geological setting and sample characterization

The investigated sample was first discovered by mineral collectors in a marl quarry used for pozzolanic concrete, at Case Montanini, near the locality of Varano Marchesi (Parma, Italy) (Fig. 1). The quarry occurs within the Contignaco Formation, which consists of the early Miocene hemipelagic siliceous marls and silty marls, with few tripoli (siliceous limestone) beds and volcaniclastic layers of rhyolitic composition. The geological setting of the area is complex: the quarry is on the northern limb of an upright faulted syncline, which belongs to a series of NNE-vergent folds affecting the middle Eocene to late Miocene epi-Ligurian succession (Ricci Lucchi 1986) (Fig. 1). The latter lies on top of the allochthonous Ligurian units, i.e., the remnants of Mesozoic oceanic and forearc deposits derived from the closure of the Ligurian-Piedmont Ocean and its continental margins (Boccaletti et al. 1971; Marroni et al. 2002). The quarry is located about 2 km south of the Salsomaggiore tectonic window, defined by the allochthonous Ligurian and the epi-Ligurian units overthrusting the Langhian to Serravallian turbiditic foredeep deposits cropping out in the Salsomaggiore anticline. The Salsomaggiore anticline was exhumed during Messinian and then covered by late Messinian-early Pliocene continental to marine deposits. The latter have been folded by younger Pliocene and Pleistocene tectonic events. During this multiphase and complex geological evolution of the Salsomaggiore area, seepage of CH_4 and other hydrocarbons occurred, as testified by a late Serravallian methane-related faunal assemblage and deposits (Conti et al. 2007) and present-day fluids rising in localized spots around the Salsomaggiore anticline (Artoni et al. 2004) (Fig. 1).

Melanophlogite is found in veins and pockets, only in the more siliceous and compact levels of the Contignaco Formation, i.e., those with apparently lower porosity (Fig. 2). It is always found in association with opal. Melanophlogite is present as euhedral cubes, from 0.1 to 1 mm in size, and occurs in veins that are never completely filled; in filled veins, only opal is found. A thin crust of opal (<1 mm) is always found between melanophlogite and the host rock (Fig. 3). Melanophlogite does not show birefringence even in thick sections; no evidence of twinning was found by optical observation. Opal is also found at the core of some melanophlogite crystals (Fig. 4).

A thin crust of melanophlogite and opal was examined by powder X-ray diffraction (XRD), and by scanning and transmission electron microscopy. The powder XRD analysis was done with a Philips PW3830 operating at 40 kV and 30 mA with Cu$K\alpha$ radiation; it showed that opal was of the CT (cristobalite-tridymite) variety and confirmed the identification of melanophlogite. SEM-EDS analysis and X-ray mapping on a polished thin section was done on a melanophlogite grain containing inclusion of opal (Fig. 4). The opal showed a slightly higher Al and Si content than melanophlogite and a corroded boundary separates the two materials. This suggests growth of melanophlogite at the expense of the opal.

Transmission electron microscopy

Transmission electron microscope (TEM) analysis was performed using a CM12 instrument operating at 120 kV. The sample was prepared by crushing a few grains of melanophlogite in an agate mortar and these were then deposited on a holey carbon film. Selected area electron diffraction (SAED) patterns of melanophlogite did not show the superstructure reflections present in the tetragonal α-melanophlogite and so the sample was indexed with cubic symmetry (Fig. 5). In the SAED pattern of Figure 5, all the spots are diffuse and elongated along [323]. The presence of such diffusion, instead of the sharp peaks that would be expected in a homogeneous cubic structure, indicates that some structural inhomogeneity is present, possibly related, as discussed below, to the tetragonal-cubic phase transition. The interpretation of TEM results in terms of the symmetry at room temperature could be affected by specimen heating caused by beam exposure. Specimen heating in the electron microscope is difficult to measure experimentally because it involves several sample- and beam-related variables, like sample size and thickness and its thermal conductivity, beam size, energy, and current. In silicates, however, the overheating is generally not expected to be higher than 10–20 °C (Williams and Carter 1996). Moreover, in an in situ high-temperature investigation on anorthitic feldspars (a framework silicate structure like melanophlogite) that was performed at the same experimental conditions as in the present study (beam current, size, sample thickness, etc.), no significant overheating was observed based on the temperature of a known phase transition (Tribaudino et al. 2000).

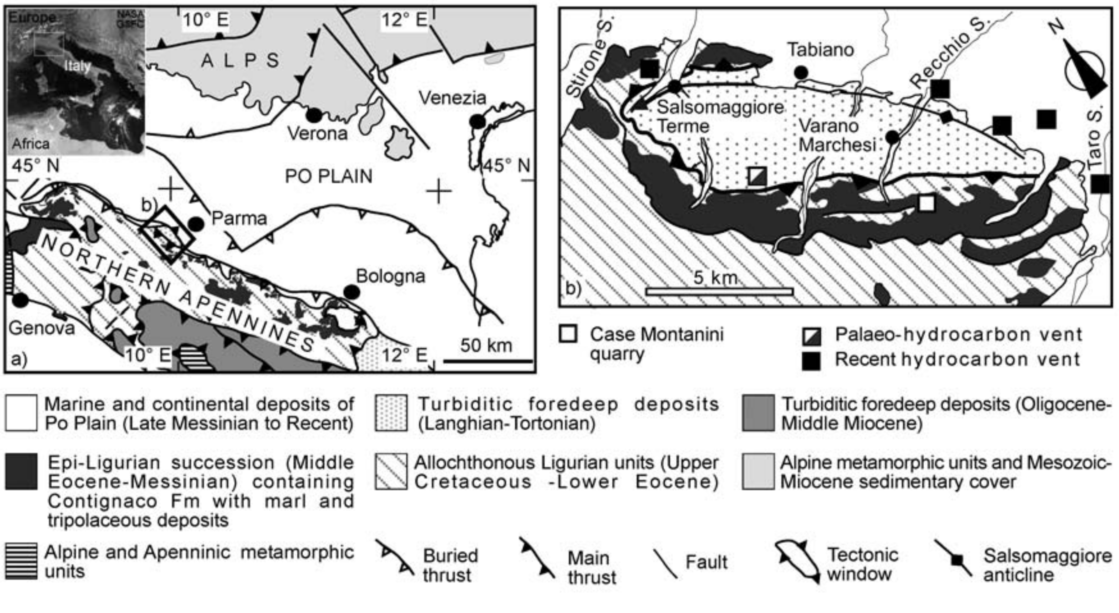

FIGURE 1. (**a**) Location and geological sketch map of the Northern Apennines; (**b**) amplified geological map of Varano Marchesi area where melanophogite samples were collected. Note the hydrocarbon vents in the area. (Modified after Artoni et al. 2004.)

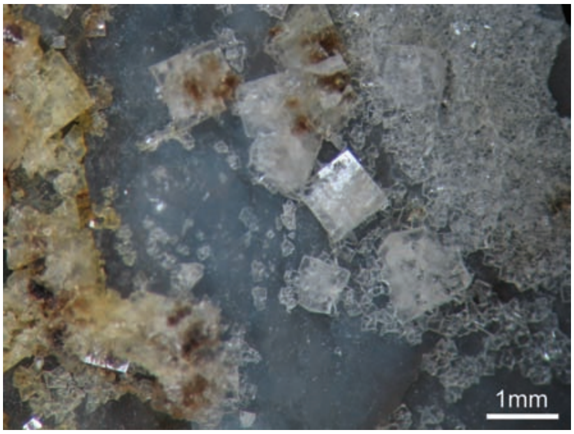

FIGURE 2. Cubic melanophlogite crystals from Varano Marchesi. The size of the larger crystals is about 1 mm.

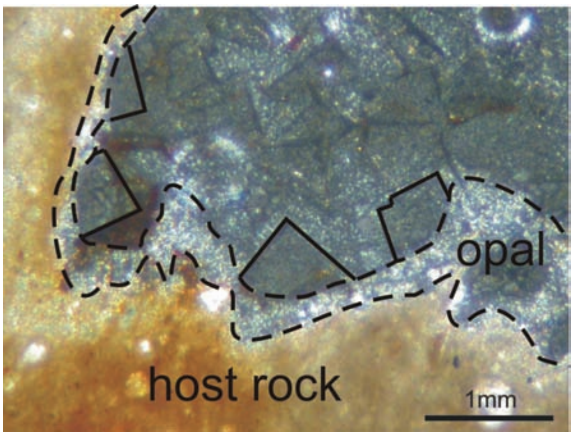

FIGURE 3. Thin section viewed in cross-polarized light of a melanophlogite-bearing vein. Brownish host rock is on the left and bottom of the image; the brown color is due to clay minerals. Transparent ovoidal zones within the host rock are made up of calcite. On the middle and top right of the image, isotropic cubic melanophlogite is present, and four grains are outlined in direct contact with the opal crust. A thin opal crust, partly birefringent, is always found between melanophlogite and the host rock. Host rock-opal and opal-melanophlogite contacts are dashed.

Raman spectroscopy

Raman spectroscopy was performed using a Jobin-Yvon Horiba LabRam microRaman apparatus, with a spatial resolution of ~1 μm and a spectral resolution of ~2 cm^{-1}. The 632.8 nm line of a He-Ne laser was used as the excitation. The laser source has a power of 20 mW, but the use of the filter wheel reduced the power to 1 mW or less on the sample. The calibration was performed with the Raman peak of silicon.

In addition to the Varano Marchesi melanophlogite, samples from the historical localities of Racalmuto (Sicily) and Fortullino (Livorno) (Grassellini Troysi and Orlandi 1972) also were examined. All samples come from Italy, but from different geological settings. No sample preparation was required for the Raman analysis; only in few cases did we need to remove some small crystals from the matrix, in order to focus the laser beam properly on the sample with the highest powered objective (100×) with small working distance. The Raman spectra were collected in a wide frequency range (100–3600 cm^{-1}) to obtain information both on the host crystalline framework and on the guest phases. Data analysis was done performing a Gauss-Lorentzian fitting of the main peaks, after a baseline subtraction, using the LabSpec software. The peak positions observed for the free gaseous molecules and for the enclathrated species, respectively, are reported in Table 1.

In the Varano Marchesi melanophlogite, the same crystal used for single-crystal investigation was studied (Figs. 6 and 7). As shown in Figure 7, the peak for CH_4 at about 2900 cm^{-1} was observed. This peak for CH_4 is reported to be at 2917 cm^{-1} for free gas at atmospheric pressure (Uchida et al. 1999). In the Varano Marchesi melanophlogite, it was found at a much lower frequency and was split with respect to the gaseous phase (Table 1), due to the cage effect, as observed by Kolesov and Geiger (2003) in Mt. Hamilton melanophlogite. In contrast to results obtained by those authors for melanophlogite from other localities, peaks for other guest phases were not observed in the present work.

In the Fortullino sample, CO_2 and faint CH_4 peaks were observed; N_2, which should be present in minor amounts from mass spectroscopic data (Gies et al. 1982), was not found. Both CO_2 peaks of the Fermi doublet are downshifted with respect to the free gas values, due to the interactions with the cage. The peaks are not split, which probably indicates that CO_2 enters only one type of cage.

In the Racalmuto sample, split peaks for both CH_4 and H_2S peaks were found (Fig. 8). We believe that the H_2S is present within the clathrate, rather than as an

TABLE 1. Position of vibrational modes of the guest molecules in melanophlogite from different locations

	CH_4		H_2S		CO_2 (I)	CO_2 (II)	N_2
Varano Marchesi	2901	2910	No	No	No	No	No
Racalmuto	2901	2911	2594	2604	No	No	No
Fortullino	No	(2915)	No	No	1279	1382	No
Mt. Hamilton*	2900	2909	No	No	1277	1378	2321
Gas	2917†	2611‡	1286*	1388*	2331*		

* Kolesov and Geiger (2003).
† Uchida et al. (1999).
‡ Charlou et al. (2004).

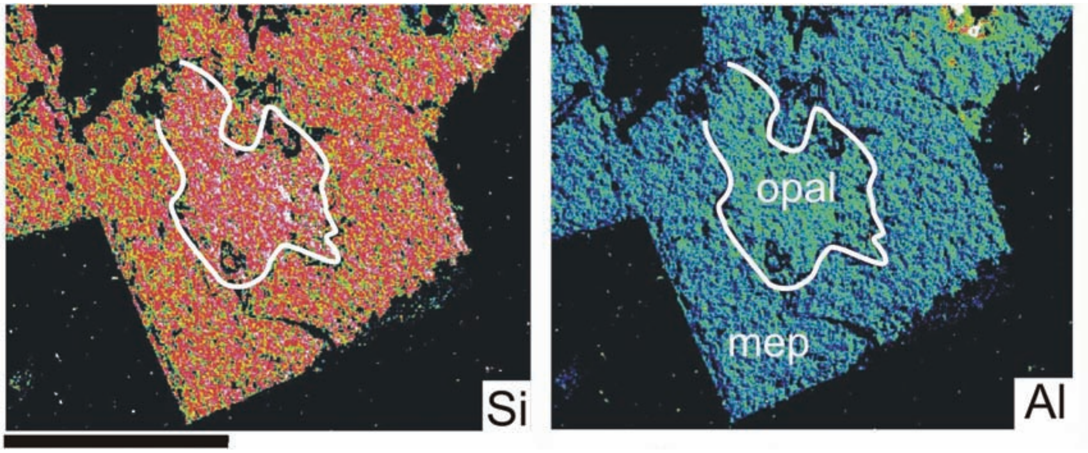

FIGURE 4. SEM-EDS qualitative X-ray map of Si and Al in a melanophlogite (mep) crystal enclosing opal. The interface between opal and melanophlogite is irregularly shaped, suggesting growth of melanophlogite at the expanse of opal. The different color of opal with respect to melanophlogie indicates a slightly higher Si and Al content. The scale bar is 400 μm.

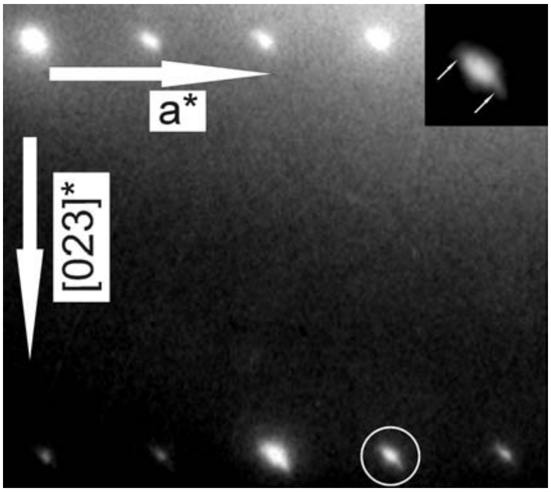

FIGURE 5. SAED pattern of melanophlogite along the [0$\bar{3}$2] direction. Superstructure reflections, indicating a transition to the tetragonal symmetry (not found here), would be present halfway between the main peaks along **a***. Note that the reflections are streaked along [323]*; the reflection enlarged in the inset is circled. In the inset, arrows indicate peak elongation.

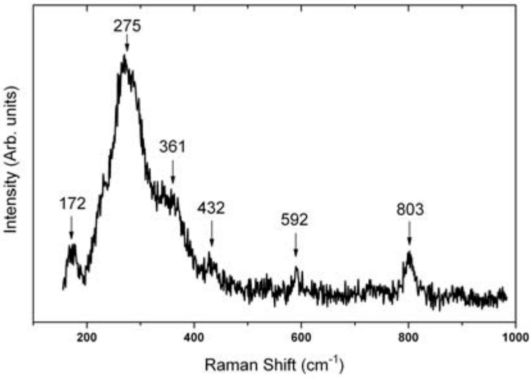

FIGURE 6. Raman spectrum of melanophlogite from Varano Marchesi in the lower wavenumber range. The vibrational modes are related to the silicate cage; the reported frequencies were obtained by Gauss-Lorentzian fitting.

organic film on the faces of the crystal, as suggested by Skinner and Appleman (1963): the H_2S peak occurs at ~2600 cm^{-1}, i.e., at a lower frequency than free H_2S at atmospheric pressure (2611 cm^{-1}, Charlou et al. 2004), and is split. The peak splitting indicates that H_2S is present in 5^{12} and $5^{12}6^2$ cavities. The observed decrease in frequency of H_2S with respect to the free gaseous molecule, albeit strong, is lower than was observed for H_2S enchlatrated in a gas hydrate by Charlou et al. 2004 (2571 cm^{-1}). In Charlou et al. (2004), the H_2S peak was unsplit, probably because it occupied only one of the two cages. In previous observations, Fyfe and Gies (1990) also showed minor CO_2 and N_2, but no H_2S, for a sample of melanophlogite from Sicily. However, it is possible that the sample investigated in the present study is not exactly from the same locality as the one probed by Fyfe and Gies (1990), and that different gaseous phases were present in the environment.

X-ray diffraction and refinement

A single-crystal XRD investigation was done at room temperature to verify the structural state of melanophlogite and the structural changes imposed on the framework by the guest phases.

A melanophlogite crystal, of cubic shape and without any opal inclusions, was chosen for single-crystal XRD. The size of the crystal was 250 × 250 × 250 µm.[1]

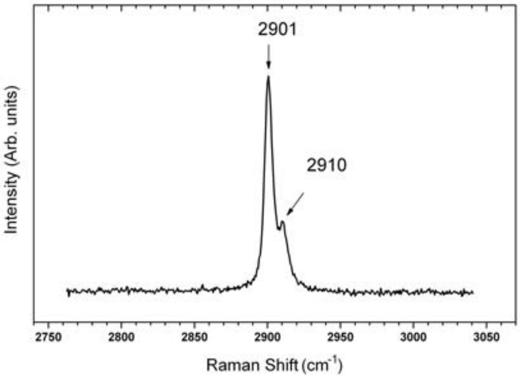

FIGURE 7. Raman modes of enclathrated CH_4 in Varano Marchesi melanophlogite.

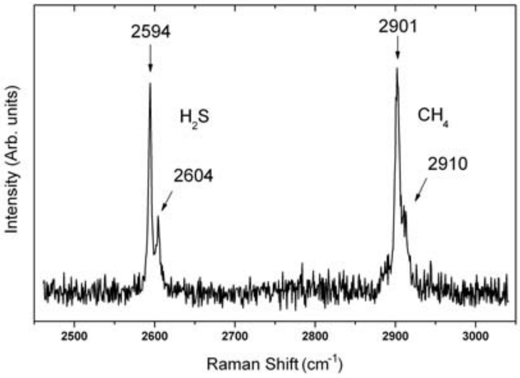

FIGURE 8. Raman modes of enclathrated CH_4 and H_2S in Racalmuto melanophlogite.

Data collection was done with a Smart CCD Brucker diffractometer, using graphite monochromatized Mo*K*α radiation (λ = 0.71069 Å). The reciprocal sphere was explored by frames, and 6317 reflections (3271 of which had $F_o > 4\sigma$) were collected with $17 \geq h \geq -17$, $12 \geq k \geq -16$, $17 \geq l \geq -7$, up to $2\theta = 57°$. The reflections were indexed using an indexing routine based on the analysis of the reflections collected in the frames, within a primitive cubic lattice, with a = 13.399(2) Å, V = 2405(1) Å^3 and the analysis of systematic extinctions confirmed the space group $Pm\bar{3}n$ proposed by Gies (1983) and Nakagawa et al. (2005) for β-melanophlogite.

The image plate data showed the presence of faint superstructure reflections between the stronger cubic ones, very few of them with intensity above 2σ. These reflections are present in tetragonal melanophlogite, due to the doubling of the cubic unit cell along the ***a*** and ***b*** axes (Zàk 1972), and could indicate the presence of tetragonal symmetry. However, the analysis of equivalent reflections needed to assign the Laue class showed reasonable agreement with cubic Laue group $m3m$ (R_{int} = 5.4 with 10.8× the observed reflections respect to the unique), and the space group $Pm\bar{3}n$ was automatically chosen by analysis of the systematic extinctions, whereas no sensible choice of a tetragonal space group was possible (progam ABSENS, McArdle 1996). Moreover, the superstructure reflections arising from the doubling along the ***a*** and ***b*** axes were not found in TEM observation. The distortion from cubic symmetry of a cell refined by imposing tetragonal lattice was hardly significant [$a/2 = b/2$ = 13.414(4) Å, c = 13.401(2)], with $a > c$, which is the opposite of what was observed for the Mt. Hamilton melanophlogite. For these reasons, as well as the lack of birefringence, the refinement was performed in the cubic structure, although it is recognized that, at least for some part of the crystal, the present cubic refinement may be pseudosymmetric. It is possible that twin domains are present at a submicroscopic scale, like observed in α-quartz close to the transition (Heaney and Veblen 1991), at least in areas of the sample that were not examined by TEM.

Weighted full-matrix, least-squares anisotropic refinements were completed using SHELX-97 (Sheldrick 1997) on 641 unique reflections; atomic scattering curves were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). The structure was refined starting with the coordinates of β-melanophlogite in Gies (1983). The coordinates and anisotropic displacement parameters of the framework Si and O atoms were first refined, down to an agreement factor $R_{4\sigma}$ = 7.7% (the agreement factor was calculated against the F_o). A residual in electron density of 4.6 e^- at the (0,0,0) position, the 5^{12} site, and of 2.0 e^- at the (0.5,0, 0.25) position (the $5^{12}6^2$ site) was observed. These positions are occupied by guest phases (Gies 1983; Nakagawa et al. 2005; Fig. 9). The other residuals are featureless (<0.6 e^-).

The refinement of the guest-phase occupancy was done by refining the occupancy of a dummy atom at the residual position, according to the procedure suggested by Nakagawa et al. (2005). In this procedure, it was assumed that the dummy atom (here C) represents the guest molecule, at least for the number of electrons. At the end of the refinement both 5^{12} and the $5^{12}6^2$ sites turned out to be overfilled, and the refined electron mean occupancy numbers were 7.1(3) and 9.1(4) e^-, respectively. Assuming that the only guest molecule is CH_4, with 10 e^-, as suggested by spectroscopy, it turns out that the 5^{12} and $5^{12}6^2$ sites have a partial CH_4 occupancy of 71(3) and 91(4)%. During this procedure, a high correlation was observed between the occupancy of the 5^{12} and $5^{12}6^2$ site with the U_{11} anisotropic displacement parameters (0.75 and 0.65 correlation, respectively). The structural coordinates and atomic displacement factors of other atoms were not significantly different after the inclusion of the guest species in the refined structure.

At the end of the 5^{12} and $5^{12}6^2$ site refinement, the residuals in a Fourier difference map are featureless. The final $R_{4\sigma}$ was 4.7% and the goodness of fit is 1.021. Atomic coordinates, anisotropic displacement parameters, and bond lengths and angles are reported in Tables 2 and 3 (structure deposited CSD no. 417910).[1]

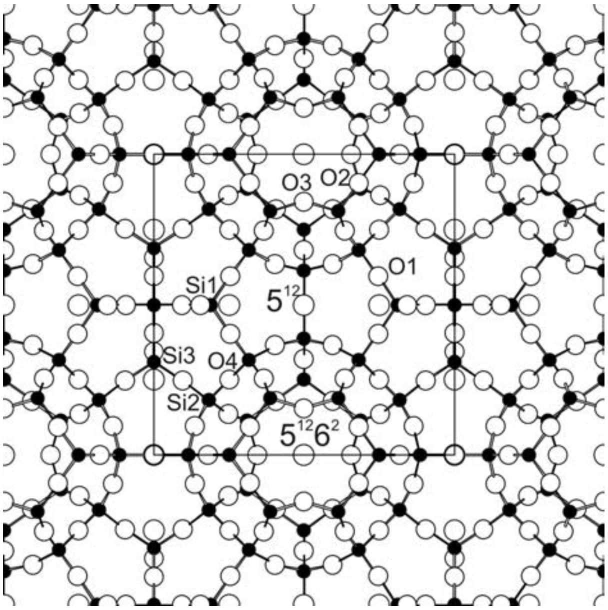

FIGURE 9. The structure of β-melanophlogite viewed along [100]. The unit cell is shown in the center. Si atoms are shown as black dots; O, 5^{12}, and $5^{12}6^2$ are shown, respectively, as open circles.

DISCUSSION

Structural features

Bond lengths and angles for the melanophlogite from Varano Marchesi and that from Mt. Hamilton (Gies 1983; Nakagawa et al. 2005) are similar, in spite of the different guest-site occupancies (Table 3). The only difference is the slightly lower value of Si1-O2 in the Varano Marchesi melanophlogite. The displacement parameters for the framework atoms determined in this work are larger than in Mt. Hamilton refinements (Table 4). This difference may be due to a higher intrinsic disorder, and/or to a pseudosymmetric cubic structure, at least in some part of the crystal. The coexistence of cubic and tetragonal domains within the same crystal could explain the presence of superstructure reflections.

The displacement parameters of the guest molecule sites are instead significantly lower than in the Mt. Hamilton melanophlogite, likely for the different site occupancy. In the Mt. Hamilton melanophlogite, CH_4 was mostly found in the 5^{12} cage, and N_2 and CO_2 had a preference for the $5^{12}6^2$ cage (Gies 1983); in the Varano Marchesi melanophlogite CH_4 is present in both cages. The lower displacement parameters for the guest molecule sites may reflect the different electron distribution for CH_4 compared with N_2 and CO_2: the CH_4 molecule can be better approximated by a spherical atom model. The site occupancies of the clathrate cages are similar [0.71(3) and 0.91(4) vs. 0.77(5) and 0.98(7) for the 5^{12} and $5^{12}6^2$ sites in this work and in the Mt. Hamilton refinement by Nakagawa et al. (2005), respectively], and suggest the presence of vacancies in the clathrate sites. The similarity in the framework structure of melanophlogites with different clathrate compositions is not surprising, as the clathrate phases have only weak Van der Waals interactions with the framework.

The clathrate composition seemingly affects the critical temperature for the α-β melanophlogite phase transition (Gies 1983). This may occur via an interaction of the clathrate molecules with the vibrational modes of the O atoms. This interaction may promote the symmetry change at the critical temperature. It appears that this interaction depends on the nature of the guest molecule.

Another possible mechanism by which the guest molecule would affect the phase transition is convergent ordering. The site occupancies in the tetragonal phase for the three sites of the degenerate $5^{12}6^2$ site are significantly different (Nakagawa et al. 2005); they would need to be equivalent to achieve the transition to the cubic symmetry. For the transition to occur those must be an exchange between the $5^{12}6^2$ subsites in the tetragonal symmetry, i.e., a convergent order-disorder process. Such convergent order-disorder would depend on the nature of the guest molecule.

Phase transitions in quartz and melanophlogite: Similarities and differences

Nakagawa and Kihara (2006) showed that the phase transition in melanophlogite is due to increasing atom disorder over multiple potential energy minima, and is strongly related to the α-β phase transition in quartz. In both the quartz and melano-

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[1] Deposit item AM-08-003, CIF (structure deposited CSD no. 417910). Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 2. Structural coordinates and isotropic displacement parameters of the Varano Marchesi melanophlogite

Atom	*x/a*	*y/b*	*z/c*	sof	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Si1	0	0.31079(5)	0.11425(5)	1	0.0427(4)	0.0243(4)	0.0348(4)	0.00000	0.00000	-0.0066(3)	0.0339(2)
Si2	0.18264(4)	0.18264(4)	0.18264(4)	1	0.0306(2)	0.0306(2)	0.0306(2)	–0.0048(2)	–0.0048(2)	–0.0048(2)	0.0306(2)
Si3	0.25	0	0.5	1	0.0177(7)	0.0225(4)	0.0225(4)	0	0	0	0.0209(3)
O1	0.09616(13)	0.24660(12)	0.13592(12)	1	0.0629(10)	0.0828(13)	0.0667(11)	0.0319(9)	–0.0101(9)	0.0123(9)	0.0708(6)
O2	0	0.40601(16)	0.18121(18)	1	0.1690(27)	0.0387(13)	0.0609(16)	0	0	–0.0309(12)	0.0895(9)
O3	0.34414(19)	0	0	1	0.0350(15)	0.0352(14)	0.0515(16)	0	0	0	0.0406(7)
O4	0.25	0.25	0.25	1	0.0904(16)	0.0904(16)	0.0904(16)	–0.0370(13)	–0.0370(13)	–0.0370(13)	0.090(2)
5^{12}	0	0	0	0.71	0.082(5)	0.082(5)	0.082(5)	0	0	0	0.082(6)
$5^{12}6^2$	0.5	0	0.25	0.91	0.368(18)	0.368(18)	0.174(15)	0	0	0	0.303(13)

Note: The refinement was done in space group $Pm\bar{3}n$ [a = 13.399(2)].

TABLE 3. Bond distances and angles for this work compared with those obtained from the refinement by Gies (1983) and Nakagawa et al. (2005) (both performed in situ at ~80 °C) of Mt. Hamilton β-melanophlogite

	This work	Gies (1983)	Nakagawa et al. (2005)
Si1-O1 ×2	1.576(2)	1.577(2)	1.573(3)
Si1-O2	1.560(2)	1.571(2)	1.572(4)
Si1-O3	1.595(1)	1.595(2)	1.595(2)
<Si1-O>	1.577	1.580	1.578
Si2-O1 ×3	1.571(2)	1.572(3)	1.575(3)
Si2-O4	1.563(1)	1.569(3)	1.566(3)
<Si2-O>	1.569	1.571	1.573
Si3-O2 ×4	1.561(2)	1.569(3)	1.560(4)
<Si-O>	1.578	1.576	1.575
Si1-O1-Si2	166.9(9)	166.9(2)	165.9(2)
Si3-O2-Si1	178.9(2)	179.0(2)	178.6(3)
Si1-O3-Si1	147.4(2)	148.3(3)	147.4(4)
Si2-O4-Si2	180	180	180
<Si-O-Si>	168.3	168.8	168.0

TABLE 4. Comparison of the B_{eq} (=$8\pi^2U_{eq}$) between Varano Marchesi and Mt. Hamilton refinements of β-melanophlogite

Atom	Varano Marchesi	Mount Hamilton	
	This work	Gies (1983)	Nakagawa et al. (2005)
Si1	2.67	1.71	1.71
Si2	2.42	1.72	1.73
Si3	1.65	1.43	1.23
O1	5.59	4.89	5.02
O2	7.07	4.78	5.50
O3	3.20	2.76	2.70
O4	7.11	5.82	5.47
5^{12}	6.47		15.4
$5^{12}6^2$	23.9		37.2
Ave*	4.51	3.54	3.64

* Average over Si and O equivalent B factors.

phlogite transitions, an increase in the dynamic motion occurs, as witnessed by the sharp increase of the atomic displacement parameters close to the transition (Nakagawa and Kihara 2006).

Diffuse reflections observed here in the SAED pattern, also were found in quartz above the α-β transition (Heaney and Veblen 1991). In quartz, an incommensurate phase is present for about 1 °C between the α and β phases. The presence of the incommensurate transition in quartz is revealed by the sharp incommensurate satellite reflections in SAED patterns, in connection with dynamically interchanging twin domains. At higher temperature, into the high-symmetry stability field, the incommensurate reflections become diffuse, but they are still present even 200 °C above the transition temperature in quartz (Heaney and Veblen 1991).

In melanophlogite, Nakagawa et al. (2006) proposed a transformation mechanism similar to that for quartz, with the formation of a complex set of domains, either in twin or antiphase relations, close to the transition. Like in quartz, these domains may become periodic and give rise to an incommensurate structure and reflection, which would become diffuse at temperatures higher than the transition. The diffuse reflections observed in melanophlogite may then be interpreted as a post-transition feature. Further high-temperature, in situ TEM investigations on melanophlogite through the tetragonal to cubic transition are desirable to look for the possible presence of an incommensurate structure.

There are, however, significant differences between the quartz and melanophlogite transitions. In quartz, the transition is a zone center one, through an incommensurate phase, and the same cell setting is retained through the transition; in melanophlogite, the transition from cubic to tetragonal occurs via a structural distortion and the formation of a superstructure. Both the structural distortion and the superstructure formation alone are able to cause the phase transition in melanophlogite, and it is not clear whether they are linked together by some kind of coupling, or if they occur at exactly the same temperature.

Constraints for melanophlogite origin

The outcrop, microstructural, and microanalytical observations provide some constraints on the genesis of Varano Marchesi melanophlogite. Melanophlogite is found in open veins, it always grows on opal, and never is in direct contact with the host rock, which suggest a formation at very mild hydrothermal conditions. A possible source of silica for the hydrothermal fluid could be the dissolution of biogenic silica from the diatom shells in the surrounding siliceous shales. The conditions of formation are within the broad range suggested by Skinner and Appleman (1963) (below 112 °C) and by Gies et al. (1982), who synthesized melanophlogite at 170 °C. Higher-temperature conditions would promote the growth of the thermodynamically stable phase of silica, i.e., quartz.

Melanophlogite is found in a fracture system related to one of the middle Miocene to Recent tectonics events. The melanophlogite is found in open veins or pockets where crystals could grow unstrained without interfering each other. It is suggested that this shear stress would cause the escape of the guest molecules and the collapse of the melanophlogite structure.

The presence of opal within melanophlogite, with corroded rims (Fig. 4), suggests that melanophlogite grew, at least in part, at the expenses of opal. A similar observation was also made for the Racalmuto melanophlogite by Skinner and Appleman (1963). This may be related to a secondary incursion of CH_4-bearing fluids, which possibly dissolved opal, and promoted crystallization of melanophlogite. The presence of melanophlogite growing on a thin opal crust (lussatite) was reported in Chvaletice (Zàk 1972) and, although not invariably, in the melanophlogite from Racalmuto (Skinner and Appleman 1963).

In the Varano Marchesi melanophlogite, the host veins were found within strata more compact and with carbonate cement between the grains, whereas in most of the outcrop melanophlogite and opal are absent. It appears that fractures occurring within the harder, cemented strata provided a trap for incoming CH_4-rich fluids, which were diffusing within the more porous marls.

The observations for the Varano Marchesi melanophlogite are consistent with the experimental constraints of Gies et al. (1982), which indicate initial crystallization of opal (and cristobalite) at the inner tube, and subsequently of melanophlogite, which may form only when conditions of higher gaseous phases saturation are achieved in a closed system.

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