CO₂ distribution in CO₂–rich melanophlogite from Fortunillo, Tuscany, Italy

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CO₂ distribution in M₁₂ and M₁₄ cages of CO₂–rich melanophlogite from Fortunillo, Tuscany, Italy was studied using synchrotron powder X-ray diffraction. Original and two heat-treated samples at 500 and 1000 °C were studied at room temperature. The diffraction patterns of these samples can be indexed as a cubic cell (Pm₃n). For the non-heated sample, CO₂ occupancy for M₁₄ cage is close to unity, whereas about 0.85 for M₁₂ cage. For the 500 °C–heated sample, the occupancies for M₁₄ and M₁₂ cages are reduced to 0.79 and 0.57, respectively. Present study showed that CO₂ has preference to M₁₄ cage, but substantial CO₂ occupies M₁₂ cage. The electron distributions obtained by MEM analysis clearly reveal orientationally ordered CO₂ distribution in M₁₂ and M₁₄ cages. Present result is also used to clarify a recently proposed interpretation for the splitting of CO₂ Raman vibrational peak for the heat-treated melanophlogite.

Keywords: Melanophlogite, Powder X-ray diffraction, Crystal structure, Site distribution, CO₂

INTRODUCTION

Melanophlogite is a rare silica mineral with a clathrate structure and is isostructural to sI clathrate hydrate (e.g., Momma, 2014). It features two large cages which can host small guest molecules such as CH₄, CO₂, N₂ and H₂S (e.g., Skinner and Appleman, 1963; Zák, 1972; Gies, 1983; Tribaudino et al., 2008; Lazzeri et al., 2017). The ideal formula for melanophlogite is 46SiO₂·2M₁₂·6M₁₄, where M₁₂ designates pentagonal-dodecahedral [5₁₂] cage made of twelve 5-membered SiO₄ rings, and M₁₄ designates tetrakaidecahedral [5₁₂6₂] cages made of twelve 5- and two 6-membered SiO₄ rings. At room temperature, melanophlogite generally takes a tetragonal cell (P4/ nbc) with 2 × 2 × 1 superstructure of cubic phase. A transition to the cubic phase (Pm₃n) takes place at relatively low temperature (<100 °C) (Gies, 1983; Nakagawa et al., 2005). On the other hand, the cubic phase of melanophlogite at room temperature has also been reported (Tribaudino et al., 2008). There are industrial and environmental interests for this mineral (Navrotsky et al., 2003) as it might be used to fix CH₄ and CO₂ which are two most notorious greenhouse gases.

Recently Kanzaki (2019) studied a CO₂–rich melanophlogite using in-situ high-temperature Raman spectroscopy up to 1100 °C and showed that degassing starts from about 450 °C. He found that vibrational peaks of CO₂ apparently split into two above 450 °C. This ‘splitting’ was reserved in the recovered samples from high temperatures. A similar split has been known for CH₄ and H₂S at room temperature without any heat treatment (Kortus et al., 2000; Tribaudino et al., 2008). These studies interpreted the split as slightly different vibrational frequencies of these molecules in M₁₂ and M₁₄ cages. Kanzaki (2019) interpreted his result of CO₂ similarly but pointed out several difficulties for this interpretation. Kolesov and Geiger (2003) has observed splitting of CO₂ vibrational peak in a CH₄–N₂–CO₂ containing melanophlogite at very low temperature (4 K), but no splitting was observed at room temperature. Adding to this, their peak assignment (to M₁₂ and M₁₄ cages) was opposite to that of Kanzaki (2019). Kanzaki (2019) observed that the peak intensity supposedly originated from M₁₂ becomes even higher than that of M₁₄ above 500 °C. As the number of M₁₂ site in the cell is a third of M₁₄ site, this observation is difficult to explain. Kanzaki’s interpretation is based on an assumption that virtually no CO₂ occupies in M₁₂ cage for the original (non-heated) sample. The strong preference of CO₂ to M₁₄ cage is suggested by
previous study of the CH$_4$-N$_2$-CO$_2$ containing melanophlogite (Gies, 1983). However, CO$_2$ molecule is supposed to work as a template for melanophlogite formation. Thus, an empty M$^{12}$ cage is unlikely. For CO$_2$-containing clathrate hydrates, the occupation of CO$_2$ in M$^{12}$ cage has been also debated in past. But now it is shown from neutron diffraction study that 50 to 70% CO$_2$ can occupy M$^{12}$ cage in sI hydrate (Chen et al., 2015). Similar situation is expected for isostructural melanophlogite. Therefore, crystal structural study of CO$_2$ occupancy of melanophlogite is essential to resolve this issue. Although structural studies for the CH$_4$-N$_2$-CO$_2$ containing samples (Gies, 1983; Nakagawa et al., 2001) and the CH$_4$-rich sample (Tribaudino et al., 2008) have been reported, there is no structural study for the CO$_2$-rich melanophlogite thus far.

In this study, the CO$_2$ occupancy in M$^{12}$ and M$^{14}$ cages of the CO$_2$-rich melanophlogite and also heat-treated samples were studied using synchrotron powder X-ray diffraction technique. Additionally, CO$_2$ distribution in the cages was visualized by maximum-entropy method (MEM). Although the electron density distributions in the cages have been reported by previous single crystal X-ray diffraction studies using differential Fourier synthesis method (Gies, 1983; Nakagawa et al., 2005), these studies used melanophlogite from Mt. Hamilton, California which has mixed guest gas molecules (CH$_4$, N$_2$, and CO$_2$). This makes interpretation not straightforward.

**EXPERIMENTAL PROCEDURES**

Natural melanophlogite samples from Fortunillo, Tuscany, Italy (obtained from N’s Mineral Co.) were used for the present study. The sample from same locality was used in our previous Raman spectroscopic study (Kanzaki, 2019). Although direct chemical analysis for gas was not conducted for the samples from this locality, they contain mostly CO$_2$ molecules based on previous Raman spectroscopic studies (Yagi et al., 2007; Kanzaki, 2019). Raman peaks of CH$_4$ and N$_2$ were very weak for the studied sample. Melanophlogite samples from other localities generally exhibit cubic shape, but the samples from this locality are clear droplet shape with diameter of 1–3 mm. Micro-focus X-ray diffraction (Rint Rapid II, Rigaku Co.) of a transparent droplet-shaped sample gave Debye rings even if the sample is not rotated. Thus, these droplets are polycrystalline aggregate. Optical microscopic observation of thin section made from the droplets revealed faint concentric stripes likely showing growth texture. Under cross polarization, the droplet is not quite black, but cross-shaped shadow zone was observed. This apparently indicates that the droplet is not optically isotropic. Powdered sample did not show clear evidence for isotropic extinction under cross polarization, but small degree of optical anisotropy will be difficult to detect. Since no suitable single crystal was available, the crystal structure is examined by powder X-ray diffraction technique.

We also studied two heat-treated samples. For those samples, a few roughly crushed fragments of the droplet were treated in a muffle furnace. In order to obtain vibrational peak-split sample, a platinum crucible with the fragments was placed in the muffle furnace which was kept at 500 °C. The crucible was taken out from the furnace after 5 min. This temperature and duration are selected consulting degassing behavior reported by Kanzaki (2019). Although the recovered fragments were still keeping original shapes, they became white, and numerous fine cracks were observed. This behavior is different from more common CH$_4$-containing melanophlogite samples which turn black after heating (e.g., Skinner and Appleman, 1963). To obtain fully dehydrated melanophlogite, these fragments were heated from room temperature to 1000 °C by 1 h, held at 1000 °C for 24 h, and cooled down to room temperature by 1 h. The recovered sample was white powder.

In order to confirm the vibration Raman mode splitting of CO$_2$ for the 500 °C-treated samples, unpolarized Raman spectra were acquired using a home-built single-monochromator micro-Raman spectrometer with 488 nm solid laser, as described in our previous study (Kanzaki, 2019). The Raman spectra of the original melanophlogite and the heat-treated sample at 500 °C for 5 min are shown in Figure 1. For the 500 °C-treated sample, vibrational modes of CO$_2$ (Fermi diad) at 1250–1400 cm$^{-1}$ as well as low-frequency broad band below 100 cm$^{-1}$ which originated from CO$_2$ librational mode are still intense, suggesting substantial CO$_2$ is still kept in the structure. For the 500 °C-treated sample, the peak at around 1380 cm$^{-1}$ apparently split. The split is less apparent for the peak near 1280 cm$^{-1}$, but a shoulder at higher frequency is visible. We also noted that the peak intensity ratio between split peaks varies from grain to grain as shown in Figure 1, suggesting heterogeneity or orientational dependence. Virtually no CO$_2$ peaks was observed from the 1000 °C-heated sample (not shown).

For structural analysis, synchrotron X-ray diffraction patterns of these melanophlogite samples were measured at BL5S2 of Aichi Synchrotron Radiation Center. A Debye-Scherrer type diffractometer equipped with four two-dimensional solid-state detectors was used (Ida, 2016). The powdered sample was loaded into a 0.3 mm-diameter borosilicate glass capillary and measured up to 95° in 2θ for 10 min. CeO$_2$ powder (NIST SRM 674b)
RESULTS AND DISCUSSION

Crystal structure of CO$_2$-rich melanophlogite

The observed synchrotron powder X-ray diffraction patterns of the samples were given in Figure 2 (red crosses). Three samples gave the similar diffusion patterns with apparent higher angle shifts for the 1000 °C-heated sample relative to other two. However, relative peak intensities between peaks at around 10° and those of 16° change significantly with increasing heat-treated temperature. From simulated powder X-ray diffraction patterns with different CO$_2$ occupancies, it becomes apparent that these intensity changes are related to changes in the occupancies of CO$_2$ molecule. Therefore, intensity ratios of these peaks could be used for qualitative measure of gas molecule abundance.

These diffraction patterns were indexed using N-TREOR09 (Altomare et al., 2009) implemented in EXPO2014 (Altomare et al., 2013). For all three samples, a cubic cell with $a \approx 13.4$ Å gave the highest figure-of-merit. It has been reported that melanophlogite at room temperature is tetragonal ($P4_2/nbc$), and it transforms to cubic phase ($Pm\bar{3}n$) at 63 °C for the case of the sample from Mt. Hamilton, California (Nakagawa et al., 2005). The sample from this locality is known to contain N$_2$, CH$_4$, and CO$_2$ gases (Gies, 1983; Lazzari et al., 2017). In order to check possible diffraction peaks due to the tetragonal cell, our patterns were compared with a simulated powder pattern using the structural parameters of $P4_2/nbc$ melanophlogite taken from Nakagawa et al. (2005). The peaks unique to the tetragonal cell are not detected in our patterns.

Present result is somewhat contradictory to previous studies of melanophlogite from same locality. Yagi et al. (2007) reported that they could index the powder X-ray diffraction pattern of their sample from Fortunillo as a tetragonal cell consistent with $2 \times 2 \times 1$ superstructure of the cubic phase, but no detailed pattern was given. Gies (1983) reported tetragonal to cubic transition at 55 °C for melanophlogite from same locality by optical observation. D’Alessio et al. (2019) studied melanophlogite from Fortulino up to 400 °C by synchrotron powder X-ray diffraction and found a transition at 97 °C much higher than that of optical measurement (Gies, 1983). They found that their pattern at room temperature cannot be fitted with the tetragonal cell ($P4_2/nbc$), but the pattern was well fitted with a monoclinic cell. These inconsistencies from same locality suggest structural variations from sample to sample may exist. We investigated more than 10 droplets by the laboratory X-ray diffractometer and found only cubic phase. Thus, rock specimen level variation was not detected. Although possibility of lower symmetry than cubic cell, also suggested from optical observation, cannot be ruled out, no discernable peak splitting was observed in our samples. Neither apparent peak broadening nor asymmetric peak suggestive of symmetry lowering was observed in our diffraction patterns. Therefore, the cubic cell was adapted in the following structural refinements.
There are several very weak peaks at about 14.2, 18.8, 24.7, and 28.4° which cannot be explained by melanophlogite (including the non-cubic cells) or dolomite (coexisting mineral). The 18.8° peak observed in the 1000 °C–heated sample only. The 14.2° peak matches with most intense peak of cristobalite, whereas the latter three cannot be indexed with any silica phases. As these impurity peaks are very weak, they are ignored during the Rietveld refinement.

Two space groups, \( Pm\overline{3}n \) and \( P\bar{4}3n \), gave best fit for Le Bail pattern fitting of EXPO2014. Although they gave an identical \( R_p \) for the pattern fitting, subsequent Rietveld refinement found that \( Pm\overline{3}n \) is more plausible as final \( R \)-factors are lower than those of \( P\bar{4}3n \). \( Pm\overline{3}n \) has been reported for space group of the high-temperature cubic form of melanophlogite (Gies, 1983) and the cubic phase observed at room temperature (Tribaudino et al., 2008), whereas Nakagawa et al. (2005) refined the structure assuming both \( Pm\overline{3}n \) and \( P\bar{4}3n \). \( Pm\overline{3}n \) is also adopted for gas-free melanophlogite samples at room temperature (Nakagawa, 2002; Ida et al., 2007).

Figure 2 shows the Rietveld refined diffraction patterns of three samples (blue lines). The obtained crystal structures are given in Figure 3, and structural parameters are listed in Table 1. Bond distances and angles are given in Table 2. The crystal structure is essentially identical to those of cubic phase reported by previous studies (Gies, 1983; Nakagawa et al., 2005; Tribaudino et al., 2008). Structure features of melanophlogite are well documented in those papers. Isotropic displacement factors for oxygens are large, but the similar large values are reported in previous studies. Smaller factor for O3 compared to others is also reproduced. On the other hand, isotropic displacement factor for M12 is close or larger than that of M14 sites in our result. However, smaller \((1/2 \sim 1/3)\) factor for M12 compared to that of M14 is reported in previous studies (Gies, 1983; Nakagawa et al., 2005; Tribaudino et al., 2008). This difference is likely due to predominant occupation of CH\(_4\) in M12 cage in their samples, as CH\(_4\) is expected to have compact electron distribution compared to that of CO\(_2\) resulting smaller factor. Anisotropic displacement factors for M14 cage are an oblate ellipsoidal shape as shown in Figure 3. Si-O bond lengths obtained from present study are somewhat smaller than expected. Similar shorter Si-O bond distances are also reported in previous studies and interpreted as a result of large amplitude of librations for oxygens (Nakagawa et al., 2005). For the 1000 °C–heated sample, the structure was essentially identical to those of other two, except no CO\(_2\) occupancies for M12 and M14 cages.

Refined CO\(_2\) occupancies for M12 and M14 cages are given in Table 1. For the non–heated sample, the occupancy of M14 is 1.000(6), and that of M12 is 0.850(11). For the 500 °C–heated sample, the occupancy for M14 is reduced to 0.790(6), whereas that of M12 is 0.568(11). This implies that the 500 °C–heated sample lost 24% CO\(_2\) compared to the original sample. Apparently, CO\(_2\) has weak preference to M14 cage over M12 cage. This tendency is similar to the occupation found in sI hydrate (Chen et al., 2015).

The gas–free melanophlogite has slightly smaller cell volume compared to that of CO\(_2\) filled samples (Table 1). This is consistent with Liu et al. (1997); but their sample was not cubic at room temperature. On the other hand, Nakagawa (2002) and Ida et al. (2007) reported that fully degassed melanophlogite at room temperature has slightly larger volume compared to the original ones. They also revealed that their recovered melanophlogite were \( Pm\overline{3}n \), changed from original \( P\bar{4}32/nbc \). These inconsistencies are partly due to difference of natural samples used. Liu et al. (1997) used a sample from Livorno, Italy, whereas Nakagawa (2002) and Ida et al. (2007) used samples from Mt. Hamilton. Based on Lazzeri et al. (2017), the sample from Livorno contains more CO\(_2\) and less CH\(_4\) compared to that of Mt. Hamilton and is closer to our sample.

M12 and M14 cage volumes are also compared in Table 2. It should be noted that ‘free space’ given by Gies (1983) for M12 and M14 cages (~ 97 and ~ 136 Å\(^3\), respectively) are not cage volumes (Navrotsky et al., 2003; D’Alessio et al., 2019). These cage volumes decrease with decreasing CO\(_2\) occupancies, and a larger change was observed for smaller M12 cage. The behavior of the cell volume and cage volumes suggest that the cages are expanded by filled CO\(_2\). No special structural difference was observed for the 500 °C–treated sample which apparently exhibits the Raman peak split.

**CO\(_2\) distribution in M12 and M14 cages by MEM analysis**

MEM–based pattern fitting (MPF) method (Momma et al., 2013) was applied for the non–heated and the 500 °C–treated samples. MEM is expected to allow us to obtain clear electron distribution even using powder X–ray diffraction data. The electron distribution of the 500 °C–treated sample is essentially identical to that of the non–heated sample, except with lower densities. Therefore, the distribution for the non–heated sample is shown in Figure 4. The electron distribution in M12 cage shown in Figure 4a reveals angular distribution, showing horn–like feature extending to outside. In three–dimensional distribution, there are total twelve horns. We noted that each horn is roughly pointing toward one of twelve Si1 sites in the cage as seen in Figure 4a. This implies that there are six (symmetrically equivalent) preferred orien-
tations for CO$_2$ in M$_{12}$ cage. In other words, oxygens of CO$_2$ in M$_{12}$ cage are statistically distributed in 12 equivalent positions (24k site) assuming C at the center. Natural question is that why Si1 site direction is favored. It might be reflecting repulsive interaction between oxygens in CO$_2$ and that in M$_{12}$ cage. Shortest distance from the center of M$_{12}$ cage to O in the cage is 4.029 Å for O1 site. When CO$_2$ is pointing to the center of the 5-membered ring, there are four O1 sites. But it reduced to 3 and 2 when it is pointing to Si2 and Si1 sites, respectively. By orientating to Si1 site direction, CO$_2$ will receive smallest repulsive force. Theoretical calculation is necessary to confirm this observation. Angular distribution was also observed by single crystal studies of Mt. Hamilton sample by Gies (1983) and Nakagawa et al. (2005). Gies (1983) recognized 12 secondary maxima in his distribu-
tion but stated that these are pointing to 'the midpoints of the pentagons', rather than Si1 site. Again, this difference could be due to the difference of guest molecules in M12 cage between their and our samples. Gies (1983) suggested that M12 cage in Mt. Hamilton sample is occupied by CH4 and N2.

The electron distribution in M14 cage is shown in Figures 4a and 4b. The distribution is predominantly extending to [100] direction, and four out of six horns are seen in Figure 4a. Figure 4b shows the distribution viewed at different depth, and a cross-like distribution can be seen. M14 cage can be regarded as an oblate ellipsoid, just like the anisotropic displacement factors shown in Figure 3, and these horns are pointing to the axes of the ellipsoid. Two of them (horizontal ones in Fig. 4a) are pointing toward the center of the 6-membered rings, but compared to other four, which are equivalent, the distribution is less extended. Nakagawa et al. (2005) reported similar result, but their electron distribution from differential Fourier map was noisy. On the other hand, Gies (1983) recognized 12 secondary maxima between 'the midpoints of the pentagon and the cage center, but not between the hexagons

### Table 1. Refined crystal structures of melanophlogite (46SiO2·2M12·6M14) at room temperature

#### Non-heated sample

| Site | x     | y     | z     | occup. | Uiso (Å²) |
|------|-------|-------|-------|--------|-----------|
| Si1  | 0     | 0.31095(11) | 0.11361(10) | 1.0 | 0.0225(4) |
| Si2  | 0.18283(8) | 0.18283 | 0.18283 | 1.0 | 0.0217(5) |
| Si3  | 0.25  | 0      | 0.5   | 1.0   | 0.0184(9) |
| O1   | 0.09606(12) | 0.24939(13) | 0.13798(14) | 1.0 | 0.0548(8) |
| O2   | 0     | 0.40479(15) | 0.18302(17) | 1.0 | 0.0653(1) |
| O3   | 0.3456(3) | 0      | 0     | 1.0   | 0.0140(10) |
| O4   | 0.25  | 0.25   | 0.25  | 1.0   | 0.0572(2) |
| M12  | 0     | 0      | 0     | 0.850(11) | 0.72(2) |
| M14  | 0     | 0.25   | 0.5   | 1.000(6) | 0.62(9) |

#### 500 °C-heated sample

| Site | x     | y     | z     | occup. | Uiso (Å²) |
|------|-------|-------|-------|--------|-----------|
| Si1  | 0     | 0.31038(9) | 0.11429(8) | 1.0 | 0.0240(4) |
| Si2  | 0.18215(7) | 0.18215 | 0.18215 | 1.0 | 0.0256(4) |
| Si3  | 0.25  | 0      | 0.5   | 1.0   | 0.0176(7) |
| O1   | 0.09666(10) | 0.24965(11) | 0.13703(12) | 1.0 | 0.0573(7) |
| O2   | 0     | 0.40456(12) | 0.18398(15) | 1.0 | 0.0700(10) |
| O3   | 0.3465(2) | 0      | 0     | 1.0   | 0.0152(8) |
| O4   | 0.25  | 0.25   | 0.25  | 1.0   | 0.064(2) |
| M12  | 0     | 0      | 0     | 0.568(11) | 0.91(3) |
| M14  | 0     | 0.25   | 0.5   | 0.790(6) | 0.688(9) |

#### 1000 °C-heated sample

| Site | x     | y     | z     | occup. | Uiso (Å²) |
|------|-------|-------|-------|--------|-----------|
| Si1  | 0     | 0.30873(11) | 0.11580(11) | 1.0 | 0.0230(5) |
| Si2  | 0.18182(9) | 0.18182 | 0.18182 | 1.0 | 0.0291(6) |
| Si3  | 0.25  | 0      | 0.5   | 1.0   | 0.0235(10) |
| O1   | 0.09725(12) | 0.24872(12) | 0.13694(14) | 1.0 | 0.0635(10) |
| O2   | 0     | 0.40620(16) | 0.18187(16) | 1.0 | 0.0706(13) |
| O3   | 0.3428(3) | 0      | 0     | 1.0   | 0.0186(11) |
| O4   | 0.25  | 0.25   | 0.25  | 1.0   | 0.073(3) |
and the cage center. This difference is again could be due to difference of molecules occupying M\(^{14}\) cage. Based on Gies (1983), M\(^{14}\) cage is occupied by N\(_2\) and lesser CO\(_2\).

In Figure 4, a bar representing O…O distance of CO\(_2\) molecule (2.31 Å by Simon and Peters, 1980) is superimposed. The electron distribution by MEM clearly indicates that there are two preferred CO\(_2\) orientations in M\(^{14}\) cage, and one less preferred orientation aligned to the center of the cage to the 6-membered ring. These electron distributions of M\(^{12}\) and M\(^{14}\) cages obtained by present study clearly reveal that CO\(_2\) is orientationally ordered in these cages. This implies that CO\(_2\) is not freely rotating in the cages. This is consistent with the observed broad Raman band at low frequency (Fig. 1), which is interpreted as librational mode of CO\(_2\) (Kanzaki, 2019).

Table 2. Bond distances and bond angles for three melanophlogite samples

| Sample | Non-heated | 500 °C heated | 1000 °C heated |
|--------|------------|---------------|---------------|
| Si1-O1 (x2) | 1.5620(19) Å | 1.5580(16) Å | 1.5528(19) Å |
| Si1-O2 (x1) | 1.563(3) Å | 1.568(3) Å | 1.573(3) Å |
| Si1-O3 (x1) | 1.590(4) Å | 1.6045(14) Å | 1.6130(18) Å |
| Si2-O1 (x3) | 1.582(6) Å | 1.578(1) Å | 1.560(7) Å |
| Si2-O4 (x1) | 1.557(7) Å | 1.573(6) Å | 1.577(9) Å |
| Si3-O2 (x4) | 1.559(3) Å | 1.553(3) Å | 1.549(3) Å |
| Si1-O1-Si2 | 168.7(15)° | 167.3(2)° | 166.3(1)° |
| Si1-O2-Si3 | 178.6(17)° | 178.1(15)° | 178.1(17)° |
| Si1-O3-Si1 | 146.1(3)° | 144.9(3)° | 147.2(3)° |
| Si2-O4-Si2 | 180° | 180° | 180° |
| M\(^{12}\) volume | 235.8 Å\(^3\) | 234.8 Å\(^3\) | 231.9 Å\(^3\) |
| M\(^{14}\) volume | 334.0 Å\(^3\) | 334.2 Å\(^3\) | 332.5 Å\(^3\) |

Clarification for CO\(_2\) vibrational Raman peak splitting

Present study clearly revealed that even in the non-heat-treated sample, CO\(_2\) molecule occupies M\(^{12}\) cage substantially. Therefore, observed peak splitting of CO\(_2\) vibrational Raman peak at high temperature cannot be explained by two different vibrational frequencies of CO\(_2\) occupying in M\(^{12}\) and M\(^{14}\) sites, proposed by Kanzaki (2019). This implies that CO\(_2\) vibrational frequencies do not change appreciably, less than the peak width of about 2 cm\(^{-1}\) between M\(^{12}\) and M\(^{14}\) cages at room temperature. For CO\(_2\) clathrate hydrate (sI), about 2 cm\(^{-1}\) difference of vibrational Raman frequencies between two cages are reported at 77 K (Chen et al., 2015).

There is no apparent structural difference between original and the 500 °C-heated samples. Thus, the splitting cannot be explained by structural change. Most likely interpretation is that these new peaks could be due to CO\(_2\) gas entrapped as inclusions formed during heating. Although we are not able to directly observe expected inclusions, Skinner and Appleman (1963) observed numerous tiny black inclusions in a CH\(_4\)-containing melanophlogite single crystal treated at 800 °C for 2 h. This interpretation can explain about 7 cm\(^{-1}\) higher frequency shifts for these new peaks relative to original peaks as CO\(_2\) gas is known to have 5-8 cm\(^{-1}\) higher vibrational frequency than those in melanophlogite (Kanzaki, 2019). As a conclusion, the Raman vibrational splitting of CO\(_2\) in the heated CO\(_2\)-rich melanophlogite proposed by Kanzaki (2019) is not real.

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Figure 4. 2D electron density maps (a × b section) including M\(^{12}\) and M\(^{14}\) sites obtained by MEM analysis. (a) Section at z = 0. (b) Section at z = 0.25. For both maps, contour starts from 0.5 and up to 5.0 e/Å\(^3\) with 0.25–step. Superimposed bar represents bond length of O–O (2.31 Å) of CO\(_2\) molecule.
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