High-temperature Raman spectroscopic study of CO$_2$-containing melanophlogite

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CO$_2$-containing melanophlogite from Fortunillo, Italy was studied using a micro-Raman spectrometer with the ability to measure the low-frequency region. A very intense and broad feature was found below 100 cm$^{-1}$. To clarify the origin of this feature in relation with CO$_2$, heat treatment experiments and in-situ high-temperature Raman measurements were conducted up to 1100 °C. As a result of the heat treatment experiments, nearly CO$_2$-free melanophlogite was obtained at 950 °C for 6 h. For shorter time duration or lower treatment temperature, CO$_2$ vibrational Raman peaks (Fermi diad) were still observed, and those peaks were split. The low-frequency feature also reduced its intensity in these degassed samples. For the in-situ study, the intensity of CO$_2$ Raman peaks started to drop at around 450 °C, and simultaneously the low-frequency feature intensity decreased. The splitting of the CO$_2$ Raman peaks started from 450 °C, and it was interpreted as redistribution of CO$_2$ molecules in two distinct cages in the structure. The low-frequency feature completely disappeared at 1100 °C. It was concluded that the low-frequency feature is originated from CO$_2$ molecules. Librational and translational modes of CO$_2$ molecules in the cages of melanophlogite would be responsible for the low-frequency feature. The high-temperature Raman spectroscopic study thus provides us insight into CO$_2$ diffusion in melanophlogite structure.

Keywords: Melanophlogite, Low-frequency Raman spectroscopy, Guest molecule, Clathrasil, CO$_2$
EXPERIMENTAL PROCEDURES

Natural melanophlogite crystals from Fortunillo, Tuscany, Italy were used for the present Raman study. According to the previous studies (Kortus et al., 2000; Yagi et al., 2007; Tribaudino et al., 2008), the samples from this locality contain mostly CO$_2$ molecules. The melanophlogite crystals have spherical shape with diameter of 1–2 mm and are colorless and transparent. For the heat treatment experiments, a single crystal was placed in a muffle furnace and heated at 900, 950, 1000, and 1100 °C for 1 to 72 h. One of the single crystals was coarsely crushed, and thin fragments were used for the in-situ high-temperature Raman spectroscopic measurement. Another single crystal was pulverized, and the resultant powder was studied by powder X-ray diffractometry. Yagi et al. (2007) reported that their melanophlogite from Fortunillo has a tetragonal cell at room temperature. To our surprise, no peaks due to the tetragonal cell were detected in our sample, revealing our melanophlogite is cubic at ambient temperature.

Unpolarized Raman spectra were acquired using a home-built single-monochromator micro-Raman spectrometer with a 488 nm solid laser, as described in our previous study (Kanzaki, 2018). One of the notable features of this spectrometer is that a low-frequency region down to ~ 10 cm$^{-1}$ can be measured using two volume holographic notch filters (SureBlock) from Ondax Inc. (Lebedkin et al., 2011). The heat-treated samples were also inspected using this spectrometer.

For the in-situ high-temperature Raman measurements, a wire-heater cell reported in our previous studies (Kanzaki et al., 2012; Kanzaki, 2018) was used. The heating was conducted at ambient atmospheric condition. A long working distance 20× objective lens (Mitsutoyo M Plan NIR) was used to avoid thermal damage from the heater. Temperature was calibrated against heating power and the resultant powder was stacked six times. This procedure was repeated up to 1100 °C. Unfortunately, this sample was lost during the cooling and cannot be inspected at room temperature. Therefore, an additional experiment was conducted, and another sample was heated to 1000 °C and was kept for 1 h using same heater and then quenched to room temperature. In order to study the CO$_2$ Raman peak splitting, yet another sample was heated to 600 °C, and was kept for 10 min, and then quenched to room temperature.

Raman shifts in the reported spectra were calibrated against 10 Raman peaks of a synthetic coesite, whose shifts were precisely calibrated against Ar$^+$ plasma lines from an Ar ion laser. This procedure is fine for most minerals, but the Raman peaks from CO$_2$ molecules are expected in a range of 1250 to 1400 cm$^{-1}$. No coesite peak is available above 1200 cm$^{-1}$. Therefore, six Raman peaks of ethanol including high frequency peaks of 1275.2 and 1453.0 cm$^{-1}$ (Ferraro and Nakamoto, 1994; Hamaguchi and Iwata, 2015) were added for the calibration. The second-order polynomial equation was used to fit the Raman shifts of coesite and ethanol against the CCD pixel position using R (R Core Team, 2018) and was used for Raman shift correction for reported spectra. A Voigt profile function was employed to fit the Raman peaks using the ‘fitky’ program (Wojdyr, 2010), and the program was also used to obtain integrated area of peaks. Overall precision will be better than 1 cm$^{-1}$ for the Raman shift reported in this paper. There was no significant background increase from thermal radiation, so no correction including background subtraction was applied for all the reported spectra, except the removal of very sharp peaks originated from cosmic rays.

RESULTS AND DISCUSSION

Raman spectrum of CO$_2$-containing melanophlogite at room temperature

The Raman spectrum of the CO$_2$-containing melanophlogite at 27 °C including the low-frequency region is shown in Figure 1. As far as we are aware, no low-frequency region (<100 cm$^{-1}$) of melanophlogite has been reported before. A very intense and broad feature below 100 cm$^{-1}$ was noted. This feature apparently has a peak top at around 20 cm$^{-1}$. However, this peak top is likely formed artificially, because of absorption by the notch filters. The intensity most likely rises continuously toward 0 cm$^{-1}$. Therefore, this will be designated as ‘low-frequency feature’ hereafter. This low-frequency feature was ubiquitously observed from all melanophlogite crystals we have measured and was not observed for other minerals in our collection measured using the same spectrometer, except for few zeolites. The feature has a shoulder at ~ 50 cm$^{-1}$. This feature is not a fluorescence, as it is seen in the anti-Stokes side (below 0 cm$^{-1}$) in Figure 1. If the sample contains glassy or amorphous portion, boson peak may appear at low-frequency region. However, boson peak of
silica glass has the maximum at 52 cm$^{-1}$ (e.g., Malinovsky and Sokolov, 1986); in addition, characteristic Raman peaks in the middle frequency range (200–1000 cm$^{-1}$) from glass/amorphous structure are not detected. Solution, such as water has low–frequency feature. If the sample contains fluid inclusions, the low–frequency feature might be explained. However, no visible fluid inclusions were observed, and Raman peaks of fluid inclusion itself were not observed. Therefore, the low–frequency feature cannot be explained by neither glass nor fluid inclusions. Thus, this feature should be intrinsic Raman scattering coming from the melanophlogite samples. Unfortunately, we are not able to obtain melanophlogite from other locality for comparison thus far.

In contrast, the Raman peaks of melanophlogite in the middle region (150–1200 cm$^{-1}$) are much weaker in intensities (see an inset of Fig. 1). These peaks are mostly broad and observed at 170, 276, 365, 483, 530, 592, 725, 803, and 1090 cm$^{-1}$. These positions compare well with the previous Raman studies of natural melanophlogite (Kortus et al., 2000; Kolesov and Geiger, 2003; Yagi et al., 2007; Tribaudino et al., 2008; Likhacheva et al., 2018), confirming the sample is melanophlogite. The identity of the sample was also confirmed by powder X-ray diffraction measurement of the powdered single crystal.

For the high–frequency region of Figure 1, Fermi resonance peaks of CO$_2$ molecular vibration (Fermi diad) at 1277 and 1380 cm$^{-1}$ are evident. These positions are within 2 cm$^{-1}$ of previously reported positions in melanophlogite (Kolesov and Geiger, 2003; Tribaudino et al., 2008), but about 5 cm$^{-1}$ lower than those of Kortus et al. (2000). These positions are about 5–8 cm$^{-1}$ lower than those of corresponding free CO$_2$ gas, suggesting a weak interaction between molecules and the cages. Additionally, hot bands at 1258 and 1400 cm$^{-1}$ are noted, which are more apparent at high temperature, as discussed below. For detailed explanation of these complicated Raman peaks by Fermi resonance and hot bands, refer to Rosso and Bodnar (1995).

We did not detect clear CH$_4$ and N$_2$ Raman peaks in our sample. Other studies (Kortus et al., 2000; Yagi et al., 2007; Tribaudino et al., 2008) reported melanophlogite sample from the same locality, and they observed intense CO$_2$ peaks and weak or no CH$_4$ and N$_2$ peaks in their Raman spectra. The weak N$_2$ Raman peak was actually detected, but it is likely from N$_2$ in air or absorbed on mineral surface. The N$_2$ peak was commonly observed using our spectrometer when the laser beam was focused to the surface of samples, and the Raman shift was exactly same to that of air. Regardless of these minor differences, we confirmed that the dominant guest molecule is CO$_2$ in our sample from Fortunillo, Italy.

**Heat treatment experiments**

The single crystals of melanophlogite were treated in the muffle furnace at 900–1100 °C for 1–72 h. Their representative spectra are given in Figure 2. The single crystals before the heat treatment were clear, colorless and transparent. Recovered samples were white in color and easily broke up to fine grains. Numerous cracks were observed under optical microscope.

For shorter time duration (1 h) or lower temperature (900 °C), vibrational Raman peaks of CO$_2$ were still observed, although their intensities were weak. For the sample treated at 900 °C, local variation in the intensity of CO$_2$ peaks was also noted, as shown in Figure 2. For
longer duration (6 and 72 h), CO₂ Raman peaks were no longer detectable, and the low-frequency feature also nearly disappeared. However, no change in the peaks at the middle frequency region was observed, confirming that melanophlogite structure is still reserved, even at 1100 °C. Neither quartz nor cristobalite was observed in those samples. For degassed melanophlogite samples, a broad peak at around 105 cm⁻¹ was noted. Same peak was also reported at 103 cm⁻¹ for a CH₄-containing sample at ambient temperature (Likhacheva et al., 2018). Therefore, this peak may exist in our sample before heating as well, but it was hidden in the intense low-frequency feature.

In previous studies, gas-free melanophlogites were generally obtained by heat treatment at around 950 °C. Liu et al. (1997) and Navrotsky et al. (2003) degassed melanophlogite (both from Livorno, Italy) at 950 °C for 6 h. Geiger et al. (2008) degassed one sample from Mt. Hamilton, California at 950 °C for 10 h and another sample from Racalmuto, Sicily at 900 °C for 24 h. Yagi et al. (2007) treated a melanophlogite sample from Fortullino, Italy at 650 °C for 7 h, but observed still remaining CO₂ Raman peaks. Žák (1972) treated a sample from Chvaltice, Bohemia at 1050 °C for 12 h. These observations are consistent with the present heat treatment study. On the other hand, Skinner and Appleman (1963) treated the samples from Argigento, Sicily at 900 to 1000 °C for few days and reported the formation of cristobalite. Geiger et al. (2008) reported the crystallization of cristobalite in their sample (Mt. Hamilton) treated at 950 °C. Likhacheva et al. (2018) observed increasing local disorder in melanophlogite structure with degassing of CH₄ in their in-situ measurements. On the other hand, our heat-treated sample and also in-situ study given below indicated more stable melanophlogite with temperature.

At moment, this discrepancy cannot be explained well, and further systematic study is necessary in near future.

**Raman spectra of melanophlogite at high temperature**

The in-situ Raman spectra of the low-frequency region below 150 cm⁻¹ during heating up to 1100 °C are shown in Figure 3. Because of complicated shape due to absorption by the notch filters at lower frequency, no fitting was conducted. To inspect a relation between this feature and temperature, Raman intensity at 25 cm⁻¹ is plotted against temperature (an inset of Fig. 3). Unfortunately, the normalization between obtained spectra was difficult for our present measurement. The shoulder at around 50 cm⁻¹ makes the interpretation further complicated. The 25 cm⁻¹ is selected to avoid this peak. The 50 cm⁻¹ shoulder seems visible up to 400 °C, but not clear at higher temperature. Despite these problems, this crude plot will still provide at least qualitative trend, since nearly the same spot was measured with the same measurement conditions, except for room temperature. Below...
400 °C, the intensity was nearly constant. At 450 °C, the intensity started to drop and became constant above 1050 °C. Above 1050 °C, the low-frequency feature virtually disappeared. The apparent peak-like feature in the low-frequency region above 1050 °C in Figure 3 is coming from the absorption of the notch filters superimposed on the background intensity. We noted a peak at around 1364 cm$^{-1}$ is due to the vibration mode for $^{13}$CO$_2$. Splitting of peaks starts above 450 °C.

At 450 °C, the intensity started to drop and became constant above 1050 °C. Above 1050 °C, the low-frequency feature virtually disappeared. The apparent peak-like feature in the low-frequency region above 1050 °C in Figure 3 is coming from the absorption of the notch filters superimposed on the background intensity. We noted a peak at around 70 cm$^{-1}$ which becomes visible when the low-frequency feature nearly disappeared at 1000 °C in another in-situ experiment (not shown). This peak would correspond to the peak found at 105 cm$^{-1}$ in the heat-treated samples at room temperature, as noted before.

The Raman spectra of the high-frequency region (≥1200 cm$^{-1}$) during heating up to 1100 °C are shown in Figure 4. With increasing temperature to 400 °C, the intensities of two Fermi diad peaks at 1277 and 1380 cm$^{-1}$ decreased, whereas the hot band intensities increased. Even the second hot band of the 1380 cm$^{-1}$ peak at 1415 cm$^{-1}$ was visible at higher temperatures. Above 500 °C, the splitting of those peaks became apparent, which is treated in next section.

To qualitatively assess the CO$_2$ degassing behavior with temperature, a total peak area of all CO$_2$-related peaks (1277– and 1380-cm$^{-1}$ peaks and their hot bands) was considered as a proxy for concentration of CO$_2$. Split peaks and hot bands are included into integrated intensities, because of the intensity partition between the main peak and hot bands with temperature. Similarly, to the case of the low-frequency feature, this will provide a qualitative trend. The total integrated area is plotted in Figure 5 as a function of temperature. The integrated area was nearly constant up to 400 °C, but it started to drop from 450 °C. This suggests that CO$_2$ degassing is starting at 450 °C. This trend is parallel to the intensity change of the low-frequency feature with temperature (the inset of Fig. 3). At 500 °C, the formation of cracks in the sample was noted visually. Similar cracks were also observed in the heat-treated samples. The formation of cracks is apparently caused by the degassing. Just after 1000 °C was reached, there is still visible CO$_2$ peaks remained, and they were slowly decreased with time. These observations are consistent with our heat treatment study in which weak CO$_2$ peaks was still observed in the heated sample at 1000 °C for 1 h.

The Raman spectra of the middle-frequency region (100–1200 cm$^{-1}$) during heating up to 1100 °C are shown in Figure 6. The Raman feature of melanophlogite was observed up to 1100 °C. This is in harmony with the present heat treatment experiment at 1100 °C (Fig. 2). Above 850 °C, a peak at around 460 cm$^{-1}$ increases its intensity. Initially this peak was attributed to the formation of quartz. However, no quartz was found in the recovered samples. Therefore, this peak likely corresponds to the 483 cm$^{-1}$ peak observed in melanophlogite at room temperature (see Fig. 1).

As noted before, our sample is cubic even at ambient temperature, so no temperature-induced phase transition is expected. According to the previous in-situ optical microscopic study, a tetragonal/cubic phase transition was observed at 55 °C for Fortunillo sample (Gies, 1983). However, no clear change in the Raman spectra between 27 and 100 °C was observed. This further supports that our sample is cubic, not tetragonal at room temperature.

The present study revealed that a relatively high
temperature (>400 °C) is necessary to drive off CO2 from melanophlogite, and melanophlogite itself is quite stable at high temperature. These properties are plausible for CO2 sequestration purpose. However, it is well known that melanophlogite (and other clathrasils) has higher solubility in aqueous solution compared to quartz, making storage in undersea or underground setting not practical.

Splitting of CO2 vibrational Raman peaks

It was noted that each of the CO2 vibrational Raman peaks was split into two peaks after the heat treatment (top spectrum in Fig. 2). The split was also observed in the spectra of the in-situ experiments (Fig. 4). However, the peak intensities in those spectra are rather weak. To obtain the better spectrum, a single crystal was heated to 600 °C using the wire-heater and was kept for 10 min and then quenched. Because of short time duration, this sample still contains substantial amount of CO2; thus providing us with a high-quality spectrum for split CO2 peaks, as shown in Figure 7 (top spectrum). There is no apparent change in peak positions for the originally existing peaks at 1277 and 1380 cm\(^{-1}\) as compared to the non-heat-treated sample (Fig. 1). New peaks at 1284 and 1387 cm\(^{-1}\) were formed at high frequency sides of those peaks, respectively. The corresponding splits were also seen in hot bands, confirming they are originated from the CO2 molecular vibrations.

The splitting of the guest gas vibrational peak in melanophlogite has been known for CH\(_4\) and H\(_2\)S at room temperature (Kortus et al., 2000; Tribaudino et al., 2008) and CO\(_2\) at 4 K (Kolesov and Geiger, 2003). But the splitting of CO\(_2\) at room temperature has not been reported. However, in retrospect, similar splitting is apparent in the heat-treated sample at 650 °C for 7 h from same locality (Fig. 2 in Yagi et al., 2007), but the splitting was not mentioned in their paper. No splitting of CO\(_2\) was observed in chibaita, recently found natural clathrasil (Scheidl et al., 2018). The splitting is generally interpreted as a result of occupancy of gas molecules in two distinct M\(_{12}\) and M\(_{14}\) sites in melanophlogite structure, in which gas molecules would have different vibrational frequencies (Kortus et al., 2000). Because of the existence of Fermi resonance, their interpretation could be complicated compared to CH\(_4\) or H\(_2\)S. We interpreted this split in a straightforward way. Based on single crystal X-ray diffraction study (Gies, 1983; Nakagawa et al., 2001), CO\(_2\) molecules preferentially occupy M\(_{14}\) site. Therefore, Fermi diad peaks at 1277 and 1380 cm\(^{-1}\) observed in the non-heated melanophlogite are from CO\(_2\) molecules in M\(_{14}\) sites. For the tetragonal phase, there are three kinds of M\(_{14}\) sites (G1, G2, and G3 in Nakagawa et al., 2001), but minor differences in three M\(_{14}\) sites would not be detectable for CO\(_2\) Raman shifts. Also, it should be noted that our sample is cubic even at room temperature. At high temperature, CO\(_2\) molecules in M\(_{14}\) are able to migrate to M\(_{12}\) through five-membered SiO\(_4\) rings, enabling occupation of CO\(_2\) in M\(_{12}\) cage, which could be responsible for the appearance of new peaks at 1284 and 1387 cm\(^{-1}\).

It seems quite reasonable interpretation. However, there are several problems for this interpretation. Kolesov and Geiger (2003) observed a split for 1378 cm\(^{-1}\)-peak at 4 K, but the split was small (2.5 cm\(^{-1}\)) compared to present study (7 cm\(^{-1}\)). Also, the split was not clear for the 1277 cm\(^{-1}\)-peak in the study of Kolesov and Geiger (2003), whereas a 7 cm\(^{-1}\) difference is observed for pres-

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**Figure 6.** Raman spectra of the middle-frequency region of melanophlogite with increasing temperature up to 1100 °C. Each spectrum was displaced vertically for clarity. Melanophlogite was stable up to 1100 °C.

**Figure 7.** Raman spectrum of a quenched sample of melanophlogite from 600 °C is shown in the top. Each spectrum was displaced vertically for clarity. The split of each of the Fermi resonance peaks and corresponding hot bands is apparent, compared to the sample without the heat treatment (Fig. 1). In-situ high temperature spectra of the sample are also shown. With increasing temperature, intensity ratio of the two split peaks changed.
ent study. Such discrepancy between the present study and that of Kolesov and Geiger (2003) is not well explained at the moment. Their sample contains CH₄ and less CO₂ than our sample, so a CO₂-rich sample should be used to confirm their result. Kolesov and Geiger (2003) interpreted the lower frequency peak as CO₂ in M₁₂ site, opposite to our interpretation. If through less CO₂ than our sample, so a CO₂ degassing. On the other hand, the di ffusion of CO₂ starting at around 450 °C (Figs. 3 and 2) was effective at these temperatures. This is in accord with the present interpretation. When the sample was quenched from 600 °C, the intensity ratio reverted to original state (similar to top spectrum in Fig. 7). This is surprising because the quench speed is high (a few hundred °C/s) for the wire-heater, and the redistribution which requires CO₂ diffusion through five-membered ring from M₁₂ to M₁₄ would not be so fast, considering the degassing behavior already mentioned. Detailed X-ray diffraction study of CO₂-rich melanophlogite is necessary to resolve this issue.

If the split is originated from CO₂ in two M sites, the split provides us additional information on CO₂ diffusion process in melanophlogite. Figure 4 revealed that a high–frequency shoulder of 1380-cm⁻¹ peak developed at around 450–500 °C, therefore CO₂ diffusion becomes effective at these temperatures. This is in accord with the degassing of CO₂ starting at around 450 °C (Figs. 3 and 5), which is also directly related to the diffusion. The M₁₄ sites share six–membered rings and form a channel running along each of the crystallographic axes. However, the M₁₂ sites are isolated one from other and are sharing five–membered rings with M₁₄. Since Kanzaki (1997) has shown that six–membered rings would have lower activation energy for molecular diffusion compared to five–membered rings, the diffusion through the M₁₄ channel would become expressway for long range CO₂ diffusion (degassing). On the other hand, the diffusion from M₁₄ to M₁₂ through five–membered ring would contribute for CO₂ peak split. Therefore, a more detailed study of the CO₂ peak intensity and peak split with temperature would provide us a better understanding of the CO₂ diffusion processes in melanophlogite structure.

**Origin of the low–frequency feature**

Both heat treatment and in–situ study revealed that the intensity of the low–frequency feature can be well correlated with the content of CO₂. Therefore, it is concluded that this low–frequency feature is originated from CO₂ molecules, not from the melanophlogite cage structure itself. Because of higher intensity of this feature compared to CO₂ Raman peaks, this feature could be used as an indicator of trace amount of CO₂ in melanophlogite as evident from Figure 2.

Most plausible explanation for the low–frequency peak is constrained rotational modes of CO₂ molecule in the cages. For free gas state, very sharp and numerous peaks of rotational Raman modes are expected at the low–frequency region (cf. Herzburg, 1945). However, for guest molecules in the cages, the interaction between the molecule and the cage will hinder free rotation, as suggested by Nakagawa et al. (2001). Weak interaction between CO₂ molecules and the cages is supported by lower frequency Raman shifts of observed CO₂ molecule compared to free molecule, as noted before. Such situation will produce librational and translational modes instead. This might be similar to a high–pressure gas where free rotation is interrupted by frequent collisions with other gas molecules. Weiler (1935) observed a broad low–frequency Raman feature for CO₂ gas at 15 and 60 bars, similar to our feature, supporting the present interpretation.

The low–frequency peak corresponds to a low–energy excitation which becomes important contribution to heat capacity at low temperature. A correlation between low–frequency Raman peak (boson peak) and low–temperature heat capacity anomaly is well known for glasses (Sokolov et al., 1993). Geiger et al. (2008) measured the heat capacities of both gas-containing (CH₄, N₂, and CO₂) and gas-free melanophlogite samples. They noted that the difference in heat capacities between gas-containing and gas-free melanophlogite samples rose from 0 to about 70 K, and it reached nearly constant value above 70 K. They suggested that the observed heat capacity behavior is controlled by the lowest energy external librational and translational modes of the CO₂, N₂ and CH₄ molecules. Our observed low–frequency feature is in accord with their interpretation.

In summary, the heat treatment and in–situ high–temperature Raman study of CO₂-containing melanophlogite revealed that the low–frequency feature is likely originated from librational and translation modes of CO₂ in the cages and provided insight of degassing behavior of mel-
anophlogite. The study also demonstrated that Raman spectroscopy is promising tool to investigate guest molecule diffusion in melanophlogite (and other clathrasils).

ACKNOWLEDGMENTS

The author thanks X. Xue (IPM) for critical reading of the manuscript. The author also thanks two reviewers and Dr. K. Momma for constructive comments and suggestions. This study was supported by JSPS KAKENHI Grant Number JP16H04076 and Operational Expense Grant from Okayama University to M.K.

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Manuscript received September 12, 2018
Manuscript accepted March 28, 2019
Published online May 22, 2019
Manuscript handled by Koichi Momma