

High-temperature Raman spectroscopic study of CO₂-containing melanophlogite

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Introduction: Melanophlogite is one of natural silica minerals with a clathrate structure. The structure has two kinds of cages which can host small guest molecules such as CH₄, CO₂, N₂ and H₂S. These are M^{12} and M^{14} cages correspond to pentagondodecahedral [5¹²] and tetrakaidecahedral [5¹²6²] units made of 5- and 6-membered SiO₄ rings, respectively. Previous crystal structural studies suggested that CO₂ is mostly locating in larger M^{14} cage. A few years ago, we found a very intense and broad peak below 100 cm⁻¹ in CO₂-containing melanophlogite. To clarify the origin of this peak in relation with CO₂ guest molecule, heat treatment experiments and in-situ high-temperature Raman spectroscopy measurements were conducted up to 1100 °C.

Experimental: Micro-Raman spectra were obtained using a home-built Raman system made of single-monochromator, CCD detector and Ondax SureBlock filters for low frequency measurement. The heat treatment was conducted using a muffle furnace, and the in-situ study was conducted with a wire-heater cell. Natural spherical single crystals from Fortunillo, Italy were crushed and small fragments were used for the experiments.

Results and discussion (origin of low-freq. peak): For the heat treatment experiments, nearly CO₂-free melanophlogite was obtained at 950 °C for 6 h, judging from intensities of CO₂ vibrational peaks (Fermi diad). Simultaneously, the low-frequency peak nearly disappeared. For shorter time durations or lower treatment temperatures, CO₂ vibrational peaks and low-frequency peak were still visible. We found that CO₂ vibrational peaks of the heat treated samples were split.

For the in-situ study, integrated total intensity of CO₂ vibrational peaks started to drop at around 450 °C, and simultaneously the low-frequency peak intensity decreased. These peaks completely disappeared at 1100 °C, while melanophlogite itself remained intact. Thus, it was concluded that the low-frequency peak is originated from CO₂ molecules, not from melanophlogite structure. Librational and translational modes of CO₂ molecules in the cages of melanophlogite would be responsible for the low-frequency peak. Thus, degassing behavior can be studied by monitoring both the low frequency band and the vibrational peaks.

(vibrational peak splitting): At about 450 °C, we noted that the vibrational CO₂ peak started to split (or more precisely, new peak appeared at slightly higher frequency and grew with temperature while the original peak became weaker). This splitting is partly quenchable, as demonstrated in the heat treated sample mentioned above. Vibrational peak splitting has been reported for CH₄ and H₂S in melanophlogites, and has interpreted as occupancy of those molecules in both M^{14} and M^{12} cages. Thus, peak splitting observed in our study can be interpreted similarly. No splitting of CO₂ has been reported before, except one report at very low temperature. From those observations, we speculated that at above 450 °C, CO₂ molecule is able to migrate from original M^{14} cage to next M^{14} or M^{12} cages. Because M^{14} cages make an infinite chain by sharing 6-membered rings, migration of CO₂ from M^{14} to M^{14} cages through the 6-membered ring will contribute to long-range diffusion (i.e., degassing). On the other hand, migration of CO₂ from M^{14} to next M^{12} through 5-membered ring will contribute to disordered distribution of CO₂ in M^{12} and M^{14} cages, which caused vibrational peak splittings. Thus, high-temperature Raman spectroscopic study could provide us more insight of diffusion behavior of CO₂ and possibly other gas molecules in melanophlogite structure.

Keywords: CO₂-containing melanophlogite, In-situ high-temperature Raman spectroscopy, Low-frequency Raman spectroscopy, clathrasil, degassing process