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Molecules in the SiO_2-clathrate melanophlogite: A single-crystal Raman study

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ABSTRACT

A Raman spectroscopic investigation of the SiO_2-clathrate melanophlogite was undertaken to investigate the enclathrated molecules. The Raman spectra show the presence of N_2, CO_2, and CH_4 molecules based on the observation of their normal stretching modes. An analysis of the spectra, together with single-crystal X-ray results (Gies 1983), demonstrates that the molecules are located in structural cages. Most of the CH_4 is partitioned into the smaller nearly spherical $[5^{12}]$ cage, while CO_2 and N_2 prefer the larger more oblate $[5^{12}6^2]$ cage. The difference in wavenumber for their stretching modes between room temperature and 4 K is minimal. There are also only small differences between the wavenumbers of the modes of the enclathrated molecules and those they possess in the free, gaseous state. The molecules are orientationally disordered in the cavities and they have weak dispersion interactions with the SiO_2 framework. Although the energetic states of the molecules are only slightly modified by being enclathrated, subtle interactions between molecule and framework are necessary to stabilize the clathrate phase. The properties and behavior of single, quasi-free molecules occurring in the cavities of beryl and cordierite are compared to the situation in melanophlogite.

INTRODUCTION

The clathrate group of phases is scientifically important for a variety of reasons. The gas hydrates have recently come under much investigation because of their possible use in CO_2 sequestration and natural gas storage and also as a potential energy resource. Members of the corresponding SiO_2 group are of interest because of their unusual physical properties, including the ability to enclathrate different types of molecules. The mineral melanophlogite is the only known natural SiO_2 clathrate. It was first described by Lasaulx (1876) from Sicilian sulfur deposits. It has now been found in several other localities worldwide in different low-temperature geologic environments, but the exact conditions needed for formation are unclear.

Melanophlogite has a microporous framework structure built up of corner-sharing SiO_4 tetrahedra that form two types of structural cages (Fig. 1a). They are labeled $[5^{12}]$ and $[5^{12}6^2]$, a notation that describes the polyhedra formed by the linkage between Si atoms. Little research has focused directly on the molecules that are located therein. Chemical analysis was the main method used to infer possible species that could be present. Skinner and Appelman (1963), in an early investigation, suggested that H_2O, CO_2, hydrocarbon molecules, and also possibly S-containing compounds were not enclathrated, but were present in organic films trapped on growth faces of crystals taken from the two type localities at Racalmuto and Lercara, Sicily (they also made infrared measurements, but did not present any spectra). Using their X-ray results, Kamb (1965) recognized the isotypic structural relationship between melanophlogite and gas hydrate I and suggested that CO_2 and H_2O occur in structural cages, and speculated that straight-chain hydrocarbons and sulfur compounds could also be present. He proposed further that these molecules are necessary for melanophlogite to crystallize. Cooper and Dunning (1972) suggested that compounds in the systems C + H + O, H + O, and C + O, including aliphatic hydrocarbons, could occur, but the exact molecular species were not quantified for their melanophlogite sample from Mt. Hamilton, California. Their chemical analyses indicated substantial variability in the concentrations of C, H, and O in different crystals. Zak (1972) studied samples from Chvaletice, Bohemia, and suggested molecules in the systems C + H ± S ± O, H + O, C + O, and S ± O ± H. The first direct investigation of the molecular species using mass spectrometry identified CH_4, N_2, and CO_2 in varying amounts in specimens from Mt. Hamilton, Racalmuto, and Fortullino, (Italy) but no sulfur compounds or H_2O (Gies et al. 1982). These workers were also able to synthesize melanophlogite at 170 °C and 150 bar starting with H_2O and $Si(OCH_3)_4$ in the presence of $CH_4 + CO_2 + N_2$.

Single-crystal X-ray refinements of melanophlogite confirm that molecules are located in both cages. Gies (1983) concluded that CH_4 is located in the smaller $[5^{12}]$ cages and CO_2 and most N_2 in the $[5^{12}6^2]$ cages, where they are orientated so as to optimize the interaction of these molecules with the van der Waals forces of the framework. Nakagawa et al. (2001) stated that the CO_2 and CH_4 molecules "move randomly inside the cages" and CO_2 in "almost arbitrary directions." The X-ray results are difficult to interpret with regard to the type, location, and orientation of the enclathrated molecules, however, and they reveal little about their energetic states. Further work is needed to clarify the behavior and properties of the different molecules in melanophlogite.

To do so, we undertook a polarized single-crystal micro-Raman spectroscopic study to address three issues: (1) what are the different molecular species in melanophlogite and where are they located? (2) do they have any preferred orientation? and (3) what are their energetic states and the nature of their

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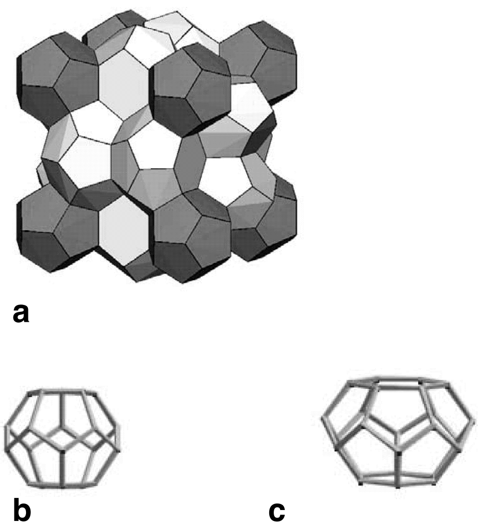

Figure 1. (**a**) Polyhedral drawing of the melanophlogite structure. The darker polyhedra are the smaller $[5^{12}]$ cages and the lighter ones the larger $[5^{12}6^2]$ cages. (**b**) and (**c**) individual $[5^{12}]$ and $[5^{12}6^2]$ cages.

interactions with the SiO_2 framework? Single-crystal micro-Raman spectroscopy is an excellent method for such an investigation, because it can be used to identify different molecules, including homonuclear ones (e.g., N_2), and describe their energetic states. In addition, in situ measurements can be obtained directly from small single crystals.

Experimental methods

The melanophlogite crystals that were investigated are from Mt. Hamilton, California, and were supplied by G. Dunning. Their geological occurrence is discussed in Cooper and Dunning (1972) and Dunning and Cooper (2002), where they describe colorless, gem-like crystals from 0.1 to 5 mm occurring as simple cubes or as multiple intergrowths. Further descriptions of the crystal habit, etc., are found in their works.

Polarized Raman spectra were recorded with a Triplemate SPEX spectrometer (focal length of the spectrograph stage, $f = 0.5$ m, and a grating with 1200 grooves per mm) with a CCD detector, model LN-1340 PB from Princeton Instruments. The laser power was about 2 mW on the sample surface over a spot of 2 micrometers diameter. We used a LD-EPIPlan, 40×/0.60 pol., Zeiss objective at room temperature and a LMPlanFl, 50×/0.50, Olympus objective that has a large working distance for the lower temperature measurements. The 514.5 or 488 nm lines of an Ar laser were used for the spectral excitation. The low- and room-temperature spectra were measured in 180° collection geometry with a Raman microscope. The low-temperature spectra were recorded by fixing the crystal on a cold finger of a helium cryostat "MicrostatHe" from Oxford Instruments. The precision of the measured temperatures is estimated to be ±1 K. All measurements were performed with a spectral resolution of 2 cm^{-1}.

Results

Polarized Raman spectra of melanophlogite at room temperature showing primarily its lattice modes are presented in Figure 2. Room temperature and 4 K spectra between 1250 and 1450 cm^{-1} and between 2200 and 2500 cm^{-1} are shown in Figures 3a and b. The intensities of two modes present in these regions, measured as a function of the crystal rotation, are shown in Figure 4. Figures 5a and b show polarized room temperature and 4 K unpolarized spectra in the wavenumber region from 2700 to 3300 cm^{-1}. The polarized spectra are labeled with a modi-

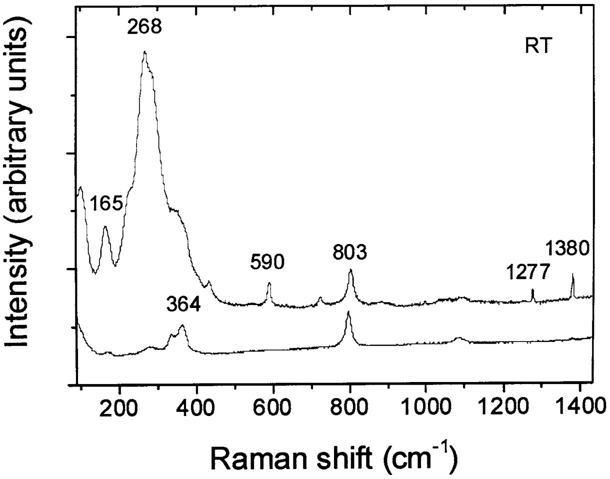

Figure 2. Polarized (XX) (top) and (XY) (bottom) spectra of melanophlogite showing primarily lattice vibrations at room temperature.

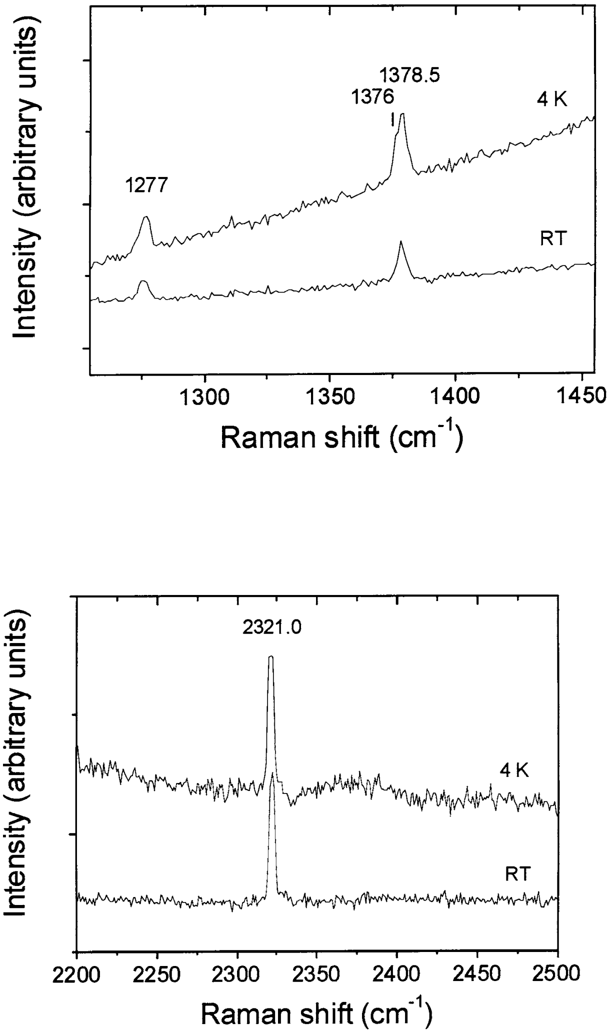

Figure 3. (**a**) Unpolarized Raman spectra between 1250 and 1450 cm^{-1} at 4 K and at room temperature. (**b**) Raman spectra between 2200 and 2500 cm^{-1} at 4 K and at room temperature.

fied Porto's notation, where the first letter in parentheses describes the polarization direction of the incident light and the second letter the direction of the scattered light relative to the crystal axes.

DISCUSSION

Liebau (1988) analyzed the structural systematics of microporous tectosilicate phases to which melanophlogite belongs. He grouped melanophlogite in the porosil class of tectosils. Its framework is built up of corner-sharing (SiO_4) tetrahedra and it has a low density of 1.89 g/cm^3 [or d_f = 19.2, where d_f (density of framework) = $n(SiO_2)$/1000 Å^3; quartz has d_f = 26.6 and stishovite d_f = 43.0 for comparison). Its formula has been given as $46SiO_2{\cdot}2M^{12}{\cdot}6M^{14}$, where M^{12} = CH_4, N_2; M^{14} = CO_2, N_2. It is tetragonal with space group $P4_2/nbc$ at room temperature (Nakagawa et al. 2001) and undergoes a phase transition around 338 K to the cubic phase with space group $Pm3n$ (Gies 1983). Figure 1a shows a polyhedral model of the cubic phase. Each unit cell has two small [5^{12}] pentagondodecahedra and six larger [$5^{12}6^2$] tetrakaidecahedra cages. The notations in brackets describe the cages formed by the Si atoms that are located at the corners of the polyhedra; the O atoms are found between any two Si cations and are near the midpoints of the lines. The polyhedra are formed by ring-like polygons containing n number of Si atoms. The polyhedra are described as [$n_{\rm i}^{m_{\rm i}}$], where $m_{\rm i}$ is the number of rings that have $n_{\rm i}$ corners, that is Si atoms (see Liebau 1988 for further discussion). The [5^{12}] cage (Fig. 1b) of topologic symmetry $m3$ is approximately spherical with a free-space diameter of about 5.7 Å and has a volume of about 97 Å^3, while the free space of the [$5^{12}6^2$] cage (Fig. 1c) with $\bar{4}2m$ symmetry can be described as an ellipsoid with d_1 ~ d_2 ~ 5.8 and d_3 ~ 7.7 Å with a volume of about 136 Å^3 (Gies 1983). He determined a population density of 90% CH_4 in [5^{12}] and 59% N_2 and 17% CO_2 in [$5^{12}6^2$] in his study of a crystal from Mt. Hamilton. Liebau (1988) pointed out that if the symmetry of a guest molecule is lower than that of the cage, the molecule should be orientationally disordered. Gies (1983) investigated the molecular orientations from single-crystal X-ray data and concluded that disorder is present, but such that the van der Waals contacts between the molecule and the SiO_2 framework are optimized. He interpreted the observed electron densities in the cages, measured from difference Fourier maps, as follows: in the [5^{12}] cage the tetrahedral CH_4 molecules are not randomly disordered, but the C atoms are located at 24 different sites slightly displaced from the special position at the cage center, with 12 surrounding sites corresponding to a superposition of eight split hydrogen positions. In the [$5^{12}6^2$] cage 12 different CO_2 orientations were observed such that the molecules are located at the midpoints between the pentagon faces and the cage center with, once again, the C atom slightly displaced. N_2 is orientated such that one atom is located approximately at the cage center, while the second can occupy 12 different surrounding positions. It is thought that only one molecule can occur in each cage in melanophlogite, but in the case of the N_2-clathrate hydrate the larger cages can be doubly occupied (Kuhs et al. 1997). There is some question as to whether the different molecules are slightly distorted from the ideal geometries that they have in the gas phase.

Low-wavenumber lattice modes of melanophlogite deriving largely from the SiO_2-framework are shown in Figure 2,

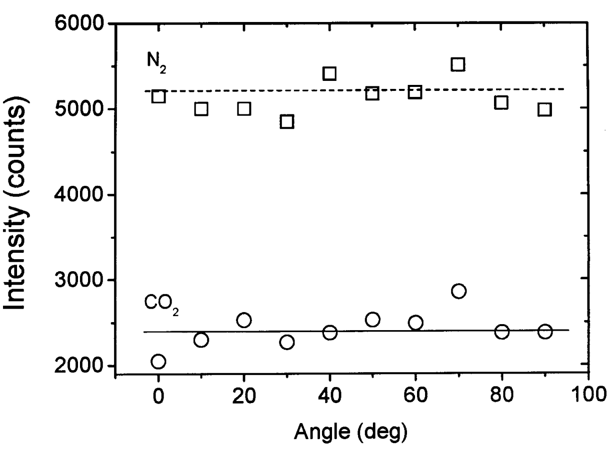

FIGURE 4. Intensities of the N_2 and CO_2 stretching modes upon rotating the crystal from the **x** axis to the **y** axis relative to the polarization direction of the laser beam.

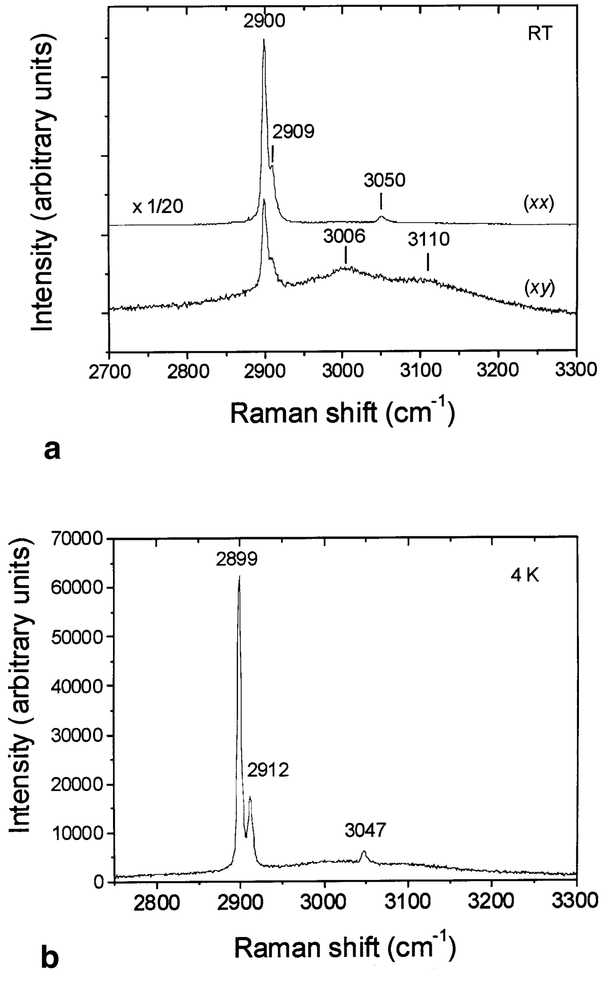

FIGURE 5. (**a**) Polarized (XY) and (XX) Raman spectra between 2700 and 3300 cm^{-1} at room temperature. (**b**) Unpolarized Raman spectrum between 2800 and 3300 cm^{-1} at 4 K.

but they will not be analyzed in this work. The spectrum above 1200 cm^{-1} contains the normal modes of the different molecular species and it is straightforward to interpret with respect to their identification. The spectrum of melanophlogite shows the presence of CO_2, N_2, and CH_4, but no H_2O or S-compound modes are observed, in agreement with the mass spectrometric results (Gies et al. 1982). Figure 3 shows spectra at 4 K and room temperature in the wavenumber region containing the stretching vibrations of CO_2 and N_2. Two CO_2 modes at 1277 and 1378 cm^{-1} are observed at room temperature. The latter is the symmetric ν_1 stretch, while the former is the first overtone of the ν_2-bending mode. Both are components of a vibrational system coupled via Fermi resonance. The symmetric band at 1378 cm^{-1} develops a shoulder at 1376 cm^{-1} at 4 K. Enclathrating a molecule lowers slightly the vibrational energy of the normal modes. The smaller the cage size, the greater the dispersive interaction with the surrounding crystal and the lower the vibrational energy of the entrapped molecule. Therefore, the lower wavenumber band is assigned to CO_2 in the $[5^{12}]$ cage, while the higher wavenumber band is assigned to CO_2 in the larger $[5^{12}6^2]$ cage. The area ratio of the two bands is approximately 1:6, and assuming that the Raman scattering cross-sections for CO_2 in both cages are the same, we conclude that about 85% of the CO_2 molecules occupy the larger cages and 15% the smaller ones. The symmetric stretch vibration for N_2 is located at 2321 cm^{-1} at both temperatures, and the band is not split (i.e., the molecule occupies only one type of cage). According to Gies (1983), N_2 is located mainly in the larger $[5^{12}6^2]$ cage. The differences in wavenumber for all modes between room temperature and 4 K are very small (i.e., 1–2 cm^{-1} and thus within the error of the spectrometer calibration). Moreover, the mode wavenumbers for the enclathrated molecules exhibit only small differences from those in the free state (i.e., gas). For CO_2 the degenerate ν_2 bending modes are observed at 667.3 cm^{-1}, the first overtone at 1285.5, and the symmetric ν_1 stretch at 1388.3 cm^{-1} (Herzberg 1991). The stretching vibration for N_2 is located at 2330.7 cm^{-1} (Herzberg 1989). The small energy differences between free and enclathrated molecules are due to very weak dispersion (van der Waals) interactions occurring with the framework. The cages are larger than the length of CO_2 (O···O distance of 2.310 Å, whereas the C-O distance is 1.155 Å in solid CO_2; Simon and Peters 1980) and N_2 (intramolecular distance of 1.05 or 1.15 Å, when corrected for thermal motion in α-nitrogen, vs. 1.0976 Å in the gaseous state; La Placa and Hamilton 1972) molecules and, therefore, the interactions do not change as the framework contracts upon cooling. Both molecules are linear and it is possible to determine their orientations. Figure 4 shows the intensity of the N_2 and CO_2 stretching modes about every 10° upon rotation of the crystal from the **x** axis to the **y** axis relative to the direction of the polarized incident light. Measurements from the **x** axis to the **z** axis give similar results. We conclude that there is no preferred molecular orientation that can be detected from our Raman measurements.

Figures 5a and 5b show polarized Raman spectra in the region of the CH_4 stretching vibrations at room temperature and 4 K, respectively. The different normal modes of a free CH_4 molecule are illustrated in Figure 6. The (XX)-spectrum, showing symmetric vibrations, contains three bands at room temperature. The band at 3050 cm^{-1} is assigned to the first overtone of the doubly degenerate ν_2-bending mode, which in a gas is located at 1523.8 cm^{-1} (Herzberg 1991). The bands at 2900 and 2909 cm^{-1} are assigned to the A_1 ν_1-stretching modes of CH_4 located in the $[5^{12}]$ and $[5^{12}6^2]$ cages, respectively. Here, the partitioning behavior between cages is opposite as in the case of CO_2, and roughly 80% of CH_4 occupies the small $[5^{12}]$ cages and 20% the larger $[5^{12}6^2]$ cages. We note that our mode assignments for CO_2 and CH_4 to the two different cages in melanophlogite are opposite to those proposed for gas hydrate I (Subramanian and Sloan 2002). For the different gas hydrate phases, they advanced the hypothesis of "the larger the cavity, the lower the frequency" for a given molecular vibration. In other words, for CH_4, for example, they assign the higher wavenumber stretching mode to the smaller $[5^{12}]$ cage and the lower wavenumber mode to the larger $[5^{12}6^2]$ cage. However, if one accepts the X-ray results of Gies (1983) and Nakagawa et al. (2001) that place CH_4 in the $[5^{12}]$ cage, our mode assignments should be correct. The (XY)-spectrum exhibits two (or more) broad bands that are assigned to combination bands consisting of CH_4-stretching and CH_4-libration-translation modes. Once again, the wavenumber difference between the normal modes of a free and an enclathrated CH_4 molecule (ν_1 = 2914.2 cm^{-1} in a gas; Herzberg 1991) and also between room temperature and 4 K is small. A summary of the energetic states of the different observed modes for all three molecules in the free state and in melanophlogite is given in Table 1.

COMPARISON TO BERYL AND CORDIERITE

The nature of the enclathrated molecules in melanophlogite can be compared to the situation in beryl and cordierite. These phases are also classified as tectosilicates and can be considered microporous, but they are structurally different from melanophlogite. In melanophlogite the SiO_2 framework is electroneutral, while in beryl and cordierite octahedral cations (Al^{3+} and Mg/Fe^{2+}, respectively) are required to charge balance the framework which consists of corner-sharing $(Si/Al/Be)O_4$ tetrahedra. Thus, in this aspect, they tend to have more struc-

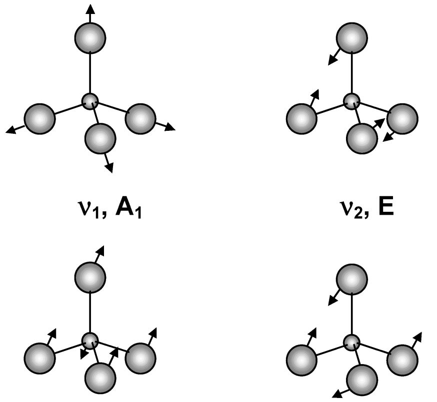

FIGURE 6. Normal vibrations of a free CH_4 molecule of tetrahedral T_d symmetry. Their wavenumbers are: ν_1 = 2914.2 cm^{-1}, ν_2 = 1523.8 cm^{-1}, ν_3 = 3020.3 cm^{-1}, and ν_4 = 1306.2 cm^{-1} (Herzberg 1991).

TABLE 1. Wavenumbers of Raman (IR)-active modes for different molecules in the free state and those measured in melanophlogite at room temperature; the wavenumbers for molecules in cordierite and beryl are also given for comparison

Phase/Molecule	CO_2 $\nu_{2(020)}$ and ν_1	N_2	CH_4 ν_1/(ν_3)
Gas*	1285.5 and 1388.3 cm^{-1}	2330.7 cm^{-1}	2914.2 cm^{-1}/(3020.3 cm^{-1})
Melanophlogite [5^{12}]	1277 and 1378 cm^{-1}	2321 cm^{-1} (?)	2900 cm^{-1}
Melanophlogite [$5^{12}6^2$]	1277 and 1378 cm^{-1}	2321 cm^{-1}	2909 cm^{-1}
Cordierite	1272 and 1383 cm^{-1}†	2324 cm^{-1}‡	(3014–3018 cm^{-1}) §
Beryl	1241 and 1387 cm^{-1}#	–	–

* Herzberg (1989, 1991).
† Kolesov and Geiger (2000b).
‡ Armbruster, pers. comm.
§ Bulbak et al. (2002).
\# Charoy et al. (1996).

tural similarity to the zeolite class of phases, because zeolites also contain extra framework cations. Both beryl and cordierite can contain nearly free N_2, CO_2, and H_2O molecules in small microcavities with a free diameter of less than 6 Å (Armbruster 1985; Kolesov and Geiger 2000a; Kolesov and Geiger 2000b). The cavities are part of infinite structural channels that run in one direction through their frameworks. The molecules are not enclathrated in a strict sense and can diffuse out of the channels, but are hindered by narrow "bottlenecks" with a free diameter of 2.6 Å made of six-membered rings of corner-sharing $Si(Al)O_4$ tetrahedra (Armbruster 1985). For cordierite and beryl, both CO_2 and N_2 molecules have a single orientation parallel to the crystallographic **x** axis (Armbruster 1985; Charoy et al. 1996; Kolesov and Geiger 2000b). It is uncertain as to whether significant amounts of CH_4 can be absorbed in the cavities (Bulbak et al. 2002). The mode energies for these molecules in both cordierite and beryl are given in Table 1. Unlike melanophlogite, the polar H_2O molecule can be incorporated in both phases and in significant concentrations. It is dynamically disordered by having an anisotropic intracavity motion. Zeolites, of course, also contain H_2O molecules, but they have hydrogen bonding of various degrees and the molecules are therefore not free. The incorporation of the polar H_2O molecule in microporous silicates may be related to the nature of the electronic charge distribution within the silicate framework, whereby in the case of electroneutral frameworks its incorporation is energetically unfavorable.

Beryl and cordierite are further unlike melanophlogite, because molecule-free crystals can be synthesized. The growth of melanophlogite crystals requires a minimum concentration of molecules in solution (Kamb 1965; Gies et al. 1982). In the laboratory melanophlogite has been shown to be unstable under pure hydrothermal conditions between 300 and 500 °C at 2.0 kbar and in the absence of molecular species it inverts to quartz (some natural crystals are found pseudomorphed to quartz; Dunning and Cooper 2002). Under dry conditions it remains metastable up to 800 °C, although molecules are lost at the higher temperatures (Skinner and Appelman 1963; Gies et al. 1982). It is concluded that although the energetic states of the different molecules are only slightly modified by being enclathrated, subtle interactions between molecule and framework are necessary to stabilize the clathrate phase.

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