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$^1262$] 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$^1262$], 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$_2$O, 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$_2$O 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 Tortullino, (Italy) but no sulfur compounds or H$_2$O (Gies et al. 1982). These workers were also able to synthesize melanophlogite at 170 °C and 150 bar starting with H$_2$O 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$^1262$] 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 interaction with the SiO$_2$ framework? To do this, 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 interaction with the SiO$_2$ framework?