Gas Hydrates

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Single Crystals of Naturally Occurring Gas Hydrates: The Structures of Methane and Mixed Hydrocarbon Hydrates

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Natural gas hydrates are clathrate inclusion compounds of water and hydrocarbons plus small amounts of other gases, such as CO_2 or H_2S,[1] with the guest molecules trapped in individual cages in the hydrate crystal lattices. Their role in the geosphere is still under investigation, with potential impact on the global energy supply, geohazards, and global climate change.[2] Three structural families are known, sI, sII, and sH, with the structure determined mainly by the largest guest molecules present.[3] All three have been identified as occurring naturally.[4] The detailed physical properties of hydrates have been studied for some time. However, in many instances recourse is taken to synthetic hydrates prepared in the laboratory.[5,6] Considerable difficulties arise in understanding a variety of relationships amongst structure, composition, and lattice parameters because of the nonstoichiometric nature of hydrates, problems in synthesizing "pure" hydrates, and the difficulty in obtaining and handling single-crystals of hydrates. It is becoming clear that hydrates should be seen as minerals. That is, their structure, composition and physical and chemical properties very much reflect the conditions under which they are formed in nature and the conditions to which they have been exposed after formation. It is still a moot point as to how characteristic synthetic hydrates are of natural hydrates, especially regarding their morphology and physical properties.

Herein, we report structures based on single-crystal diffraction data of hydrate samples recovered from the Cascadia margin.[7,8] In both cases, the work reported represents the first single-crystal diffraction analyses of recovered natural methane and higher hydrocarbon hydrates. As this work points out both the advantages and limitations of such studies, it should serve as a benchmark for a variety of other studies on clathrate hydrates as well as provide lattice parameters that most closely reflect natural gas hydrates.

The hydrates for which structures are reported were both recovered from the Cascadia Margin, off the shore of Vancouver Island. One sample is associated with a cold seep (A in Figure 1), at Integrated Ocean Drilling Program (IODP) Site U1328. The gas is of biogenic origin, and a variety of its properties have been reported recently.[4] The second (B in Figure 1) is associated with an oil seep in Barkley canyon, and the gas is of thermogenic origin.[4] Gases of biogenic and thermogenic origins generally are of different composition, biogenic gas being predominantly methane and thermogenic gas generally containing hydrocarbons with two or more carbon atoms in concentrations greater than 1%. Hydrates formed from biogenic gas are almost exclusively sI, whereas hydrates formed from thermogenic gas can be quite diverse structurally with the possibility of all three common hydrate families, sI, sII, and sH, occurring. After recovery, both sets of samples were stored in liquid nitrogen and were transported to the laboratory in cold, dry-shippable containers. It was a great challenge to find a hydrate single crystal of sufficient quality for this work. Sometimes several tens of crystals were selected and screened. The crystal on which qualitative data were obtained was found in association with massive gas hydrate that had not experienced dissociation.

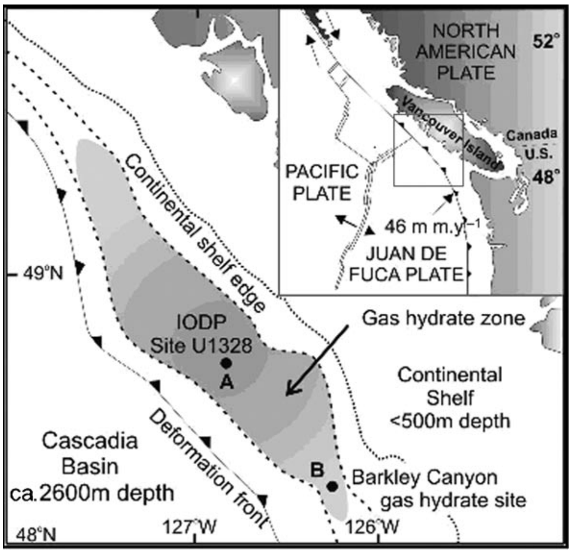

Figure 1. The locations of the studied samples (A, associated with a cold vent; B, associated with an oil seep); m m.y.$^{-1}$ refers to the moving rate of the Juan de Fuca plate in meters per thousand years.

Natural methane hydrate was found to be in the form of cubic structure I (Figure 2, space group $Pm\bar{3}n$, $a = 11.857(1)$ Å). Cubic structure I ($6T{\cdot}2D{\cdot}46H_2O$, where T are the tetrakaidecahedra and D the pentagonal dodecahedra)

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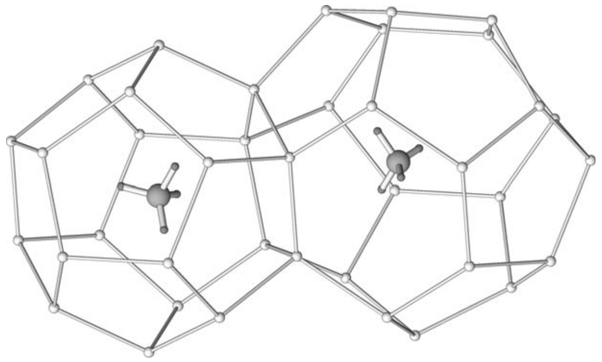

Figure 2. Structure of natural methane hydrate (only two connected D and T cages are shown).

consists of columns of tetrakaidecahedra parallel to cube edges. Formed by pairs connected through hexagonal rings, the tetrakaidecahedral columns are closely packed, and the rest of the space is occupied by pentagonal dodecahedra. The latter are oriented in a pseudo-body-centered fashion where a central pentagonal dodecahedron is turned by 90° corresponding to pentagonal dodecahedra at the corners of the unit cell.

The natural hydrate of methane, ethane, and propane was found to be cubic structure II (Figure 3, space group $Fd\bar{3}m$, $a = 17.141(1)$ Å). Cubic structure II ($8\,H\cdot 16\,D\cdot 136\,H_2O$, where the H are hexakaidecahedra) is built of layers of pentagonal dodecahedral cages which alternate with layers built of hexakaidecahedral and pentagonal dodecahedral cages. These layers are stacked in an ABC manner in the [111] direction. The unit cell of this structure can be considered as diamond-like, where carbon atoms are substituted by centers of the hexakaidecahedra.

In all cases the large cages of both cubic structures I and II are found to be 100 % occupied with guest molecules. In the case of the mixed hydrate of methane, ethane, and propane, 100 % occupancy of the large cage was assumed in order to calculate partial occupancies for ethane and propane. It was found that ethane occupied 77.6 % of the large cages and propane 22.4 %. Methane fully occupies the small cages. In the case of natural methane hydrate, the small cages are 89.8 % occupied with methane; the rest of the small cages are vacant. All cages consist of nearly planar, hydrogen-bonded hexagonal and pentagonal faces.

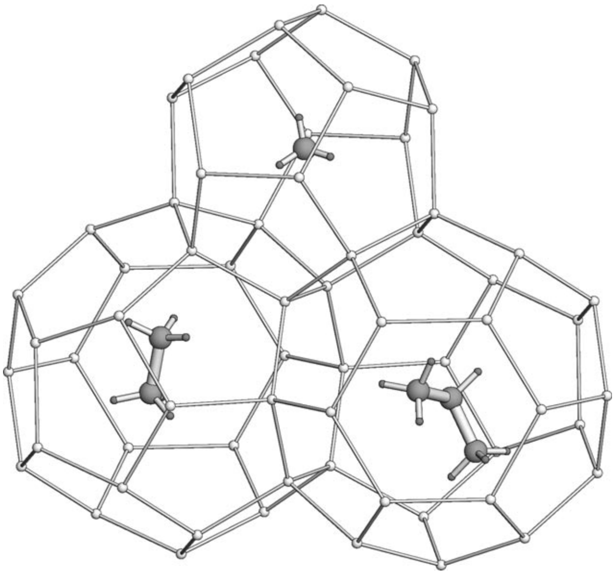

Figure 3. Structure of natural hydrate structure II (only three connected D and H cages are shown).

The maximum deviation from the plane is 0.161 Å observed for the pentagonal faces common to two large cages of cubic structure I methane hydrate (0.071 Å for pentagonal faces of the small cage). The deviation from the plane for the hexagonal face in structure II is 0.058 and 0.012 for the pentagonal faces common to the large and small cages of cubic structure II. The hexagonal face in cubic structure I and pentagonal faces common to the two small cages of structure II hydrate are planar within experimental error.

In all cases, guest molecules lie off the geometrical center of the cage and form van der Waals contacts with water molecules. The propane guest positions are very close to those found for a synthetic propane hydrate. Deviations between the positions in the two crystals are less than 0.59 Å. Only two of the carbon atom positions we found in the natural hydrate are close to those reported by Kirchner et al.,[6] where the propane molecule with a C–C bond length of 1.33 A and a C-C-C angle of 148° was constrained to lie in a special position (Figure 4). The position of the C3 atom (the leftmost atom of the guest molecule in Figure 4) is 0.98 Å away from the one we determined for natural hydrate and 1.48 Å away from the C3 position of synthetic propane hydrate. As for methane in the small cage of structure II found by Kirchner et al., it is difficult to build a tetrahedral molecule from the hydrogen atoms around the carbon atom. The hydrogen positions reported in fact form a hexagonal prism around the carbon atom with two additional hydrogen atoms in special positions at the top and bottom of prism. Probably, the authors were not able to move the guest molecules out of special positions because of an incomplete data set.

We note that for the structures reported by Kirchner et al., although they give a good idea of the hydrate structures, the guest positions and cage occupancies are not well described, and the quality of the structures is not nearly

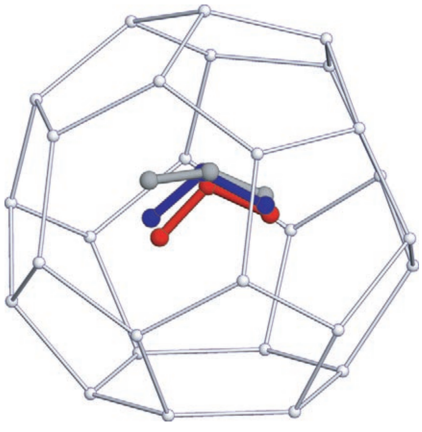

Figure 4. Propane positions found in natural hydrate (blue) synthetic propane hydrate (red) and synthetic propane hydrate (grey) reported by Kirchner et al.[6]

as good as that reported herein. Thus the oligocrystallographic approach[5] has considerable limitations as far as structural details are concerned. The pure natural methane hydrate and the synthetic propane hydrate structures are of unprecedented quality, the residuals (R_1) being less than 0.7 %. For the natural sII hydrate, the structure is not as good as that for natural sI hydrate, with an R_1 value around 4 %. The probable reason for this situation is the presence of mixed sets of guest molecules. We note that the bulk hydrate sample also contained isobutane and butane,[3] which are both large cage occupants in sII hydrate, and that the large cage also contained methane. Thus, the unresolved contributions of these three additional guests may well lead to the larger residual.

Experimental Section

The initial pressure and temperature conditions for the recovered hydrate samples can be estimated as follows: because both samples were recovered either from the seafloor or from sediment at a shallow depth below the seafloor, the pressure–temperature (P–T) conditions of the seafloor can be applied. For the cold vent-field hydrate $T \approx 3.0\,°\mathrm{C}$, $P \approx 12.6$ MPa; for hydrate associated with oil seepage $T \approx 3.2\,°\mathrm{C}$, $P \approx 8.6$ MPa. Recovered core samples, or massive hydrate, were handled in liquid nitrogen. The core samples were split open, also revealing sections of massive hydrate. Single crystals of natural hydrate samples were selected and mounted on a plastic holder under the microscope in a dry, cold atmosphere and than placed on a goniometer head. During these manipulations, the sample temperature never was higher than −80 °C.

Propane hydrate was synthesized in a sealed tube from a mixture of propane and degassed water in molar ratio of 1:12 (excess propane). The mixture was cooled down until formation of solid and then warmed up to melt about 50 % of the crystals, and this procedure was repeated several times. The tube was then left at −40 °C for six months. Hydrate crystals of appropriate size grew on the walls of the tube, and were handled the same way as the crystals of recovered natural hydrate.

The X-ray diffraction data were collected with $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $2\theta_{\max} = 57.5°$, ω scan mode) on a Bruker SMART CCD diffractometer at 125 K. The structure was solved by direct methods using the SHELXTL suite of programs.[9] The composition of the gas in the hydrate structure and the fractional occupancies of molecules in each cavity were found from the experimental X-ray data refinement. The experimentally obtained large cage occupancy for structure I hydrate was found to be close to 100 % (depending on isotropic thermal parameters it was (100 ± 2) %). For structure II hydrate it was assumed that the large cage site occupancy was 100 %, consistent with previous knowledge. After that, refinement of site occupancies for ethane and propane molecules was made based on the experimentally determined electron density in the large cage. The site occupancy of methane in the small cages was found from structure refinement with isotropic and anisotropic thermal parameters.

All non-hydrogen atoms and hydrogen atoms on water and methane were found from the electron density map. Hydrogen atoms on ethane and propane were placed in calculated positions and allowed to ride on the parent atoms. To resolve disorder in the large cage of structure II hydrate, all peaks which appeared in special positions at the beginning of the refinement were assigned to carbon atoms. The structure was refined with fixed isotropic thermal parameter to 0.05 and variable site occupancies allowing carbon atom to be out of special positions. After the restriction on the carbon atoms was removed, we found the propane molecule with a geometry that was close to expected. Bond lengths and angles in the propane molecule were fixed at this stage and the refinement was continued. Then the two strongest peaks in the large cage were assigned to ethane. Refinement was continued with fixed thermal parameters for ethane and variable site occupancy (with the assumption that the large cage should be 100 % filled). After the site occupancy was determined, refinement was continued with anisotropic thermal parameters. No restraints were applied to methane in the small cage of structure II. For structure I hydrate, only soft restraints (same C−H and H−H distances) were applied for the methane molecules.

Natural methane hydrate ($\mathrm{CH_4 \cdot 5.90\,H_2O}$): cubic, space group $Pm\bar{3}n$, $a = 11.857(1)$ Å, $V = 1666.8(2)$ Å^3, $\rho_{\mathrm{calcd}} = 0.950\ \mathrm{Mg\,m^{-3}}$, crystal size $0.5 \times 0.5 \times 0.45\ \mathrm{mm}^3$, $T = 125$ K, $Z = 2$, GOF on $F^2 = 1.28$. Final R indexes ($I > 2\sigma(I)$): $R_1 = 0.0068$, $wR_2 = 0.0155$ (18760 total reflections, 454 unique, 79 parameters).

Natural hydrate of methane, ethane, and propane ($\mathrm{2\,CH_4 \cdot 0.776\,C_2H_6 \cdot 0.224\,C_3H_8 \cdot 17\,H_2O}$): cubic, space group $Fd\bar{3}m$, $a = 17.141(1)$ Å, $V = 5036.2(5)$ Å^3, $\rho_{\mathrm{calcd}} = 1.071\ \mathrm{Mg\,m^{-3}}$, crystal size $0.5 \times 0.3 \times 0.25\ \mathrm{mm}^3$, $T = 125$ K, $Z = 8$, GOF on $F^2 = 1.20$. Final R indexes ($\mathrm{I} > 2\sigma(I)$): $R_1 = 0.0396$, $wR_2 = 0.1180$ (14610 total reflections, 382 unique, 88 parameters).

Synthetic propane hydrate ($\mathrm{C_3H_8 \cdot 17\,H_2O}$): cubic, space group $Fd\bar{3}m$, $a = 17.166(1)$ Å, $V = 5058.3(6)$ Å^3, $\rho_{\mathrm{calcd}} = 0.920\ \mathrm{Mg\,m^{-3}}$, crystal size $0.5 \times 0.5 \times 0.45\ \mathrm{mm}^3$, $T = 173$ K, $Z = 8$, GOF on $F^2 = 1.125$. Final R indexes ($I > 2\sigma(I)$): $R_1 = 0.0134$, $wR_2 = 0.0352$ (4787 total reflections, 356 unique, 57 parameters).

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