Storage and handling of natural gas hydrate

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Abstract: Gas hydrate samples that are recovered from natural deposits usually need to be preserved for subsequent analysis in a laboratory setting remote from the recovery site. The preservation of integrity of the gas hydrate and the quality of the subsequent sample analysis will depend on the details of sample storage and handling. Previously, massive gas hydrate samples, both natural and synthetic, have been stored in liquid nitrogen without apparent ill effects. We propose this method also for sediment-rich natural samples that are recovered for the analysis of fundamental gas hydrate properties; liquid nitrogen storage is safe and convenient as long as some care is taken with the detailed handling procedure. This is rationalized in terms of the current state of knowledge of the dynamics and reactivity of gas hydrate and ice.

Résumé : Les échantillons d'hydrates de gaz récupérés dans les dépôts naturels doivent généralement être conservés pour être analysés ultérieurement dans un laboratoire éloigné de leur site de prélèvement. La conservation de l'intégrité de ces échantillons et la qualité de l'analyse dépendront de la méticulosité avec laquelle les échantillons auront été transportés et manipulés. Dans le passé, les échantillons d'hydrates de gaz massifs, naturels ou de synthèse, étaient conservés dans de l'azote liquide, apparemment sans conséquence désastreuse. Nous proposons l'utilisation du même procédé pour conserver les échantillons naturels riches en sédiments récupérés en vue de l'analyse des propriétés fondamentales des hydrates de gaz; l'azote liquide est un produit sûr et pratique dans la mesure où il est manipulé avec précaution et minutie. Cette méthode de conservation dans de l'azote liquide est valable dans l'état actuel des connaissances sur la dynamique et la réactivité des hydrates de gaz et de la glace.

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SCOPE OF PAPER

This paper examines some of the methods used for the storage of recovered natural gas hydrate samples, and, in light of the current state of knowledge, suggests that storage in liquid nitrogen is the best option for preserving the gas hydrate. For subsequent quantitative analysis by physico-chemical methods, a simple procedure needs to be followed in order to remove adsorbed gases upon removal of gas hydrate samples from liquid nitrogen.

INTRODUCTION

As the recovery of natural gas hydrate samples from terrestrial and marine sources becomes more common, it is worth revisiting the various techniques used for sample storage. These include storage of gas hydrate in pressure vessels at various subambient temperatures either under autogenous pressure or under the pressure of a gas used to back-fill the void space over the sample, and storage in liquid nitrogen. There has not been a serious analysis of the various storage options, although it is easy to see why some methods are inherently unsatisfactory. Storage in a pressure vessel at any temperature where gas hydrate decomposition occurs at a reasonable rate will cause the gas hydrate to decompose to the extent that the pressure of the guest gases reach the equilibrium decomposition pressure of the gas hydrate. This is a reasonable option if the dead space over the sample is minimal and the sample has a high gas hydrate content. Decomposition is not prevented by the filling of the dead space over the sample by a 'neutral' gas such as helium, as the gas hydrate will still decompose until the partial pressure of the guest gas is equal to the decomposition pressure. Back-filling the pressure vessel with a gas that is able to occupy guest sites in the hydrate will lead to the incorporation of this gas into the hydrate, as the gas hydrate and gas re-equilibrate. Unless the gas used for back-filling has exactly the same composition as the gas already in the hydrate, the composition (and properties) will be changed. Our companion paper illustrates that the gas hydrate from the Mallik site is quite heterogeneous, with considerable local variability in composition (Tulk et al., 1999), so that any storage options where hydrate reformation reactions can take place are inherently unsatisfactory.

Storage of synthetic gas hydrate samples in liquid nitrogen has been the usual practice in the National Research Council (NRC) laboratories since the 1960s, and natural gas hydrate from the Blake Ridge, samples from offshore Guatemala, and from the Gulf of Mexico have been stored and transported in liquid nitrogen also. Because the technique is relatively simple and undemanding in terms of equipment, we examine it from the point of view of the available information on the reactivity of ice and gas hydrate at low temperatures. Although knowledge is still incomplete, we propose a storage and handling protocol that should be generally suitable for most recovered natural gas hydrate if the aim is to preserve the hydrate for analysis of structure, composition, and pressure-temperature (P-T) characteristics.

DYNAMICS OF WATER MOLECULES IN ICE AND HYDRATE FRAMEWORKS

The stability of ice and hydrate at 77 K ultimately depends on the rate that recrystallization or other transformations can take place, which in turn depends on the dynamics of the constituent water molecules.

The dominant structural feature of ice and hydrate frameworks is that they consist of hydrogen-bonded networks where each water molecule has four nearest neighbours. Ice Ih, ice Ic, other ices, and hydrates of Structure I, II and H also share the fact that the hydrogen atoms are disordered so that each bond can be denoted either as O-H- -O or O- -H-O. In pure ices and most hydrates, this disorder is frozen in to very low temperatures. The dynamics of water molecules can be probed directly by techniques such as calorimetry (Yamamuro and Suga, 1989), dielectric relaxation, nuclear magnetic resonance (NMR) spectroscopy, and vibrational spectroscopy (Davidson,1974).

Two fundamental dynamic processes that have been identified in ice networks are reorientation and diffusion (Onsager and Runnels, 1969). The first process is dielectrically active (Auty and Cole, 1952), the second is not; both can be followed by NMR spectroscopy (Davidson and Ripmeester, 1978). Activation energies for reorientation and diffusion in Ice Ih are 55.2 kJ/m and 58.1 kJ/m, respectively. The mechanism for these processes generally is thought to follow a defect mechanism. For reorientation, the Bjerrum defects have been proposed (Bjerrum,1952). These come in D and L forms, the D defect being a doubly occupied H bond, the L form an empty H bond. As the defects migrate through the H-bonded network, the water molecules are left in a different orientation. Centre-of-mass diffusion is thought to occur via a different defect mechanism. The activation energies are therefore associated with the ease of defect formation. The activation energies reported can be considered to be for intrinsic defects, so that at 77 K the associated dynamic processes will be extremely slow in a 'pure' ice lattice.

The processes that occur in ice also have been observed in hydrate (Davidson, 1974; Garg et al., 1974; Ripmeester, 1976), with similar kinds of defect mechanisms proposed. The added feature of the hydrate, of course, is the guest molecule. One pronounced effect attributed to the guest molecule has been the observation of an increased rate of water reorientation that depends on the nature of the guest molecule (Davidson, 1974; Davidson and Ripmeester, 1984). The fastest processes have been observed for guest molecules containing oxygen atoms with activation energies ~27–36 kJ/m much less than for ice Ih (Davidson, 1974; Davidson and Ripmeester, 1984). This is attributed to the formation of transient H bonds of the guest molecule with the host, thus injecting Bjerrum defects into the lattice. Calorimetric measurements on hydrate with oxygen-containing guest molecules also show glass transition behaviour at ~80 K as evidence of the freezing in of water motions (Yamamuro and Suga, 1989). For guest molecules that do not contain oxygen, the polar nature of the guest molecule is still expected to have

an effect. Gas hydrate with non-polar guest molecules is the least different from pure ice as far as water dynamics is concerned. Activation energies for centre-of-mass diffusion appear to be much less sensitive to the nature of the guest molecule (Davidson and Ripmeester, 1978).

Ice and gas hydrate structures that are doped with impurities such as KOH also are known to have shortened relaxation times because of the presence of defects that enhance the mobility of water molecules. Some doped ice and gas hydrate structures are known to order even at very low temperatures (Tajima et al., 1982; Oguni et al, 1987).

REACTIVITY OF GAS HYDRATE AT LOW TEMPERATURES

The mobility of water molecules in gas hydrate and ice structures should have a direct bearing on the 'reactivity' of such materials. The most reactive pure ices are probably the amorphous ices. These are indefinitely stable at 77 K (actually metastable, but essentially stable because of slow kinetics) and transform via a glass transition at ~135 K and recrystallize to cubic Ice Ic at ~150 K. Amorphous ices can be produced by a number of methods, including the low-temperature vapour deposition of pure water (Burton and Oliver, 1935) (or water together with other vapours), or by hyperquenching pure water (Bruggeler and Maier, 1980) (or aqueous solutions (Tulk et al., in press)). Features of such amorphous phases include significant numbers of 'dangling' hydrogen bonds (Devlin and Buch, 1997) in addition to the H-bonded networks. Much has been learned about the reactivity of water networks by following the crystallization of these metastable phases by calorimetry, diffraction, vibrational spectroscopy, and NMR spectroscopy (Sceats and Rice,1982; Hallbrucker et al., 1989a, b; Fleyfel and Devlin, 1991; Fisher and Devlin, 1995; Johari et al., 1996; Hernandez et al., 1998). Amorphous codeposits of non-polar guest molecules (O_2, Xe) and water do not recrystallize below the temperatures observed for pure amorphous ices either (Maier and Hallbrucker, 1989; Ripmeester et al., 1994). On the other hand, guest molecules such as ethers and thin films of ice are known to transform at lower temperatures (Richardson et al., 1985). Also, codeposits of water and methanol transform at temperatures as low as ~115 K to give various crystalline phases depending on the exact composition (Nakayama et al., 1997). Metastable phases of tetrahydrofuran (THF) and water (Zakrzewski et al., 1994), and codeposits of water and formaldehyde (Ripmeester et al., 1996), are known to crystallize at significant rates, even at 77 K over a period of some months. It is likely that the presence of molecules that are able to inject Bjerrum defects is the main factor in the conversion of these unstable phases even at very low temperatures.

Based on these observations, we can conclude that when gas hydrate is at the stable phase at 77 K it is quite unlikely to transform, and this will be especially true for hydrocarbon hydrate. For pore gas hydrate the situation is more complex. The limited amount of data available suggests that gas hydrate in pores is less stable than bulk gas hydrate (Handa and Stupin, 1992), although one must go to pore sizes less than ~ 1 micron before these effects become noticeable (Uchida et al., 1998). However, even at 77 K the crystal hydrate in pores will still be the stable phase, and again it is not likely to transform. For ice in pores it is reported that the layer of water next to the pore wall does not crystallize, although motional processes still freeze in (*see* for example, Bellisent-Funel and Dore, 1994). Currently, nothing is known about this surface layer in pore hydrate. In general, we note that the effect of confinement on the fundamental properties of matter (e.g. melting, freezing, phase changes) is a prominent topic in the literature today, so that it would be presumptuous to suggest that all of the important factors related to the effect of pore confinement are understood. Other factors that remain unknown are the role of salinity, and the possibility that pure CO_2 hydrate is absolutely unstable at low temperatures.

A PROTOCOL FOR HYDRATE STORAGE

From the previous sections we may conclude that without Bjerrum or other more complex defects, gas hydrate and ice lattices are quite inert below ~150 K. The only naturally occurring guest molecule that is likely to show activity in this respect is CO_2, and so far it has been seen only as a minor component of guest gases in natural gas hydrate samples. This relative inertness is corroborated by the many observations of the decomposition of various gas hydrate samples recovered from natural sources as well as synthetic gas hydrate (Handa, 1988; Handa et al, 1997). These observations allow us to propose a general protocol for sample storage and recovery. The 'danger zone' for hydrate taken outside its stability region is defined by two processes: hydrate decomposition (or formation), and ice/hydrate recrystallization, as discussed above. On the other hand, considering the uncertain nature of pore-wall phases, it would be prudent to slow down dynamics even in the phases that may well be more glass-like. Therefore, cooling well below the glass transition is recommended. Recovered hydrate should be frozen as quickly as possible to temperatures below ~120 K.

During storage in liquid nitrogen, the surface of the hydrate, ice, and minerals is in intimate contact with liquid nitrogen. There is no danger of new hydrate formation under the conditions of storage. Samples may be handled, and loaded into sample cells for X-ray diffraction, Raman spectroscopy, or NMR spectroscopy. However, sample analysis that requires warming above ~120 K, such as differential scanning calorimetry or gas evolution experiments, requires another step, as a surface layer of adsorbed nitrogen gas will remain, especially in small pores. This could lead to hydrate formation when the sample is warmed to temperatures where significant ice recrystallization may occur, i.e. above the glass transition. The adsorbed gas layer must therefore be removed by exposing the samples to dynamic vacuum, still at temperatures well below the glass transition, say 120 K. As noted above, actual hydrate decomposition does not occur below ~150 K at significant rates.

We emphasize that the protocol proposed above is designed to preserve the samples for subsequent analysis of fundamental properties of the hydrate portion of the sample.

If, on the other hand, preservation of the core and its pore structure is the issue of greater importance, for instance, for the study of engineering properties, than recourse must be taken to methods that do not give rise to excessive freezing or thawing. As suggested in the introduction, another option that is least likely to change the nature of the gas hydrate is to allow the decomposition of some of the sample into the dead space over the sample. The dead space can be minimized by adding inert material (glass, metal, but not plastics, as the latter can sorb considerable amounts of gas) as fill.

In this context, a few words should also be said about gas hydrate self-preservation. This effect is based on the observation that gas hydrate can exist for some time on warming samples outside its normal P-T zone of stability. This effect has been observed in laboratory experiments on both natural and synthetic gas hydrate (Davidson et al, 1986), and now also forms the basis for a commercial scheme for gas hydrate storage and transport (Gudmundson et al., 1994). One way that this may occur is by the decomposition of the outer hydrate layer on gas hydrate particles, leaving an ice layer that is relatively impermeable to methane gas diffusion. So far, there is no quantitative information on the effectiveness of the self-preservation effect. Results obtained on the gas evolution from gas hydrate in sediments suggest that self-preservation is not very effective for samples that have been stored in liquid nitrogen. Possible reasons include thermal fracturing of the samples, especially at interfaces between gas hydrate and mineral particles where the coefficients of expansion of the phases in contact are likely to be very different. At the current state of knowledge it is best not to rely on self-preservation when handling samples that are to be used for quantitative studies related to the physico-chemical properties of the gas hydrate.

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