Preservation of Methane Hydrate at 1 Atm

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Gas hydrates, the most common terrestrial example being methane hydrate (CH4.nH2O where n ≥ 5.75), are crystalline solids formed from the association of water and gas under certain conditions of relatively high pressure (P) and low temperature (T). They continue to generate considerable interest as globally distributed deposits harboring potential hydrocarbon reserves, as icy minerals of predicted outer-solar-system occurrence, as manufactured materials with novel industrial applications, as potential players in global issues of climate and seafloor stability, and as troublesome blockage-formers in gas pipelines.1 Due to the remote and complex environments in which they occur, however, many of the properties and influences of gas hydrates remain unknown or poorly constrained. Likewise, the effects of geochemical, thermal, mechanical, and other environmental influences on the stability of gas hydrates or on the kinetics of their dissociation to water + gas are poorly understood.

Recently, a number of observations of incomplete or delayed dissociation have been reported for a variety of gas-hydrate-bearing specimens of both natural and synthetic origin.2–9 Such “self-preservation” occurs well above the 1-atm equilibrium temperature for hydrate breakdown, but below the H2O ice point. Practical exploitation of this behavior requires an ability to preserve the hydrate in a predictable and controllable manner. However, critical comparison of the extent of preservation, expected gas yields, and equilibrium phase relations among the previously reported cases is problematic. This is largely due to (1) insufficient or unavailable information describing the precise composition and stoichiometry of the original hydrate, (2) the difficulty in comparing synthetic and thermal histories of samples, (3) the common presence of large fractions of ice as a secondary phase, and (4) in the case of natural hydrate, the unknown extent of decomposition and alteration undergone during retrieval and transport. In the cases cited above, shielding effects provided by the contaminant ice or by the formation of ice rinds on the surface of decomposing hydrate have been invoked as the principal mechanisms for incomplete dissociation.2–9 A common and substantiating observation is that warming the preserved material through the ice point induces both ice melting and full decomposition of the residual hydrate.

To address these issues further, we refined a “pressure-release” method that enables reproducible bulk preservation of pure, porous, methane hydrate at conditions 50 to 75 K above its equilibrium T (193 K) at 1 atm. The amount of hydrate preserved by this method appears to be greatly in excess of that reported in the previous citations, and is likely the result of a mechanism different from ice shielding.10 In common with the other reports, however, warming of the preserved material through the ice point induces its complete and rapid dissociation. Consequently, predictable and potentially large amounts of gas can be released through just modest heating of the pressure-released material. Details of the experimental techniques and the underlying physical chemistry of preservation are reported elsewhere,10 this communication is simply intended to highlight a few key aspects of “anomalous preservation” for those interested in its implications for gas fuels.

In this study, polycrystalline methane hydrate was grown in the lab by warming granular (200 µm) H2O ice in a pressurized CH4 atmosphere.11,12 The resulting material is essentially pure methane hydrate (> 99 vol %) of composition CH4.5.89H2O, with highly reproducible grain texture.13 Additional samples were synthesized with equal volumes of methane hydrate and quartz sand, with the sand distributed either homogeneously throughout the hydrate or as discrete layers alternating with those of pure hydrate (as shown in Figure 4 in ref 13). Dissociation rates and/or sample stoichiometry were then measured on over 65 samples.10,14 Each test moni-
CH$_4$ gas are decomposition products, and high external fluid bath. The remaining vented to 0.1 MPa over about 8 s. The vent is then the sample to an isothermal test just above the equilibrium curve, then equilibration of involves initial reduction of sample pore pressure to that hydrate actively dissociates at 0.1 MPa. Pressure release "for quickly accessing thermal regions where regions occur at both low methane hydrate stability field. These sharply bounded predicted from the greater thermal overstepping of the company increasing test temperatures, as would be characteristic dissociation behavior (Figures 1 and 2). In two samples: "temperature ramping" for precise measure-

tored CH$_4$ release by use of a custom-built gas flowmeter and collection instrument connected directly to the sample chamber. Most samples were tested immediately after synthesis to avoid any structural, compositional, or reproducibility problems caused by intermediate handling or cryogenic transfer procedures. A typical 30 g sample releases nearly 6 L of CH$_4$ during dissociation, all of which is collected in the flowmeter (Figure 1, inset).

Two general methods were used to destabilize samples: "temperature ramping" for precise measurement of stoichiometry and gas yield, and "pressure release" for quickly accessing thermal regions where hydrate actively dissociates at 0.1 MPa. Pressure release involves initial reduction of sample pore pressure to that just above the equilibrium curve, then equilibration of the sample to an isothermal test T maintained by an external fluid bath. The remaining P is then rapidly vented to 0.1 MPa over about 8 s. The vent is then quickly closed while simultaneously opening the sample to the flow meter, allowing collection and flow measurement of the hydrate-forming gas.

Results of pressure release tests conducted between 195 and 290 K identified three thermal regimes of characteristic dissociation behavior (Figures 1 and 2). In two regions, monotonically increasing dissociation rates accompany increasing test temperatures, as would be predicted from the greater thermal overstepping of the methane hydrate stability field. These sharply bounded regions occur at both low T (195–240 K) where H$_2$O ice + CH$_4$ gas are decomposition products, and high T (272 K) where liquid water + gas are products (Figure 2). Between 241 and 271 K, however, lies a regime of anomalous behavior in which dissociation rates decay rapidly within several seconds of the pressure-release treatment, resulting in large fractions of hydrate remaining preserved for extended duration. The change in behavior between the systematic vs anomalous regimes is dramatic; more than 90 vol % of a pure methane hydrate sample dissociates within 10's of seconds when pressure-released at 239 K, whereas > 90 vol % hydrate can be retained for at least 10's of hours when depressurized at 268 K. While dissociation rates of hydrate + sediment samples were measurably faster than those of pure methane hydrate, all samples tested in the preservation regime dissociated at rates that were orders of magnitude slower than those predicted from extrapolation of the low-T tests (Figure 2, dashed curve). Dissociation rates in the preservation regime are likewise depressed well below those measured in higher-T tests, but such comparison is complicated by the significantly greater influence of heat flow systematics on hydrate dissociation above 273 K.

While some variation occurs on a sample-to-sample basis, the general expression of dissociation exhibited in virtually all tests was surprisingly reproducible. The fine detail of the T dependency within the preservation regime (255–264 K) is also well-resolved experimentally. It should also be noted that the preservation behavior described here is thermally altered at low T; preserved material can be slowly cooled from 270 to 190 K without any increase in dissociation rate, but upon rewarming above 195 K, the hydrate systematically dissociates over the range 205–215 K as in temperature-ramping tests discussed in ref. 10.

Such anomalous preservation of methane hydrate at temperatures just below the ice point, coupled with the ease of controlled recovery of a predictable gas yield by just modest heating of the preserved material, may enable development of new strategies for (1) the temporary low-pressure transport and storage of natural gas, (2) retrieval of naturally occurring gas hydrate from remote settings, or (3) controlling gas yield rates from natural
hydrate-bearing deposits or from artificially produced hydrates. It is also an effect that has not been critically evaluated for stability issues involving deep water drilling into hydrate-bearing sediments, or models of seafloor stability where rapid pressure-release associated with slumping, submarine landslides, or along fault vents may occur.

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