

## POLYCRYSTALLINE METHANE CLATHRATE: A NEW METHOD OF *IN SITU* SYNTHESIS, AND ITS PHASE STABILITY AND RHEOLOGY AT HIGH PRESSURES,

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Methane is an important molecule in the outer solar system and is expected to form the icy clathrate structure (CH<sub>4</sub>·6H<sub>2</sub>O) in appreciable amounts on the solid planets and moons of the outer solar system where both water and methane are abundant. Methane clathrate also occurs commonly in offshore methane-bearing sediments, and is the largest untapped hydrocarbon source on Earth. Prior work on this compound has been hampered by the difficulty in synthesizing cohesive polycrystalline aggregates suitable for physical property measurement. We have successfully made such aggregates, deformed them at low temperatures and elevated pressures and examined their deformation microstructures as guides to the deformation processes that control their rheology. We found that the growth and deformation properties of this compound to be very peculiar and interesting.

Our sample-fabrication apparatus enables routine production of polycrystalline clathrate test specimens with controlled grain size, random grain texture, and near-zero porosity. We fabricate large volume (50 cm<sup>3</sup>), cylindrical samples of methane clathrate from CH<sub>4</sub> gas and melting H<sub>2</sub>O "seed" ice grains, by promoting the reaction CH<sub>4</sub> (g) + 6H<sub>2</sub>O (s→l) → CH<sub>4</sub>·6H<sub>2</sub>O (s) at controlled conditions of pressure and temperature allowing undisturbed, *in situ* crystallization of methane clathrate. Complete reaction was most readily achieved at conditions approaching the clathrate dissociation curve, by raising the temperature from 0°C to 16°C at methane pressures of 25 to 30 MPa over a time interval of approximately 8 hours (Fig. 1).

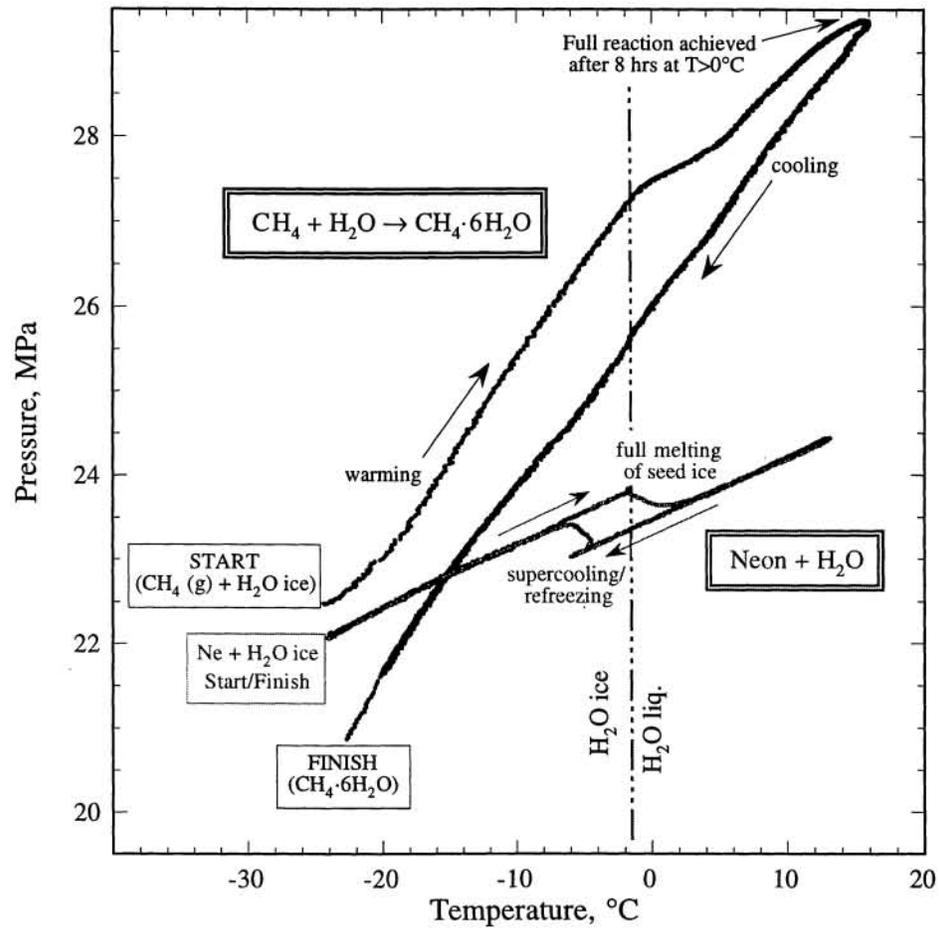
Although sample-fabrication records show that the rates of clathrate formation slow down with time at temperatures just above the metastable ice melting curve, we demonstrate that overdriving the clathrate-forming reaction at temperatures well above the melting curve greatly improves reaction kinetics and facilitates full reaction at rates that are practical in the laboratory. Significantly, partially reacted samples do not show evidence for significant melting of the unreacted ice, despite lengthy exposure at temperatures well above the H<sub>2</sub>O melting curve. We propose that under these conditions of *in situ* growth in which the system is apparently nuclei-deficient, development of a hydrate mantle surrounding each ice grain affects reaction kinetics by suppressing melt nuclei and impeding the hydrate formation rate (1). Moreover, effective "armoring" of the ice grains also appears to be coupled with the extraordinary persistence of superheated ice as the clathrate-forming reaction proceeds to completion. Control experiments comparing this behavior of ice in the presence of a hydrate-forming gas (CH<sub>4</sub>) vs a non-hydrate-forming gas (Ne) verify that ice melts detectably near its melting curve when no clathrate is forming (Fig. 1). This result confirms that H<sub>2</sub>O ice in the presence of methane can persist metastably at temperatures well in excess of its melting point under conditions favorable to clathrate hydrate formation.

Deformation tests also reveal intriguing behavior. Methane clathrate samples were shortened in constant-strain-rate deformation experiments at T= 140-200 K, P<sub>c</sub>= 50-100 MPa, and ε̇= 3.5 x 10<sup>-4</sup>-10<sup>-6</sup> s<sup>-1</sup>. While measurements in both the brittle and ductile fields show that methane clathrate is comparable in strength to H<sub>2</sub>O ice, stress-strain curves of deforming clathrate differ markedly from those of H<sub>2</sub>O ice in that they exhibit extensive strain-hardening behavior (Fig. 2). Furthermore, x-ray diffraction analyses of deformed clathrate samples showed development of significant fractions (25-30%) of water ice during testing. A gas collection system detected no CH<sub>4</sub> gas evolving from deforming samples either during or after testing, however, suggesting that methane clathrate undergoes a form of solid-state unmixing to ice plus another clathrate during deformation at conditions well within its nominal stability field. Clathrate phase instability under nonhydrostatic stress may be of particular interest regarding terrestrial environments such as those underlying continental shelves and in associated accretionary prisms prone to regional tectonic influences, where the presence of hydrates strongly influences the mechanical properties, stability, and porosity of hydrate-cemented sediments.

<sup>1</sup> Hwang, M.J., D.A. Wright, A. Kapur, and G. D. Holder, An experimental study of crystallization and crystal growth of methane hydrates from melting ice, *J. Inclusion Phenom.*, 8, 103-116, 1990.

**Figure 1.** Sample fabrication run record (black circles) showing initiation of the clathrate-forming reaction from  $\text{CH}_4$  gas +  $\text{H}_2\text{O}$  ice grains as temperature is raised above the  $\text{H}_2\text{O}$  melting curve (dot-dashed line). Full reaction is accompanied by a 1.8 MPa reduction in pressure which attends the volumetric reduction.

Parallel experiments using a non-hydrate-forming gas (neon, shown in grey circles) demonstrate our ability to detect the melting of the seed ice from the associated pressure discontinuities, and verifies the metastable persistence  $\text{H}_2\text{O}$  ice at temperatures well above its melting point when under clathrate-forming conditions.



**Figure 2.** Deformed methane clathrate exhibits prominent strain hardening behavior, in contrast to the yield, strain softening, and steady-state flow in deforming  $\text{H}_2\text{O}$  ice at comparable conditions.

