

PRELIMINARY COMPARISON BETWEEN THE DISSIPATION IN CO₂ CLATHRATE HYDRATES AND WATER ICE. M. Choukroun, J.C. Castillo-Rogez, J.B. Young, R.E. Mielke. Jet Propulsion Laboratory, 4800 Oak Grove Dr, MS 79-24, Pasadena, CA 91109. E-mail: mathieu.choukroun@jpl.nasa.gov.

Introduction: Clathrate hydrates (hydrogen-bonded H₂O skeleton forming cages that trap individual gas molecules) have long been suggested as a medium for storage and release of volatiles in planetary environments. Specifically, dissociation of methane clathrate hydrates associated with cryovolcanism is a likely mechanism for Titan's atmospheric methane replenishment [e.g., 1-3]. On Enceladus, the dissociation of mixed N₂-CO₂-CH₄ clathrate hydrates is possibly the source of most species detected in the South Pole plumes [e.g., 4,5].

However, besides the stability of these phases, their thermomechanical behavior is also of major importance for modeling the response of an icy shell containing ice and clathrate hydrates (among other compounds) to tidal forcing and convection. Little is known on the mechanical properties of clathrate hydrates, except under high confining pressure and large differential stresses [6-8]. To date, no experimental data have been obtained at conditions relevant to icy satellites, and the attenuation properties of water ice have just started being investigated over a wide range of conditions. Obtaining such data has been the motivation for developing the JPL *Planetary Tides Simulation Facility* [9].

The purpose of this study is three-fold: 1) achieve the capability to synthesize and characterize samples of water ice and clathrate hydrates; 2) compare the microstructures of ice and clathrate hydrates synthesized and understand the implications for icy satellites; 3) conduct mechanical measurements on these samples to obtain data relevant to the tidal response of icy satellites with icy shells containing non-water ice components, as Enceladus's likely is.

Sample synthesis: De-ionized liquid H₂O is frozen, ground, and sieved at the Extraterrestrial Materials Simulation Laboratory (EMSIL, JPL) and/or at the Mars and Ice Simulation Laboratory (Caltech), to generate ice seeds of a known size. We synthesize clathrate hydrate by reaction of the ice seeds with high-pressure gas within a high pressure – low temperature system, recently developed at JPL [10,11] to synthesize clathrate hydrates of CO₂, CH₄, N₂, and inert gases or mixtures. The phase diagram of Figure 1 shows the stability curve of relevant clathrate hydrate species, as well as the pressure – temperature – time paths followed to convert H₂O ice into the clathrate hydrate of interest. The procedure is similar to that described in

[6], except that it is restricted to temperatures lower than the melting point of H₂O to avoid intense recrystallization of the samples and changes in grain size.

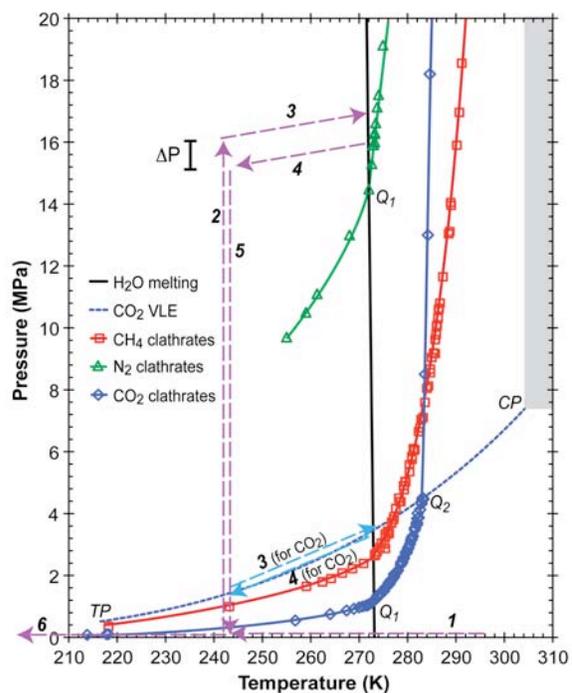


Figure 1. Phase diagram and procedure for the synthesis of clathrate hydrates. Clathrate hydrates of a given gas are stable on the left of the corresponding stability curve. *CO₂ VLE*: CO₂ vapor-liquid equilibrium. *Q_i*: quadruple point clathrate – gas – ice – liquid water. *Q₂*: quadruple point clathrate – gas – liquid (guest molecule) – liquid water. *TP*: triple point (CO₂). *CP*: critical point (CO₂). ΔP : pressure drop observed upon clathrate formation, not observed for CO₂ as pressure is buffered by the VLE. After [11].

Prior to conducting mechanical measurements (whether on clathrate hydrates or on water ice), it is necessary to reduce the porosity of these samples to negligible values. We achieve this by compacting the ice seeds or the as-grown clathrate hydrates in a stainless steel pressure vessel up to 100 MPa, at dry ice temperature (-78.2 °C), for several hours.

Characterization: We use optical, elemental, and spectroscopic methods to characterize the clathrate and ice samples. With these methods, we can assess the

nature and the microstructure of these samples, as well as survey the evolution of the samples through time.

Optical characterization: We use an Olympus BX51 polarizing microscope equipped with a Linkam LTS 350 liquid nitrogen – cooled cryostage to discriminate clathrate hydrate (cubic, i.e. always extinct under crossed-polarized light) from water ice (hexagonal, with 90° repetitive extinction patterns). We also use a FEI XL30 Scanning Electron Microprobe (cryo-SEM) to analyze the microstructure of the samples, which are maintained at cryogenic temperatures using a Polaron stage (Quorum Technologies).

Elemental characterization: The cryoSEM is equipped with an X-ray Energy Dispersive Spectrometer, which provides energy spectra from which the atomic abundances can be derived. Hydrogen cannot be detected by this method, pure water ice appears with a ~ 100% at. C composition. CO₂ clathrate hydrates are found to display atomic compositions of 10-12 at% C for 88-90 at% O, which is consistent with the theoretical formula (CO₂, 5.75 H₂O).

Spectroscopic characterization: We also use Raman spectroscopy to characterize clathrate hydrates. A 632.8 nm He-Ne laser is fiber-coupled to a Kaiser (MI) holoprobe microRaman system with a thermoelectrically cooled CCD detector, to obtain the spectra within the Linkam LTS 350 cryostage. The Raman spectra obtained show the signature of the H₂O skeleton similar to ice Ih, and the signature of gaseous CO₂. The relative intensities of CO₂ and H₂O signatures are consistent with pure CO₂ clathrate hydrates. More details on the characterizations methods can be found in [11].

Microstructure, Mechanical Measurements and Implications: Figure 2 compares cryoSEM images obtained with a beam acceleration of 15 kV and a working distance of 10.2 mm on polycrystalline H₂O ice and CO₂ clathrate hydrate samples, before (1, 2) and after (3, 4) cold compaction. Three distinct scales of organization of the microstructure can be identified in all samples: 1-3 μm (sub-grain structures, potentially individual crystals), 8-12 μm (grains), 17-25 μm (clusters). Clathrate hydrate seeds (2) retain the overall shape and the size of the starting ice seeds, although clathrate seeds appear slightly more rounded than ice seeds. The compaction into negligible porosity samples yields another scale of grain size, of ~ 60-100 μm in H₂O ice samples, which is the footprint of the starting ice seeds. In clathrates the size of these remnants is 30-40 μm. The extreme conditions the samples are subject to (0 – 100 MPa, 200 – 270 K) encompass and exceed those at depth in icy satellites, and the similarity in microstructure may represent a similarity in viscous

behavior. We are presently conducting experiments to measure the viscoelastic properties and the dissipation in such samples with the JPL *Planetary Tides Simulation Facility*, and will present results at the meeting.

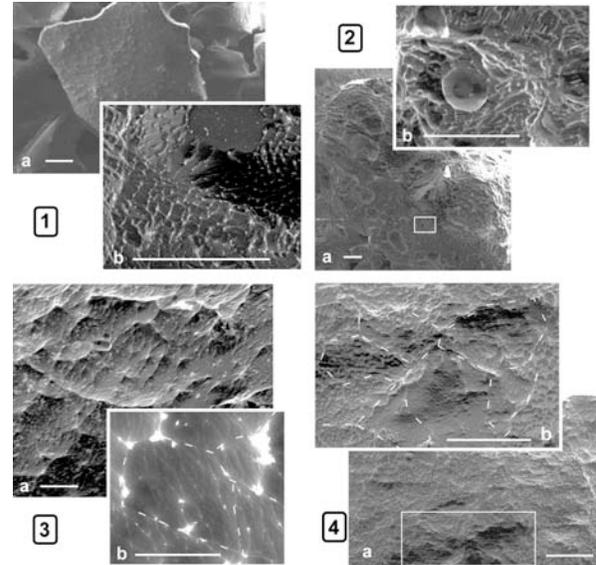


Figure 2. CryoSEM images at low (a) and high (b) magnification of: 1) H₂O ice seeds; 2) CO₂ clathrate hydrates as grown; 3) 100-MPa compacted H₂O ice; 4) 100-MPa compacted CO₂ clathrate hydrate sample. Scale bars all represent 20 μm.

Acknowledgements: The authors would like to acknowledge F. Zhong and H. Engelhardt for their technical support, C. McCarthy for advice on the compaction system, and M. Barmatz for administrative support and management of facilities. MC is supported by a NASA Postdoctoral Program Fellowship, administered by Oak Ridge Associated Universities. This work has been conducted at the Jet Propulsion Laboratory, California Institute of Technology, under contract with NASA, and has been supported by internal JPL Research and Technology Development Funds. Copyright 2009, California Institute of Technology. Government sponsorship acknowledged.

References: [1] Lunine J.I. and Stevenson D.J. (1987) *Icarus* **70**, 61-77. [2] Tobie G. et al. (2006) *Nature* **440**, 61-64. [3] Choukroun M. et al. (in press) *Icarus*, doi: 10.1016/j.icarus.2009.08.011. [4] Kieffer S.W. et al. (2006) *Science* **314**, 1764-1766. [5] Fortes A.D. (2007) *Icarus* **191**, 143-148. [6] Stern L.A. et al. (1996) *Science* **273**, 1843-1847. [7] Durham W.B. et al. (2003) *J. Geophys. Res.* **108** (B4), 2182. [8] Durham W.B. et al. (2005) *Proc. 5th Intl. Gas Hydr. Conf.*, Trondheim, Norway. [9] Young, J.B. et al. (in preparation) *Rev. Sci. Instr.* [10] Choukroun M. et al. (2009) *LPS XL*, Abstract #2313. [11] Choukroun M. et al. (submitted) *Geophys. Res. Lett.*