NEW GROWTH SETUP OF PLANETARY CLATHRATE HYDRATES ANALOGS FOR PHYSICAL PROPERTIES MEASUREMENTS. M. Choukroun, M. Barmatz, and C. Sotin, NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr, Mail Stop 79-24, Pasadena, CA, 91109, E-mail: mathieu.choukroun@jpl.nasa.gov.

Introduction: Clathrate hydrates are inclusion compounds, with an ice-like structure that consists in an arrangement of ice cages in which guest gas molecules are trapped individually. These structures are stabilized by van der Waals interactions between the gas and the cages [e.g. 1]. Their potential ubiquitous occurence in the Solar System [e.g. 2] has strong implications in various domains: quest for future energy resources [3], climatology of the Earth [4] and Mars [5], astrophysics [6] and outer planets and icy satellites compositions [7]. Clathrate hydrates could especially play a significant role on the evolution and in the dynamic processes occurring on icy satellites, such as methane outgassing from the interior on Titan [e.g. 8,9]. Addressing the physical properties (mechanical behavior, thermal conductivity, density) of these compounds is essential to improve our current understanding of geophysical properties of icy satellites. We present a new high-pressure apparatus for the generation of clathrate hydrates with relevant compositions to icy satellites. Expected results on clathrate hydrates thermo-physical properties from measurements conducted on these samples are also presented.

Clathrate hydrates and implications for the behavior of volatiles in icy satellites: Clathrate hydrates are thought of as a likely trap for volatiles in the outer presolar nebula, prior to planets and satellites accretion [e.g. 7,10]. These icy structures can contain up to 14 percents of gas, these significant amounts being compatible to some extent with planetary abundances expected on giant planets and their moons. Particularly, large amounts of N_2, CH_4, CO_2, and noble gases (Ar, Xe) may have been accreted in planetesimals and satellitesimals and could thus have contributed significantly to the volatile budget of icy satellites [10].

Influence on the thermal evolution of icy satellites: The density contrast between clathrate hydrates and other species (ammonia hydrates, salt hydrates, high-pressure phases of ice, etc) within the H_2O-dominated interior of icy satellites could have led to the early formation of a segregated layer of clathrate hydrates. Density, but also stability and thermal conductivity of clathrate hydrate depend highly on the nature of the guest gas, or of the gas mixture in equilibrium with clathrate hydrates. As an example, the density of clathrate hydrates varies from 0.92 (methane clathrate) to 1.25 or more (CO_2 clathrate). Therefore, segregated layers of clathrate hydrates can exist above or below the primordial ocean in the icy moons of Jupiter and Saturn. A recent study [9] has shown that the heat release of Titan through time decreases drastically if an outer clathrate hydrate shell is present, thus delaying crystallization of the internal ocean. As the thermal conductivity of clathrate hydrates is up to five times smaller than that of ice [e.g. 1 and references therein], even the presence of small amounts of clathrate hydrates within an icy shell would have a significant impact on the thermal behavior of the crust. Furthermore, tidal heating is a key issue in the development of convective plumes within the icy shells [e.g. 11]. Therefore, good knowledge of the mechanical properties of clathrate hydrates is also essential to understand the dynamics of icy satellites and their thermal evolution.

Role in volatile release from the interior via cryovolcanism: Observation of potentially cryovolcanic features on Titan [12,13], as well as measurements of large amounts of CH_4 and CO_2 in Enceladus' plume [14] by the instruments onboard the Cassini spacecraft, raise the problem of volatile outgassing from the interior in icy satellites. Methane clathrate hydrates dissociation at depth has long been a hypothesis for Titan's atmospheric methane replenishment [e.g. 15]. Recent experimental [8,16] and numerical [9] studies have shown that such dissociation can only occur at a local scale and through a succession of events involving reaction with ammonia-water cryomagmas at shallow depth [16]. Dissociation of clathrate hydrates containing a gas mixture (CO_2, CH_4, N_2) has also been proposed as the source of Enceladus plume volatiles [17]. However, these studies only focused on the dissociation at equilibrium. Experimentally, dissociation of methane clathrate hydrates has been observed within their stability field during mechanical measurements [18]. Understanding the mechanical behavior of clathrate hydrates and its potential impact on the stability of these structures can thus bring new constraints on cryovolcanic processes and the release of volatiles on the icy moons of Jupiter and Saturn.

Experimental setup for clathrate hydrates generation: The apparatus under development for clathrate hydrates generation consists of a high-pressure vessel, cooled by a refrigerated circulator. Indeed, generation of clathrate hydrates is much easier to achieve under pressure, and reaction kinetics is improved.

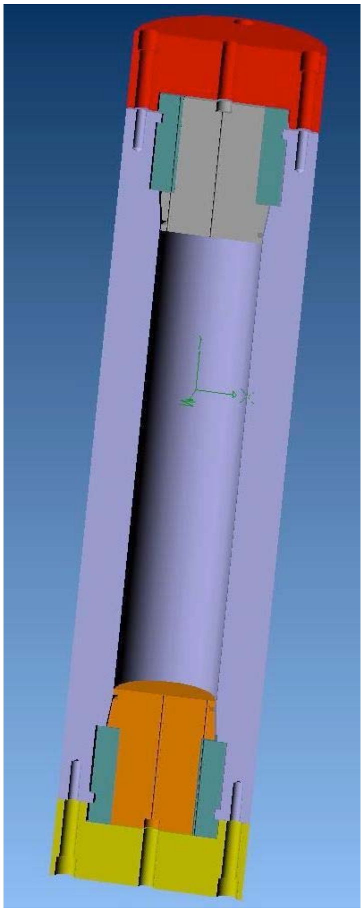

Figure 1. Preliminary design for the high-pressure autoclave. An O-ring type closure system with two lids and a bolted cover will be used for rapid access to the samples after formation.

High-pressure vessel: The high-pressure vessel is a custom-built autoclave, developed with Autoclave Engineers. A 3D view of the item ordered is presented in Fig. 1. The 1-liter autoclave has a maximum allowable working pressure of 200 bars, with a 316-type stainless steel body that can sustain temperatures down to 240 K under pressure. It is equipped with two inlet/outlet valves, for pressurizing the system with sample gas (CO_2, CH_4, N_2). Internal dimensions of the vessel are 2.5 in. diameter and 12 in. length. A Pt100 probe will be placed in the allocated thermowell to provide an external temperature control to the Lauda RP-855 C that will be used to cool the system.

Procedure: Due to the slow kinetics of clathrate hydrates formation, the programming capabilities of the RP-855C circulator will be used to perform temperature cycles around the dissociation curve of clathrate hydrates with corresponding composition. Growth of the crystals will be controlled by the temperature ramping and initial size. The procedure followed will be similar to that described in [1].

Expected results: Pure clathrate hydrates of CH_4, CO_2, and N_2, will be generated with this apparatus. Preservation of the samples will be ensured by transport in a liquid nitrogen-cooled container. The initial large clathrate sample will be cut to appropriate size for several types of measurements with the facilities available at the JPL Cryoices Lab [19]: *1)* thin sections will be observed within an Instec cryostage placed under a microscope, for characterization and structural analysis of the grains; *2)* samples with a length of 2 in. will be used for mechanical measurements using an Instron 5848 system; *3)* samples with a length of 0.25 in. will be used for thermal conductivity measurement following the method described by [20].

Mechanical measurements to be conducted with the Instron 5848 System at cryogenic temperatures include determination of the Young's modulus, creep properties, stability under differential stress, and cyclic loading at icy satellites conditions [21]. These new results, combined with thermal conductivity measurements, will help constrain the mechanical and thermal state of a mixed ice-clathrate crust on icy satellites, with implications on their evolution and the cryovolcanic processes that can take place.

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