NEW GROWTH SETUP OF PLANETARY CLATHRATE HYDRATE ANALOGS FOR PHYSICAL PROPERTIES MEASUREMENTS. M. Choukroun, M. Barmatz, J.C. Castillo-Rogez, 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 satellite 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 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, currently under development at the NASA Jet Propulsion Laboratory. Expected results on clathrate hydrates thermo-physical properties from measurements conducted on these samples are also presented.

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

High-pressure vessel: The high-pressure vessel is a custom-built autoclave, developed with Autoclave Engineers. A 3D view of the vessel 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 Proline RP-855 C that is used to cool the system.

Clathrate generation system: Figure 2 is a schematic view of the whole system. Gas is supplied to the high-pressure autoclave from a pressurized gas bottle. The maximum pressure that can be achieved with the system is 160 bars, the bottle pressure of CH_4 or N_2. Higher pressures would require the installation of a gas compression system upstream of the vessel. The high-pressure vessel is cooled by a Lauda Proline RP855 C circulator, which provides thermal control via a Pt100 PRT inserted in the thermowell. Both an internal and an external copper coil are used to ensure good heat transfer between the cooling fluid and the vessel. The temperature range for regulation is -50 to 50 °C. Under pressure of a few bars, such temperatures are low enough to generate clathrate hydrates. At this stage, the apparatus is in its final test phase and will soon be used to generate clathrate hydrate samples.

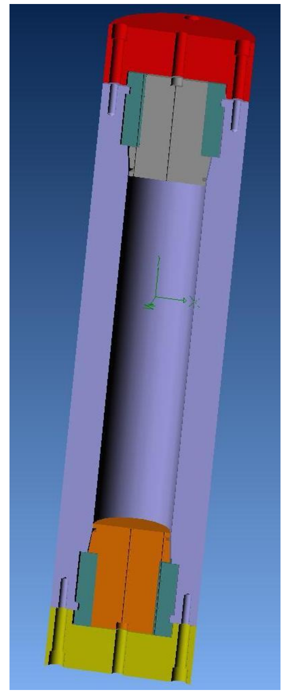

Figure 1. Design of the high-pressure autoclave. An O-ring type closure system with two lids allows fast access to the samples.

Procedure: The growth procedure will be similar to that described in [1] and [2]. Fine-grained polycrystalline ice seeds with a diameter of 500 microns will be prepared with Professor Herman Engelhardt at the Division of Geological and Planetary Sciences at Caltech. These seeds will be loosely packed in a plexiglass tubes. To generate long clathrate hydrate samples, the tubes will be inserted in the autoclave under cold conditions. Then high-pressure gas will be brought into the high-pressure vessel. The temperature will be varied from ~ -20 °C to 0 °C. Being close to the melting point of ice has been shown to improve the reaction time and to ensure the reaction of all the ice crystals with the gas [10]. Nonetheless, due to the slow kinetics of clathrate hydrates formation, the programming capabilities of the circulator will be used to perform temperature cycles around the melting curve of ice and the dissociation curve of clathrate hydrates with corresponding composition. Growth of the crystals will thus be controlled by the temperature ramping and initial grain size of the ice.

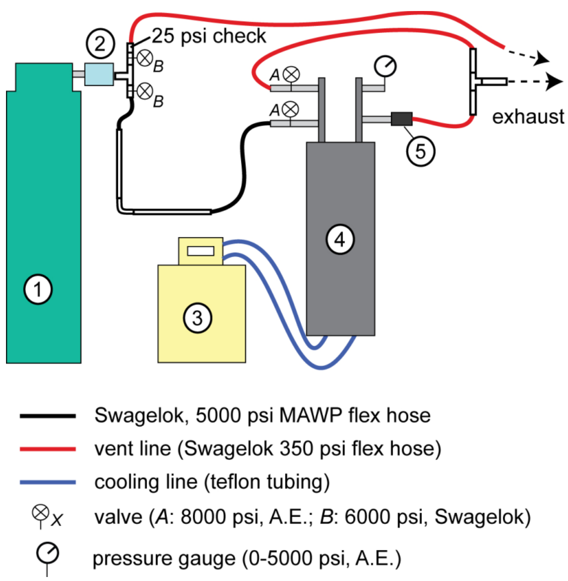

Figure 2. Schematic view of the whole facility for growth of polycrystalline clathrate hydrate samples. 1: Airgas gas bottle at 160 bars (CH_4, N_2) or 50 bars (CO_2); 2: High-pressure regulator (Airgas), with a tee, two valves and a check valve for going into the high-pressure line and/or exhaust; 3: Lauda RP855 C circulator; 4: High-pressure vessel; 5: rupture disk (220 bars).

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: *1)* thin sections will be observed within an Instec cryostage placed under a microscope, for characterization and structural analysis of the grains; *2)* thicker sections will be cut for analysis with a cryo-ESEM (Environmental Scanning Electron Microprobe); 3) samples ~ 1 in. in diameter and 2 in. long. will be used for mechanical measurements using an Instron 5848 system.

Mechanical measurements to be conducted with the Instron 5848 System at cryogenic temperatures include determination of the elastic modulus, creep properties, stability under differential stress, and cyclic loading at icy satellites conditions. The apparatus and its characteristics have been described elsewhere [11], however significant improvements on the thermal stability now allow achieving stresses lower than 0.1 MPa, and cycles with a period corresponding to that of Europa (3.55 days).

In a first stage, CO_2 clathrate hydrate samples will be generated, and their creep properties will be measured under low stress. This will provide a comparison with previous studies [e.g., 12]. Then cyclic loading tests will be conducted at low frequencies on these samples to investigate their attenuation properties. These initial measurements will provide some information on the state of clathrate hydrates containing significant amounts of CO_2, as expected on Enceladus. The new results that will be obtained on clathrate hydrates will help constrain the mechanical 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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