Rapid Heat Induced Clathrate Dissociation Events - A Planetary Context.

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Introduction: Gas clathrates (hydrates) consist of guest molecules such as carbon dioxide, methane, or nitrogen trapped in a cage-like structure of water molecules. Clathrates have become more than a research curiosity as they have posed dangers to industrial operations on Earth, and have recently been investigated in a planetary science setting. Dissociation of clathrate is an endothermic reaction, and thus self-limiting as the clathrate stability field falls in the low temperature, moderate pressure region.

Clathrate dissociation may be caused by depressurization, thermal stimulation, chemical inhibition, decreasing guest molecule concentration, or a combination of these effects. Gas releases possibly associated with clathrate dissociation events have been suggested on Mars, Titan, Eurpora, and Enceladus. Here the thermal stimulation aspect of dissociation will be examined in detail, constrained by experimental data.

Gas release on planetary bodies, especially stochastic releases, could be a result of rapid heat induced clathrate dissociation. Heating could come from subsurface sources such as dike swarms or hot fluid flow through fractures in the rock. Heating could also result from extra-planetary interactions such as small impact events or changes in solar radiation flux.

Methane plumes have been seasonally observed on Mars [1]. It has been proposed that heat induced dissociation may provide a mechanism to dissociate near surface clathrate reservoirs and produce the observed plume foot print [2]. Clathrates on Mars may be within tens of meters of the surface at all latitudes due to relaxed temperature-pressure requirements with the addition of hydrogen sulfide to the system [3].

Plumes of CH_4, N_2, CO_2, and H_2O have been observed by the Cassini spacecraft on Enceladus. It has been proposed that subsurface clathrates are undergoing depressurization via tectonically introduced cracks in the south polar terrain [4]. While depressurization is likely the dominant mechanism, heat transfer may also play an important role. Heat transfer could occur through gas advection in rock fractures and does not require liquid or an interior which is convective in nature [5].

Titan has also been the subject of clathrate studies since the 1980's when hydrate was unexpectedly found to be an important phase. Recent work [6] shows that in the expected ammonia-methane-water system of Titan, clathrate may be the source for significant methane outgassing. For this outgassing to occur, heat from the interior is required along with the addition of ammonia to the system.

Europa is also believed to have clathrates of SO_2, CO_2, H_2S, and CH_4 stable on the surface and in the oceans. According to Galileo spacecraft data, clathrates will be stable at the surface of Europa. Some of the hydrates are calculated to be buoyant in the ocean, while some will sink to the ocean floor. Heat transfer or heat trapping beneath clathrate layers may result in dissociation, possibly associated with cryovolcanic events [7].

Experimental Design: Heat induced dissociation experiments were conducted at Oak Ridge National Laboratory in the 72 liter Seafloor Process Simulator (SPS) [8]. A heat exchanger was embedded in quartz sand. The sand was saturated with water, and the system over pressurized with methane into the hydrate

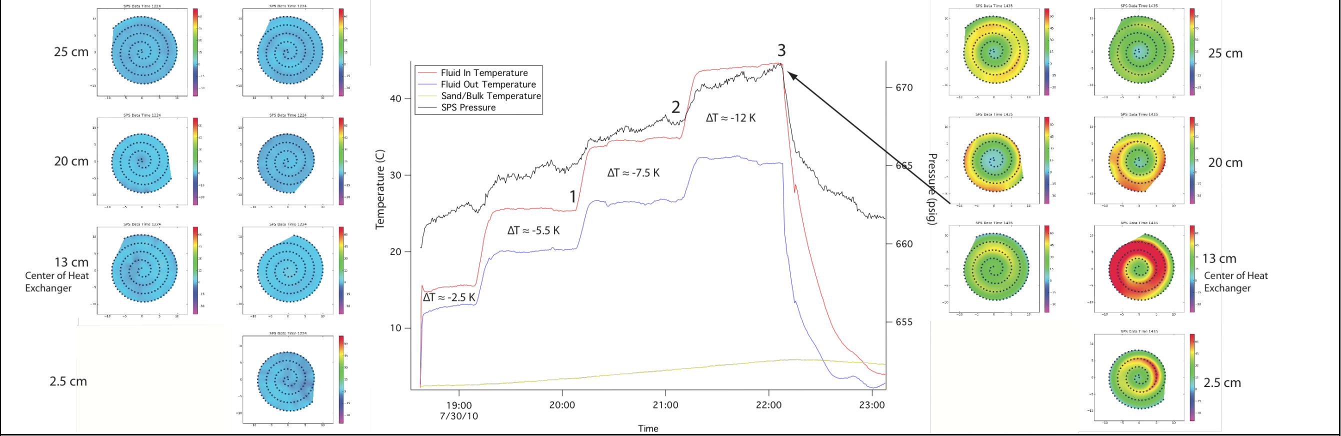

Fig 1 -When heat is introduced into the system through the heat exchanger, the bulk vessel pressure rises steadily; a sharp rise is also observed after each increase of heat input. The DSS plot on the left shows the initial conditions of the system before heat was introduced. These measurements indicate a homogeneous temperature distribution, indicating the system was at equilibrium. The DSS plot on right is after the system was subjected to four heating steps over a period of about 3.5 hours. The sharp gradient observed is the boundary between the sand/hydrate heated by the heat exchanger. Areas where hydrate has dissociated are indicated by cool areas due to the endothermic nature of hydrate dissociation.

stability field. The temperature was lowered to ~275K, inside the hydrate stability field, forming pore filling clathrate.

Heated ethelyene glycol was pumped through the heat exchanger, while the input and output temperatures were monitored. Four grids of fiber optic distributed sensing (DSS) cables embedded within the sand-hydrate system measured temperature-strain conditions at1cm intervals [9].

Results: When heat was added through the heat exchanger to the hydrate-sediment system the SPS bulk pressure increased almost immediately, indicating clathrate dissociation (Fig.1). Endothermic hydrate melting was further supported by decreased temperature conditions surrounding the heat exchanger observed by the DSS. The temperature of the heat exchanger was increased in steps through 283, 293, 303, and 310K resulting in associated pressure rises observed due to further dissociation.

After each temperature step, the system quickly reached steady state; additional energy was used to maintain the volume of dissociation and possibly to induce fluid convection cycles in the sediment with fluid resulting from dissociation. Similar fluid flow has been inferred from seismic volume analysis in teresstrial hydrate reservoirs [10].

Conclusions: Events common in planetary settings can result in short-duration heating which may result in rapid gas release from subsurface clathrate reservoirs. Heating events appear to evolve gas very rapidly, but incompletely dissociate the reservoir. Depressurization events result in a slow release of gas, but have the potential to decompose an entire body of clathrate. Both processes are likely at work in most settings, otherwise the system would reach a steady state quickly due to overpressurization or endothermic cooling.

References:

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