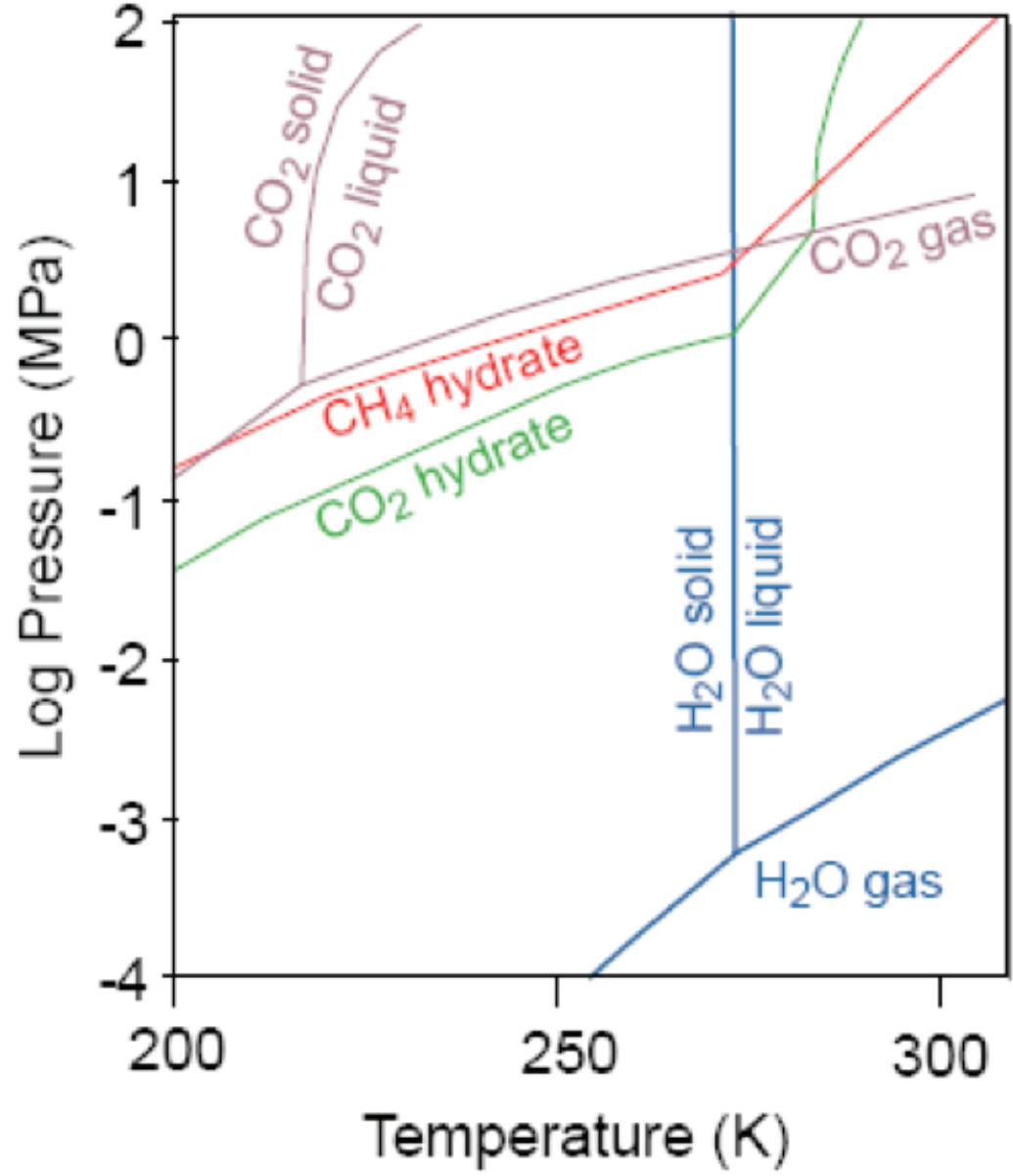


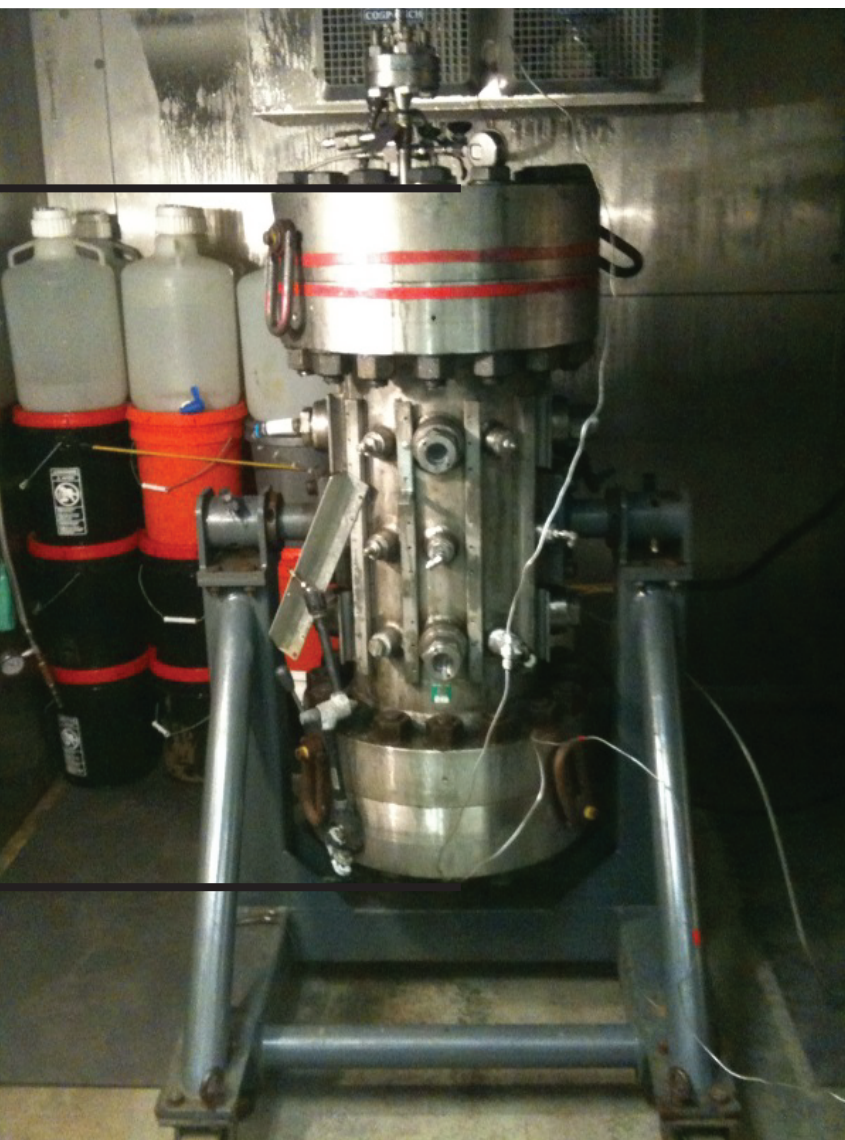
Introduction

Gas releases possibly associated with clathrate dissociation events have been observed on Mars, Titan, and Enceladus. Gas clathrates (hydrates) consist of guest molecules such as carbon dioxide, methane, or nitrogen trapped in a cage-like structure of water molecules. Clathrate dissociation may be caused by depressurization, thermal stimulation, chemical inhibition, decreasing guest molecule concentration, or a combination of these effects. Dissociation of clathrate is an endothermic reaction, and thus self limiting as the clathrate stability field falls in the low temperature, moderate pressure region.

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.

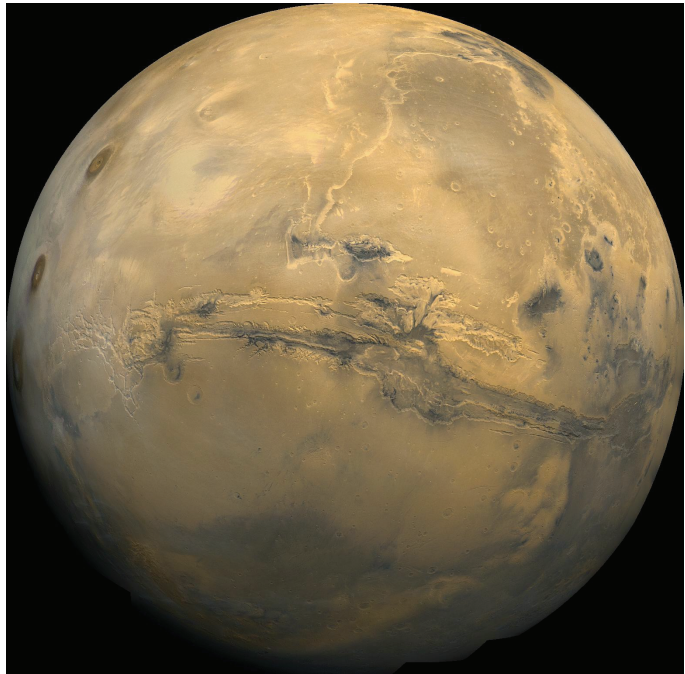


Experiments were conducted in the Seafloor Process Simulator (SPS) located at Oak Ridge National Laboratory (ORNL) to analyze the effects of heat flow in hydrate-sediment systems and attempt to produce a data set to constrain and aid in modeling planetary heat flow. Novel sensing techniques using fiber optic Bragg gratings allowed for a robust interpretation of conditions inside the sediment.

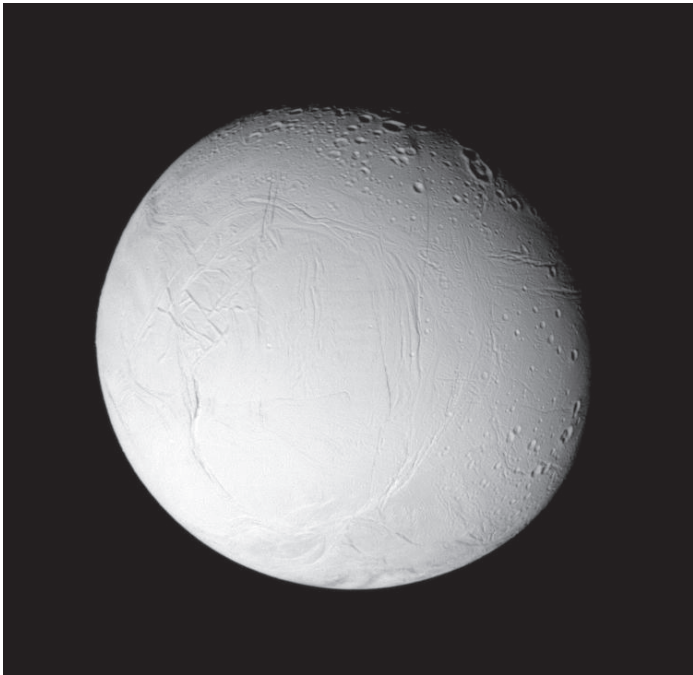


Planetary Context

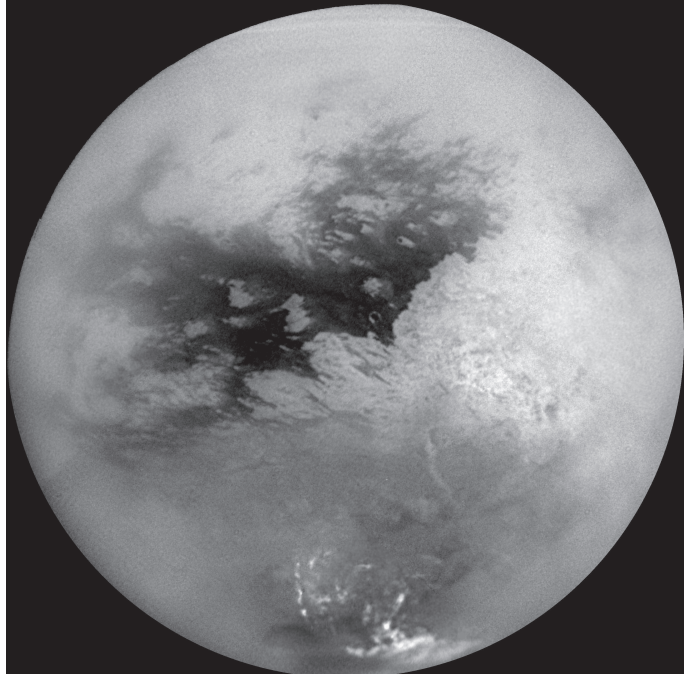
**Mars** exhibits observable seasonal methane plumes [1]. Methane clathrate may be found within tens of meters of the surface of Mars, even at low latitudes if hydrogen sulfide is also present [2]. Heat induced dissociation of these potential gas hydrate reservoirs has been proposed as a source of the these plumes [2] [3].



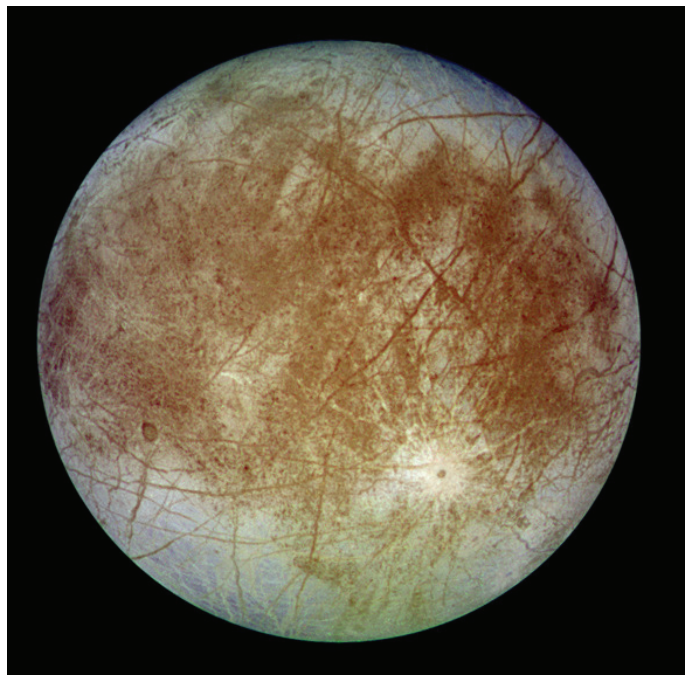
**Enceladus** Plumes of CH<sub>4</sub>, N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O have been observed by the Cassini spacecraft on Enceladus. Subsurface clathrate dissociation due to depressurization via tectonically introduced cracks in the south polar terrain has been proposed as a volatile source [4]. While depressurization would likely be the dominant mechanism, heat transfer may also play an important role. Heat transfer could occur through gas advection in rock fractures without a convective liquid or an interior[5].



**Titan** has been the subject of clathrate studies since the 1980's when, hydrate was first discovered in terrestrial petroleum systems. Recent work [5] shows that clathrate may be the source for significant methane outgassing in the expected ammonia-methane-water system of Titan. For this outgassing to occur, heat from the interior is required along with the addition of ammonia to the system.

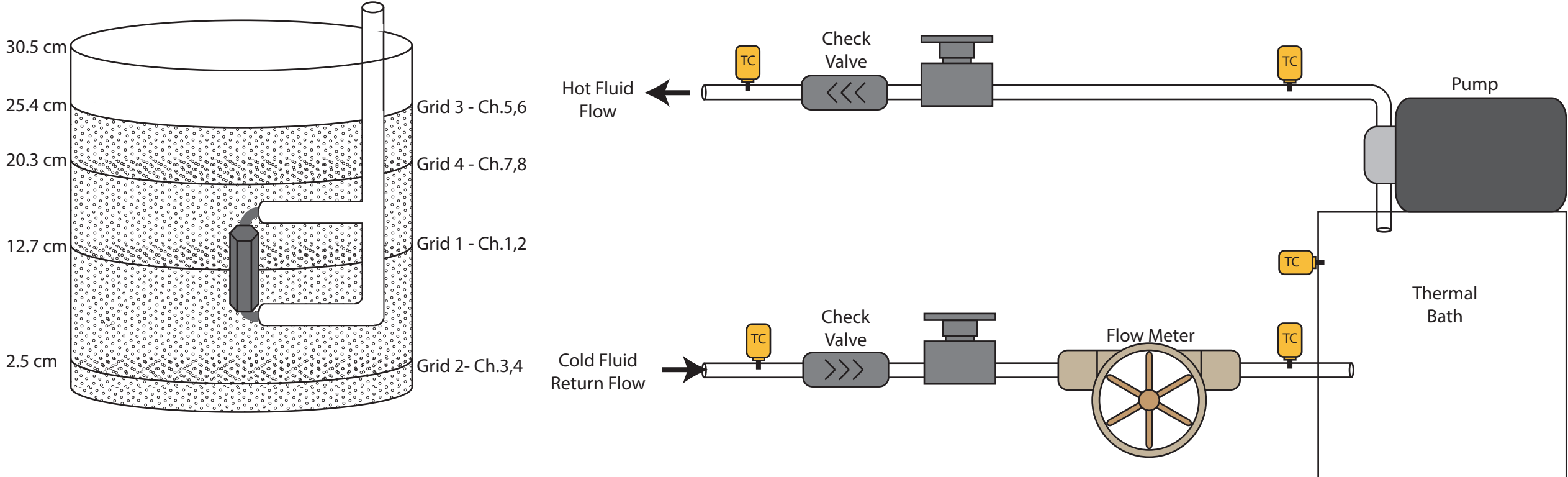


**Europa** is believed to have clathrates of SO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> stable on the surface and in the oceans. Depending on the composition, some hydrates phases are expected to be buoyant in the ocean, while others will sink to the ocean floor. Heat transfer or heat trapped beneath clathrate layers may result in dissociation, possibly associated with cryovolcanic events [6].



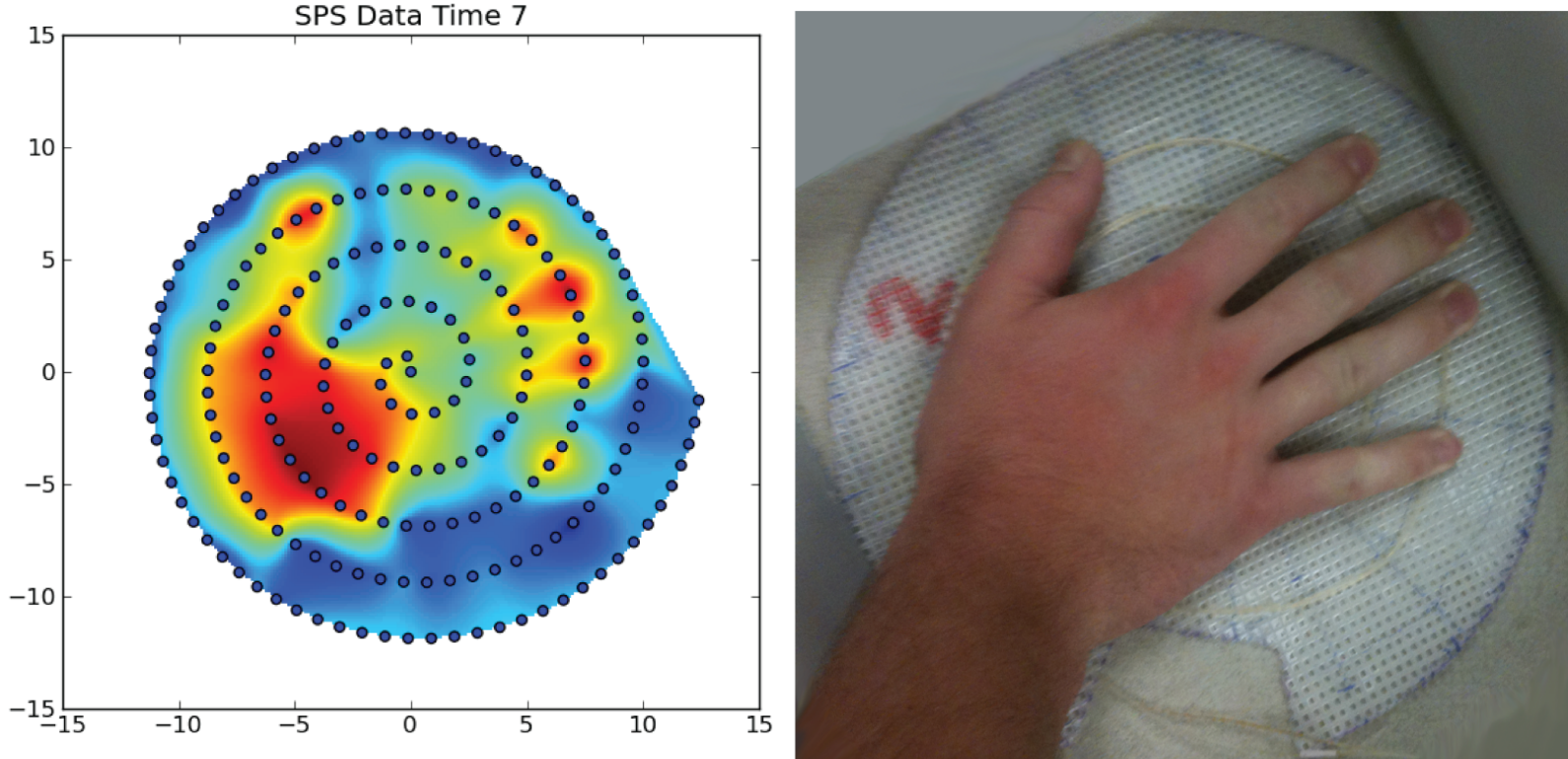
Experimental Design

In this study a hydrate-sediment system was constructed inside the Oak Ridge National Laboratory's Seafloor Process Simulator (SPS). A heat exchanger was embedded inside a sediment column and heat introduced to study possible mechanisms for heat induced clathrate dissociation. The experiment was monitored with a novel fiber optic system that allowed the measurement of a hybrid temperature strain value throuought the system [7][8].



Four distributed sensing system(DSS) grids were layered within the sediment with two fibers on each grid. The fluid was heated in a computer controlled thermal bath and pumped into the SPS heat exchanger. The temperature was monitored at the vessel input/output lines, at the pump output and after the return flow meter to examine heat loss in the system. SPS bulk temperature and pressure were monitored by a seperate LabView driven system.

The sand was saturated with water, and the system over pressurized with methane into the hydrate stability field. The temperature was lowered to ~275K, inside the hydrate stability field, forming pore filling clathrate.

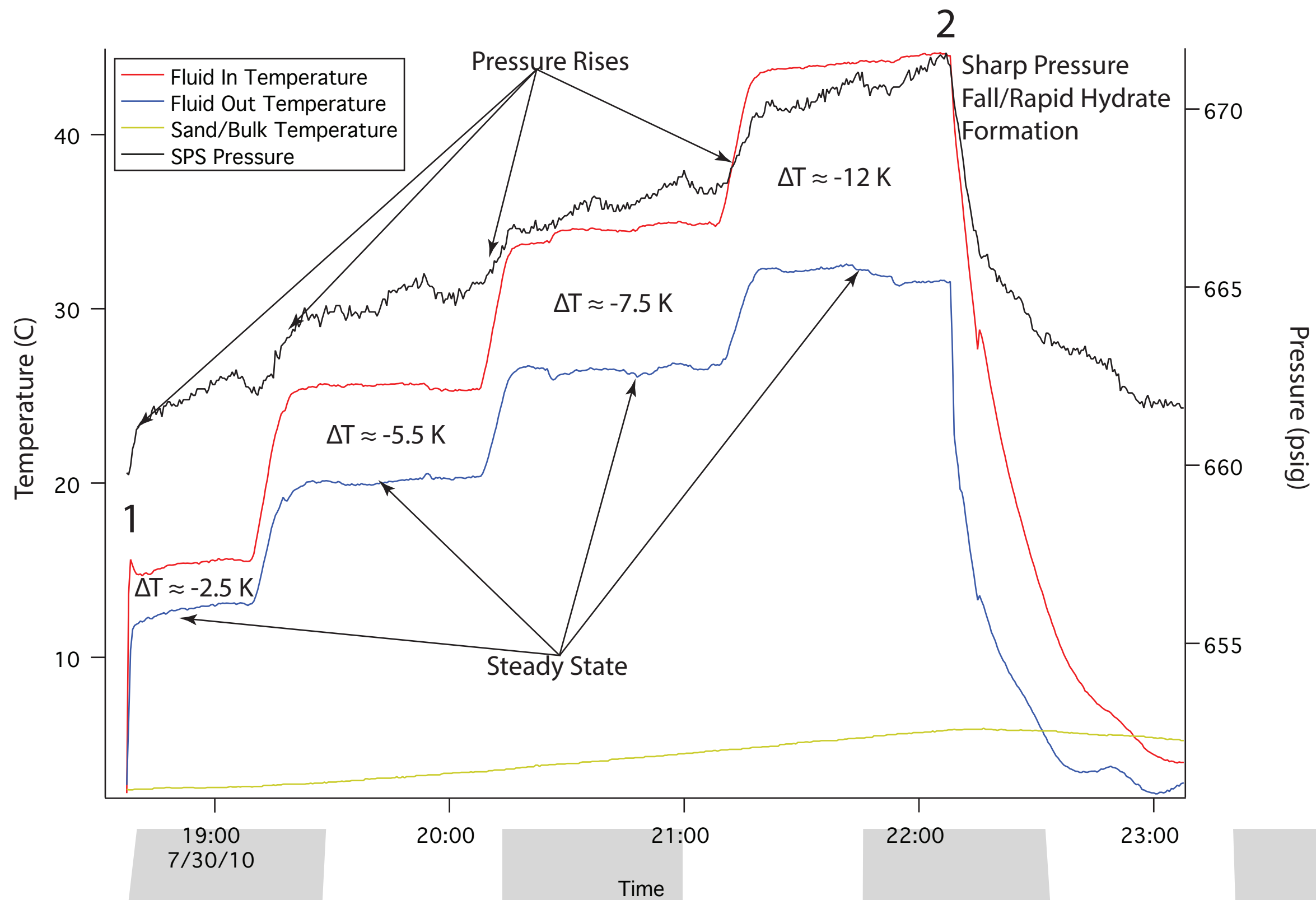


A hand placed on a LUNA DSS fiber produces a firm signature in the temperature contour plot.

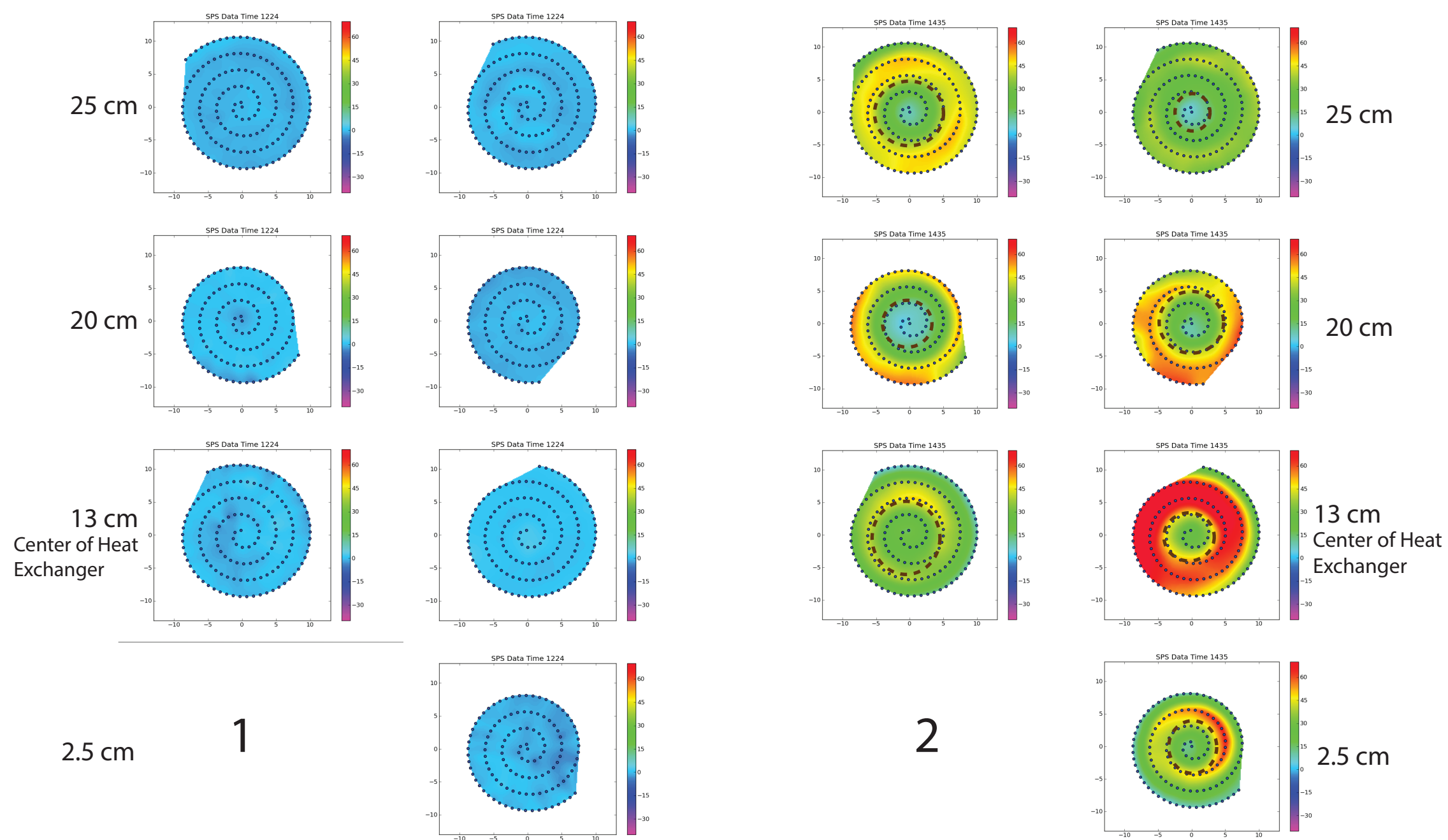
Results

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 increase observed due to further dissociation.

After each temperature step, the system quickly reached steady state; additional energy was consumed maintaining 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 teresstial hydrate reservoirs [9].

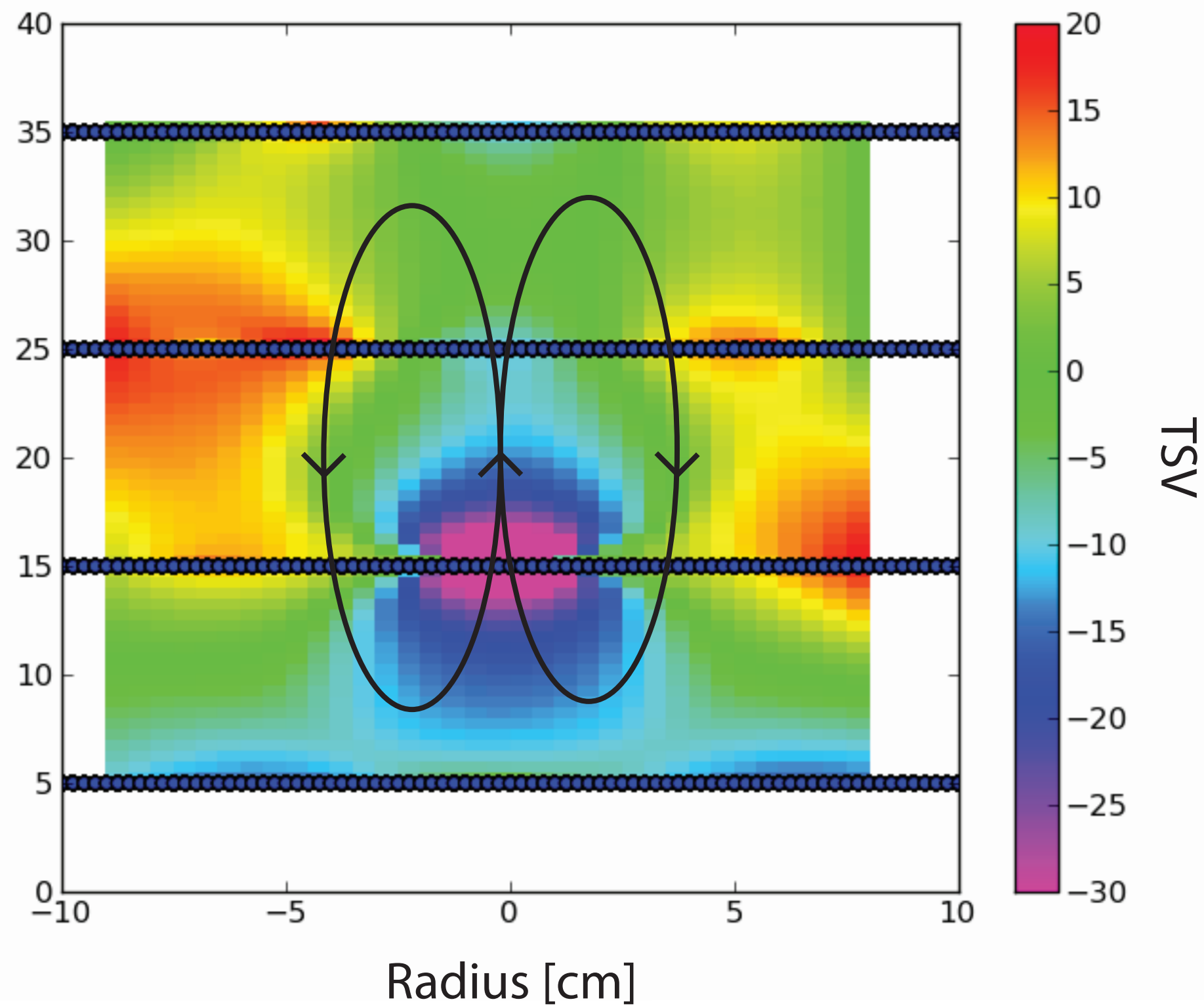


Results (cont.)



The difference between the output and input fluid temperature ( $\Delta T$ ) increases each time the input temperature is raised, confirming that more energy is being transferred to the system. Expansion due to increased temperature of the bulk sand cannot account for the total rise in pressure observed at each fluid temperature increase. Also note how the pressure drops quickly as soon as heat is removed from the heat exchanger, despite the relatively slow decrease in the bulk temperature. This suggests rapid clathrate reformation as soon as the heat source is removed.

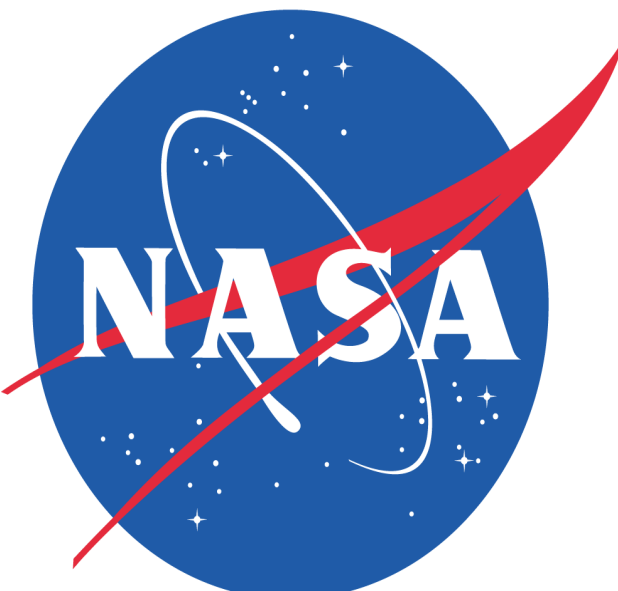
The DSS plots on the left (#1 above) show the initial conditions of the system before heat was introduced. These measurements show a homogeneous temperature distribution indicating the system was at equilibrium. The DSS plots on the right (#2 above) are after the system was subjected to four heating 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 (indicated by dashed lines). Areas where hydrate has dissociated are indicated by cool areas due to the endothermic nature of hydrate dissociation.



A vertical cross section through the sediment column. The area in-between DSS planes suffers from some interpolation artifacts due to the large ratio of vertical sensor spacing to horizontal sensor spacing. The area around the heat exchanger exhibits cold TSV values indicating hydrate dissociation. The nearly symmetric TSV profile suggests that convective fluid movement likely plays an important role in heat distribution in addition to conductive heat transfer.

Conclusions

Events common in planetary settings such as dike swarms, hot fluid flow through fractures in the rock, and extra-planetary interactions such as small impact events can result in short-duration heating which may result in rapid gas release from subsurface clathrate reservoirs. Short heating events appear to evolve gas very rapidly, but incompletely dissociate the reservoir. Depressurization events result in a slow release of gas [10], but have the potential to decompose an entire body of clathrate. Heating and depressurization are likely at work in most settings, otherwise the system would reach a steady state quickly due to overpressurization or endothermic cooling.



[1] Mumma M. J. et al. (2003) Science, 323, 1041- 1045. [2] Elwood Madden M. E. et al. (2010) Planetary and Space Science, In Press. [3] Root M. J. et al. (2010) LPS XXXI, Abstract #1705. [4] Kieffer S. W. et al. (2004) Science, 314, 1764-1766. [5] Choukroun, M. et al. (2010) Icarus, 205, 581-593. [6] Prieto-Ballesteros, O. et al. (2005) Icarus, 177, 491-505. [7] Rawn C. J. et al. (2011) Review of Scientific Instruments, In Press. [8] Leeman, J.R. et al. (In Review) Computers and Geosciences. [9] Hornbach M. J. et al. (2008) Journal of Geophysical Research, 113. [10] Leeman, J.R. et al. (2010) LPS XXXI, Abstract #1418.

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