ORNL Capabilities for Studying Clathrate Hydrates

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ORNL Gas Hydrates Workshop
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OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

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Prior Funding and Ancillary Equipment

- LDRD (FY01 and 02) support for building a pressure cell to be used for collecting in-situ neutron diffraction data
- Fossil Energy support - for purchasing ancillary equipment to study natural samples
  - Low Temp XRD
  - 2nd pressure cell for Raman (Michael Lance)
  - Low temperature stage for Raman (Michael Lance)
  - Diamond Anvil Cell for experiments at NSLS
  - Thermophysical properties (Hsin Wang)
  - SANS (Jane Howe and Camille Jones)
  - Natural Samples provided by Roger Sassen

Transporting, Storing, and Handling of Samples

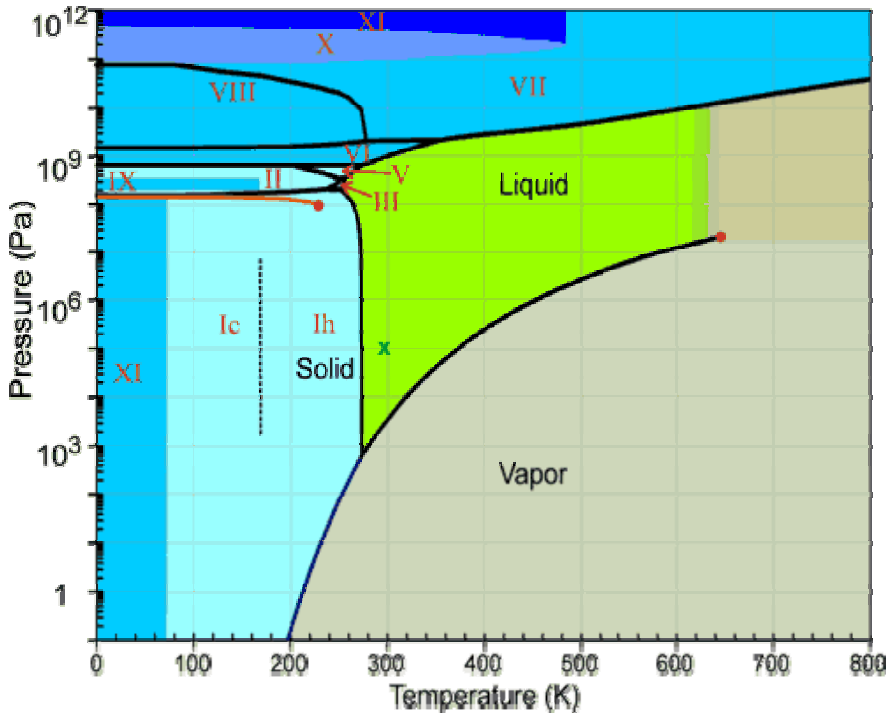
Hydrate-filled V cans were quickly removed, sealed, then stored at LN temperatures for subsequent transport in a dry shipper.

Samples are loaded for data collection in flowing He.

Diamond Anvil Cell (DAC) for high pressure studies

Cold loading of methane hydrates

Used on Beamline X17C at NSLS

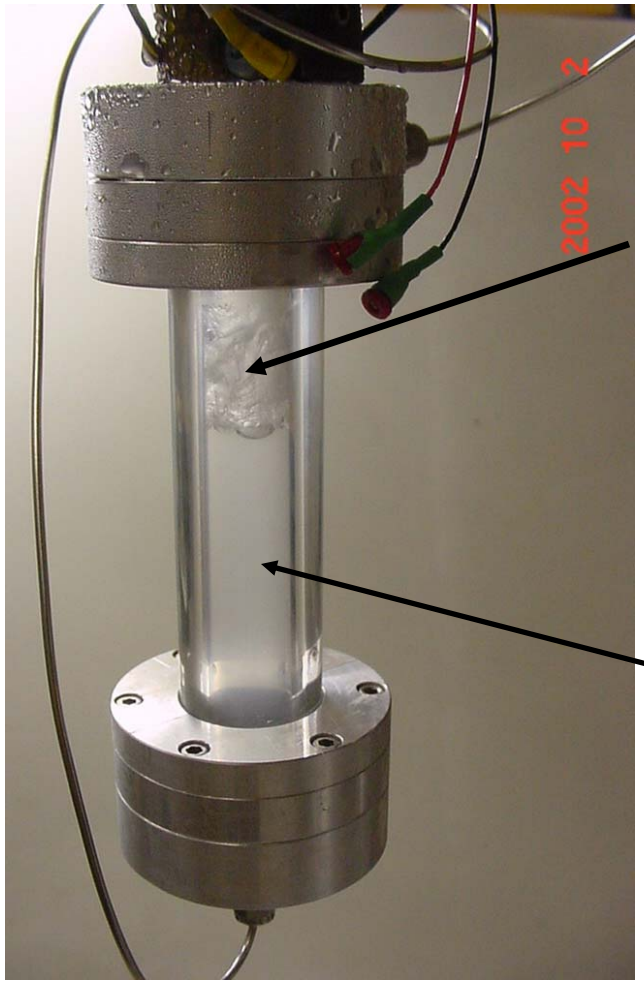


data collected above 4 GPa on mixture of H_2O and trimethylene oxide

A pressure cell for the synthesis of gas hydrates from water and gas has been constructed and tested

The pressure cell is constructed from a machined single crystal of sapphire and is designed to study samples using in-situ neutron powder diffraction.

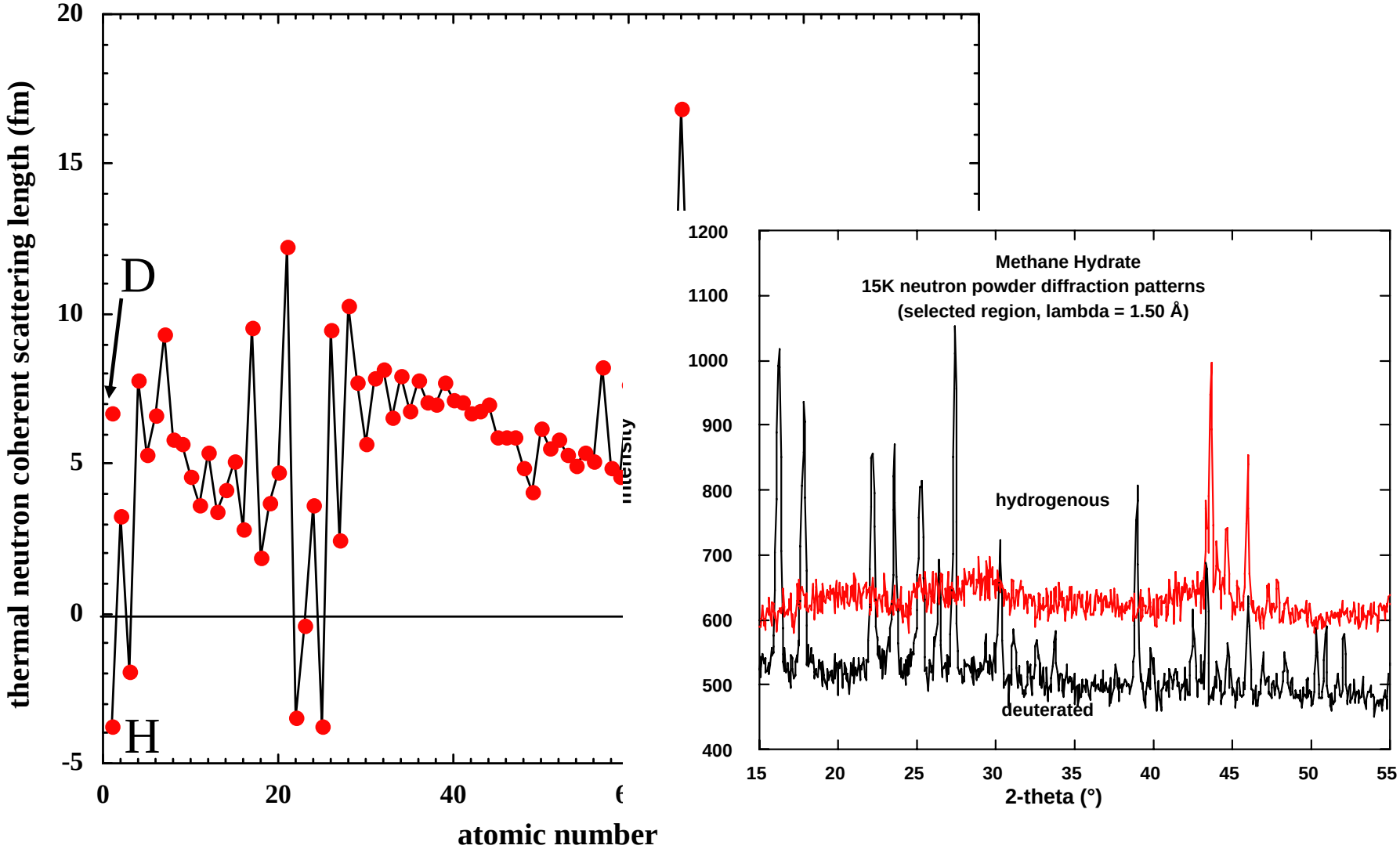
- This cell will allow us to study
  - the formation and decomposition of gas hydrates as a function of pressure
  - how the atomic structure changes as a function of pressure
    - from unit cell refinements we can calculate the bulk moduli
- This cell is available to researchers from US industry and academia through DOE user programs (HFIR, HTML).



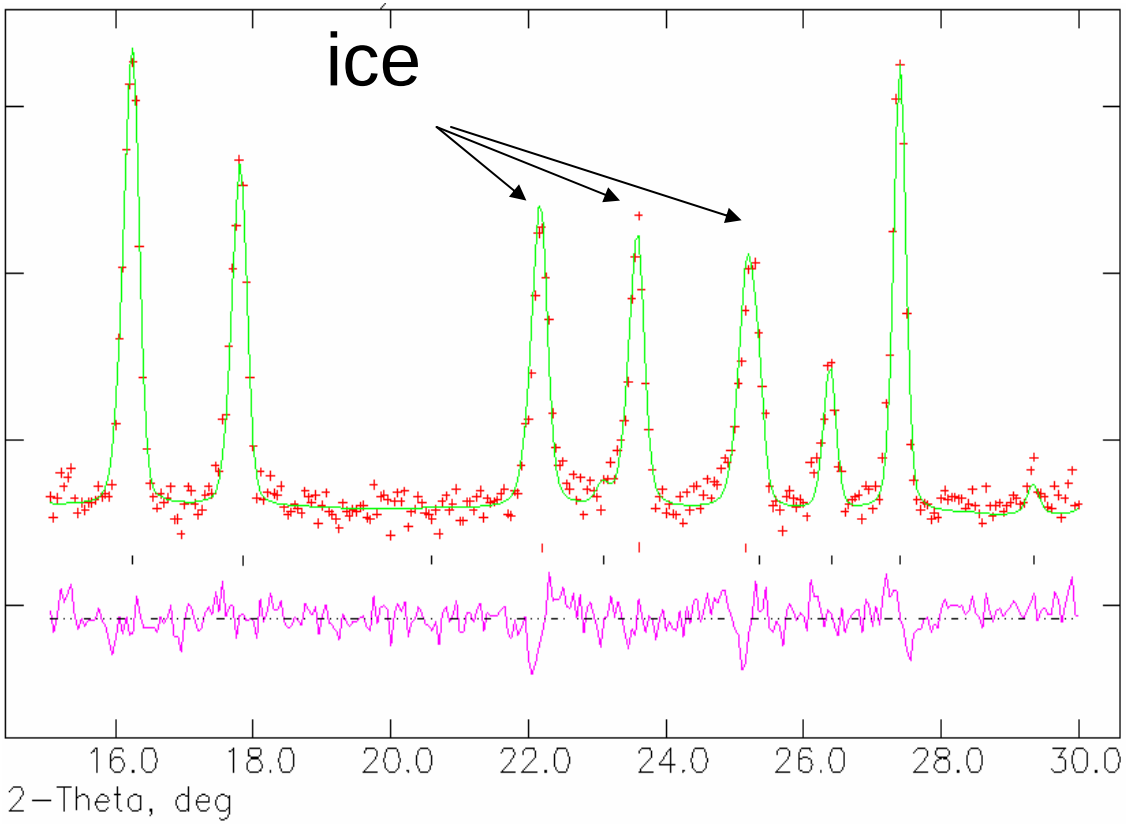
Methane hydrate forming at 2000 psi, 280K

Water

Neutron powder diffraction is an ideal technique for studying samples synthesized with D_2O



In some of the laboratory synthesized samples both gas hydrate and ice were present



47 variables, including variables associated with ice as a secondary phase,were used in the Rietveld refinement

ORNL data

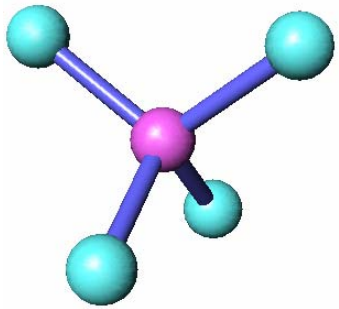
Temp (K)	*a* (Å)
11	11.832(1)*
35	11.834(2)
60	11.840(2)
85	11.848(2)
110	11.858(2)
135	11.868(2)
160	11.870(2)
175	11.873(2)
185	11.872(2)
190	11.873(2)
195	11.873(2)
200	11.874(2)
205	11.875(2)

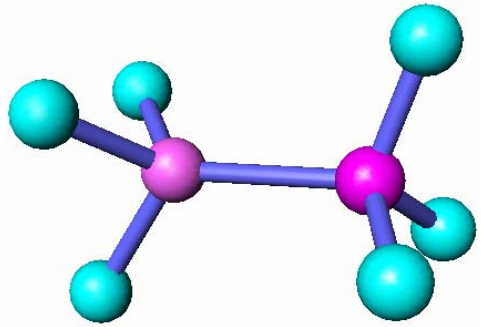
***esd 3σ**

Rotational disorder of the guest molecules have been modeled by describing them using the rigid-body formalism

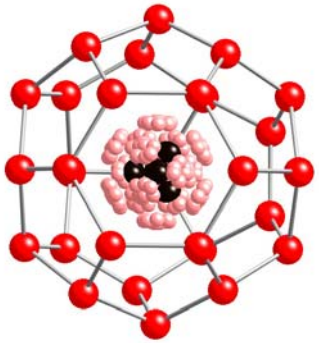
Geometrical constraints are applied to the molecules, with translational, librational, and screw motion tensor descriptions.

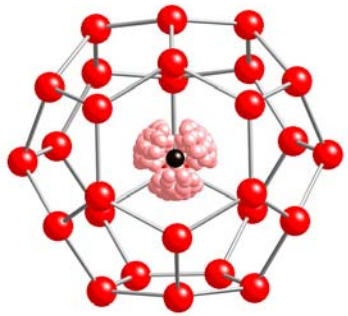
CH_4

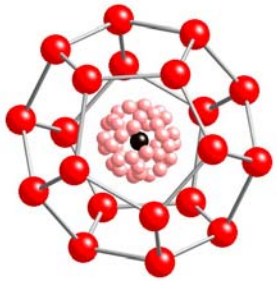




C_2H_6







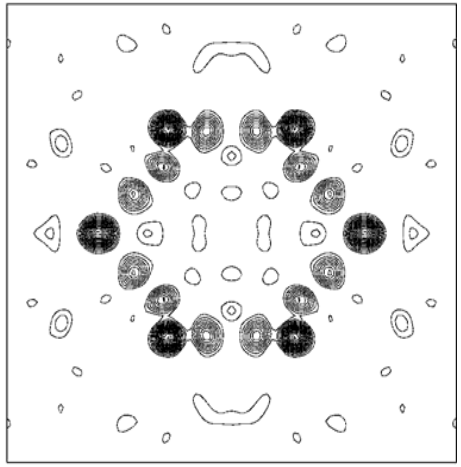
Describing caged molecules modeled with rigid body formalism

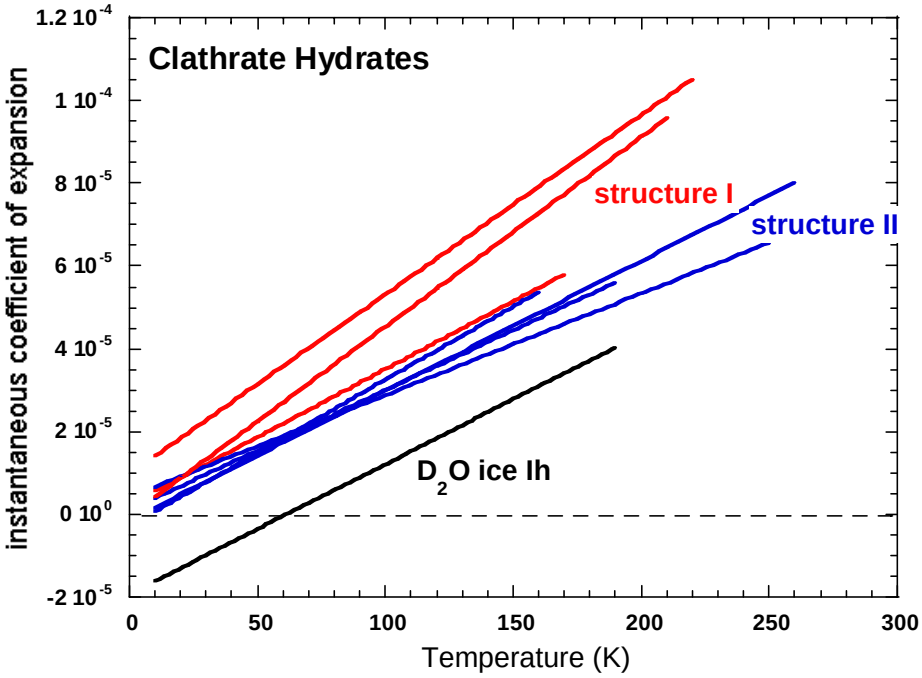
- Accounts for preferred positions within cages
- Yields bond length changes in caged molecules
- Yields mean-square displacement of cage occupant
- The temperature dependence of the T tensor yields another measure of the positional disorder

In-situ Neutron Diffraction Studies of Clathrate Hydrates

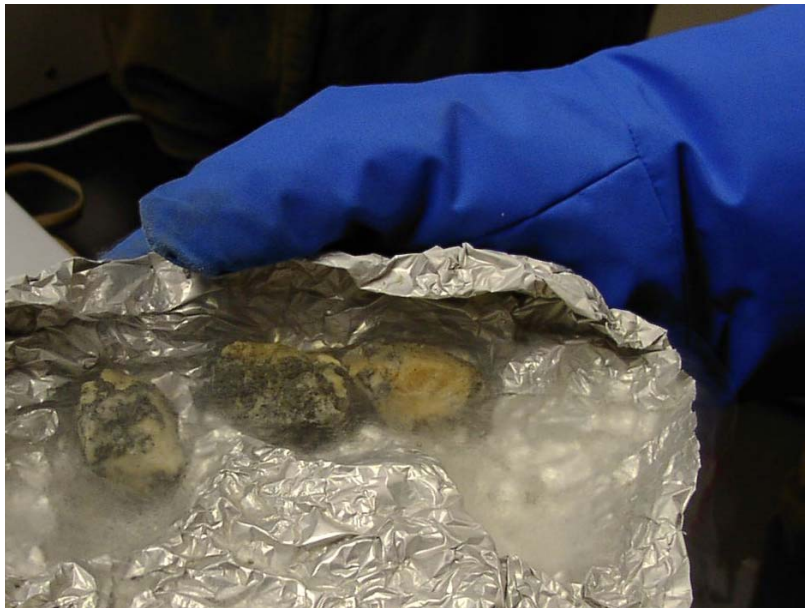
- Seven different laboratory synthesized clathrate hydrates have been studied using low temperature neutron powder diffraction.
- From the low temperature neutron diffraction data the lattice parameters as a function of temperature have been determined. From this data the thermal expansion has been calculated.
- Decomposition of gas hydrates as a function of temperature
- Determine the amount of ice present as a secondary phase
- Determined cage volumes and atomic displacement parameters as a function of temperature

F_{obs} map of a hexagonal face CO_2 hydrate at 100 K





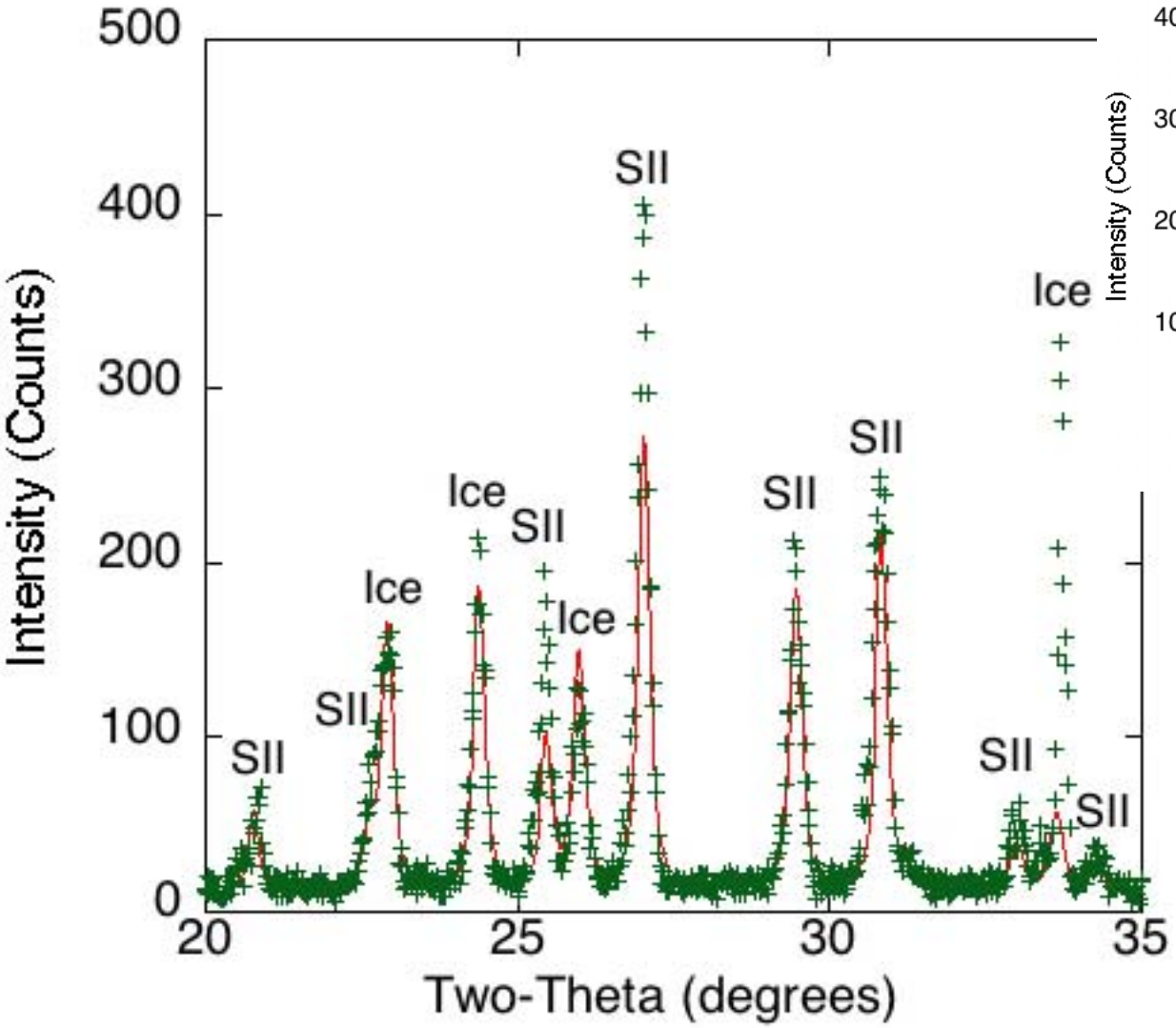
Complementary techniques were used to study natural samples formed from seawater

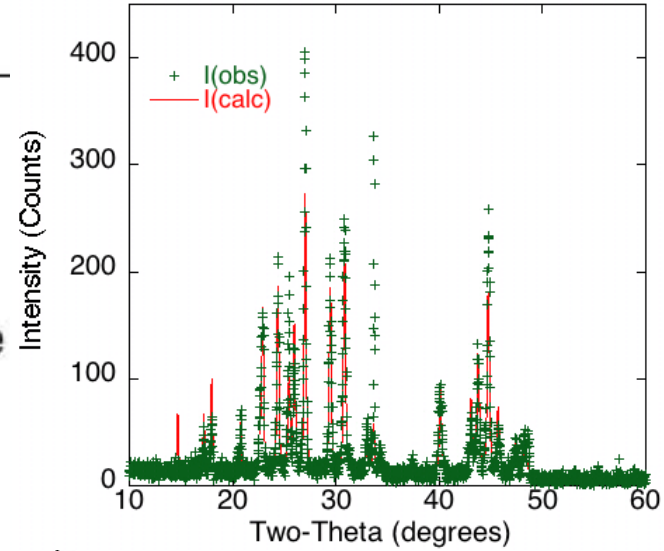


Natural Samples - GC232 and GC234
Recovered from the Green Canyon in the
Gulf of Mexico continental slope, southwest of the Mississippi Delta
Courtesy Prof. Roger Sassen, Texas A&M University

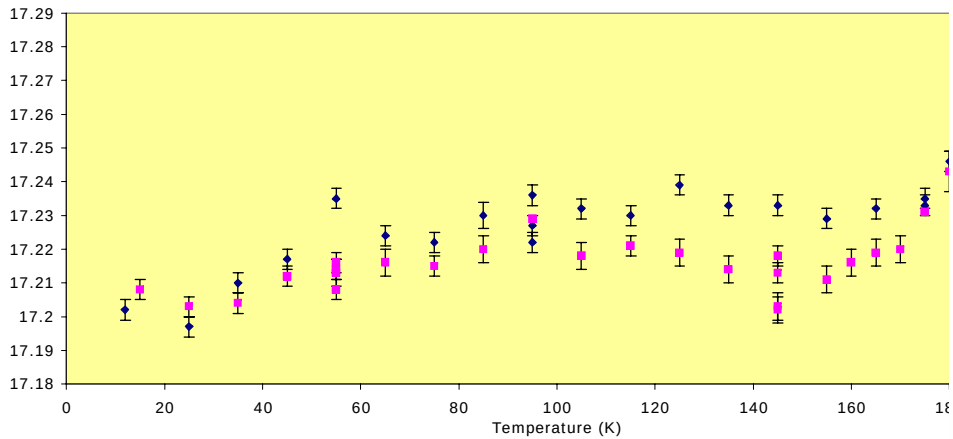
http://www-gerg.tamu.edu/menu_RGD/index.asp.

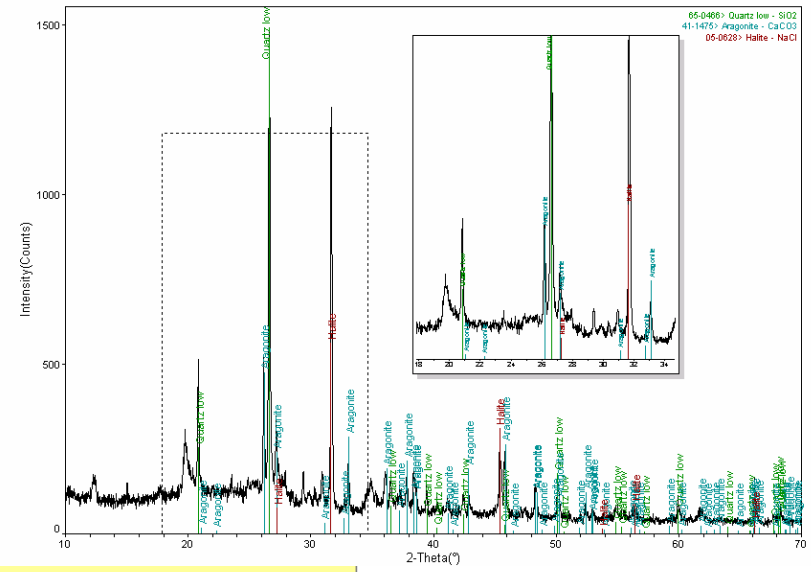
Low temperature x-ray powder diffraction was used to study natural samples

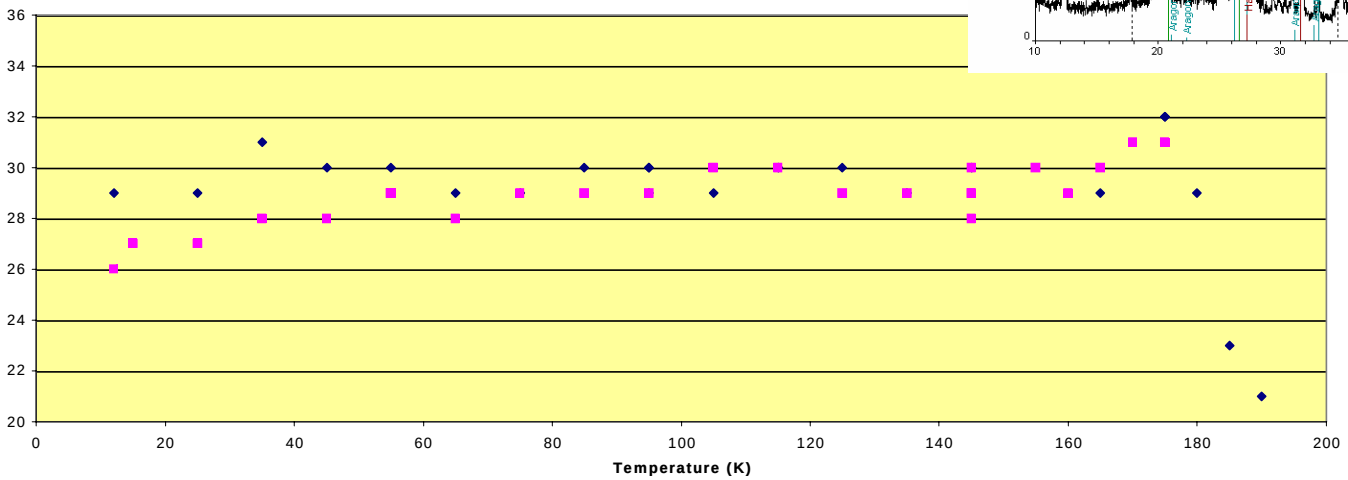




Low temperature x-ray diffraction results indicated that the samples decomposed at approximately 190 K and had SiO_2, NaCl, and $CaCO_3$ are present from the sediment







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Summary

- LDRD money support the construction of high pressure cell to synthesize and study gas hydrates in-situ.
- FE money supported the purchase and installation of ancillary equipment to study natural gas clathrates as a function of pressure and/or temperature.
  - Raman
  - LTXRD
  - Thermophysical properties
  - DAC
- This equipments is available for collaborations.

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