Oil & Natural Gas Technology

DOE Award No.: DE-FE0009897

Quarterly Research Performance Progress Report (Period ending 9/31/2013)

Hydrate-Bearing Clayey Sediments: Morphology, Physical Properties, Production and Engineering/Geological Implications

Project Period (10/1/2012 to 9/30/2016)

Submitted by:
J. Carlos Santamarina

Georgia Institute of Technology
DUNS #: 097394084
505 10th street
Atlanta , GA 30332
e-mail: jcs@gatech.edu
Phone number: (404) 894-7605

Prepared for:
United States Department of Energy
National Energy Technology Laboratory

Submission date: 10/31/2013

Office of Fossil Energy

ACCOMPLISHMENTS

Context – Goals. *Fine grained sediments host more than 90% of the global gas hydrate accumulations. Yet, hydrate formation in clayey sediments is least understood and characterized. This research focuses on* *__hydrate bearing clayey sediments__*. *The goals of this research are (1) to gain a fundamental understanding of hydrate formation and ensuing morphology, (2) to develop laboratory techniques to emulate "natural" formations, (3) to assess and develop analytical tools to predict physical properties, (4) to evaluate engineering and geological implications, and (5) to advance gas production alternatives to recover methane from these sediments.*

Accomplished

The main accomplishments for this period include:

- X-ray CT system improvement and regulatory requirements
  - Interlock and alarm light design
  - PI and Student safety training and system control
  - First images acquired
  - Optimization of system parameters, trade offs
- Continued literature review and analyses
  - Hydrate topology differences among Indian, Korean, and US sites
- In-Lab CO_2 hydrate formation in clay
  - Hydrate formation in mini samples
  - Hydrate formation in unsaturated clay
- In-Lab THF hydrate formation in clay
  - Hydrate formation in a clay paste

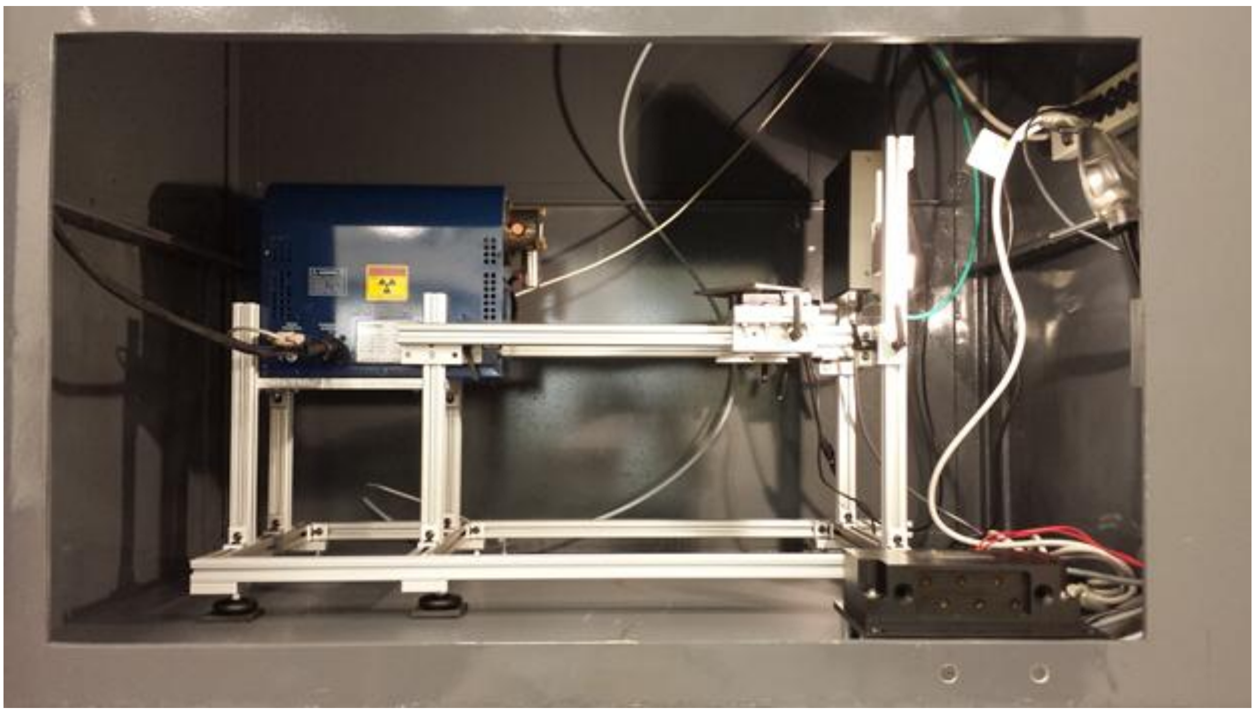
Plan - Next reporting period

Optimize the X-ray CT system and scanning procedure. Design and construct a new chamber especially for the hydrate formation in clay while considering constraints placed by both the X-ray CT system and pressure-temperature requirements. Further formation of THF hydrate in clay will be completed to better analyze hydrate lens morphology and topology. Additional CO_2-CH_4 hydrate replacement trials will be conducted.

Research in Progress

Imaging System: MicroCT for high pressure specimens

The X-ray microCT scanner has been completely assembled and has been certified through Georgia Tech's Office of Radiological Safety. Proficiency in the automation software for the simultaneous control of the x-ray source, detector, and rotary stage is being developed. As well, the experimentation of various software programs for the visualization and eventual analysis of the images is being performed.



Equipment	**X-ray Source**	**X-ray Detector**	**Rotary Stage**
Brand and Model	ThermoScientific PXS10	Varian PaxScan 1313	Zaber T-RSW Motorized Stage

Figure 1. Close up of tomographic system inside shield cabinet.

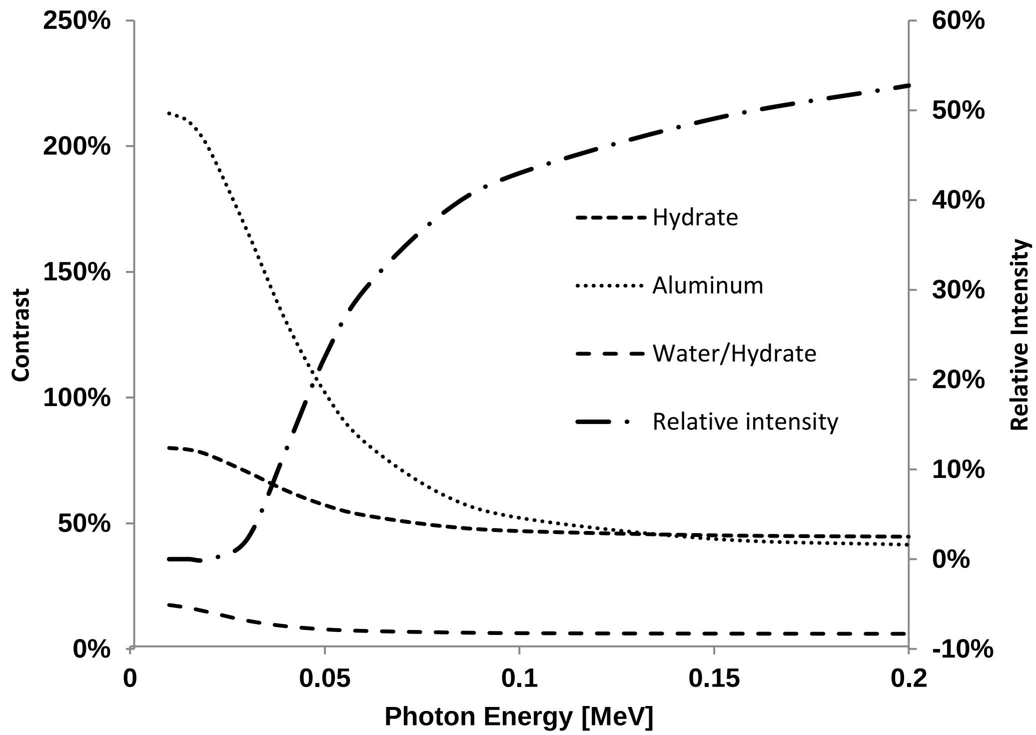


Figure 2. Tradeoff between contrast and signal intensity (Data Source: NIST)

Relative intensity is defined as the intensity penetrating the specimen over the original intensity. Here the specimen is wet kaolinite (water content 50%, no gas phase assumed) in an aluminum tube. The thickness of the chamber is 4.8 mm (two walls), and the thickness of the kaolinite sediment is 20 mm.

Comparison of Hydrate Topology at Blake Ridge, Ulleung Basin, and Krishna-Godavari Basin.

Understanding the topology of hydrate-filled fractures in nature is critical to the methodology by which hydrates are formed in the laboratory. Three distinct sites, Blake Ridge, US, Ulleung Basin, Korea, and Krishna-Godavari, India, where the existence of hydrates have been extensively characterized, were chosen for a comparison study to better understand why hydrate lenses form in the orientations in which they do.

Table 1. Topology comparison of hydrate-filled fractures at various sites

Location	Depth to Sea Floor [m]	GHSZ [mbsf]	Dip Angle	Dip Direction
Blake Ridge, US (a,b)	2700	200-450	55°	
Ulleung Basin, Korea (c)	1800-2100	5-150	43°-63°	W-SW
Krishna-Godavari Basin, India (d,e)	1000	Variable, 56-94,106-210, 170-200,	60°	Varying

a) Holbrook et al. 1996 b) Hornbach 2008, c) Kim et al. 2013, d) Riedel et al. 2010, e) Cook 2010

The resolution by which in-situ hydrate formations can be effectively evaluated improved by the implementation of the Resistivity-at-the-Bit (RAB) imaging, whereby the resistivity around the drill bit is continuously recorded while drilling occurs, which provides much more conclusive evidence of detailed fractures versus more traditional seismic reflection studies. Additional, x-ray computed tomography scanning of pressure core samples allows for even higher resolution images of fractures, and proves the existence of fine, horizontal fractures that RAB and seismic reflection images fail to resolve. Specifically, Blake Ridge has only been analyzed using seismic reflection data, while both Ulleung and Krishna-Godavari basins have been evaluated using all three of the before mentioned tools. Data in Table 1 are averaged data obtained using only seismic reflection for Blake Ridge, and RAB data for the other two locations. The dip direction correlates well with the stress field.

CO_2 Hydrate Formation in Clay

Water saturated and unsaturated specimens with ice lenses were subjected to various P-T paths (example bellow). Careful observation of the P-T and photographic record reveals:

- The heat liberated during the CO_2 hydrate formation (391-418kJ/kg) is greater than the latent heat absorbed during the ice melting (334kJ/kg); this excess heat facilitates ice-to-hydrate transformation.
- The temperature when hydrate forms from ice is lower than the melting temperature of ice (clear evidence starting at about -1.7 °C).
- Hydrate formation nucleates on ice surfaces and pulls water from the surrounding environment to sustain hydrate growth.
- The final hydrate lens has a different shape than the original ice lens.

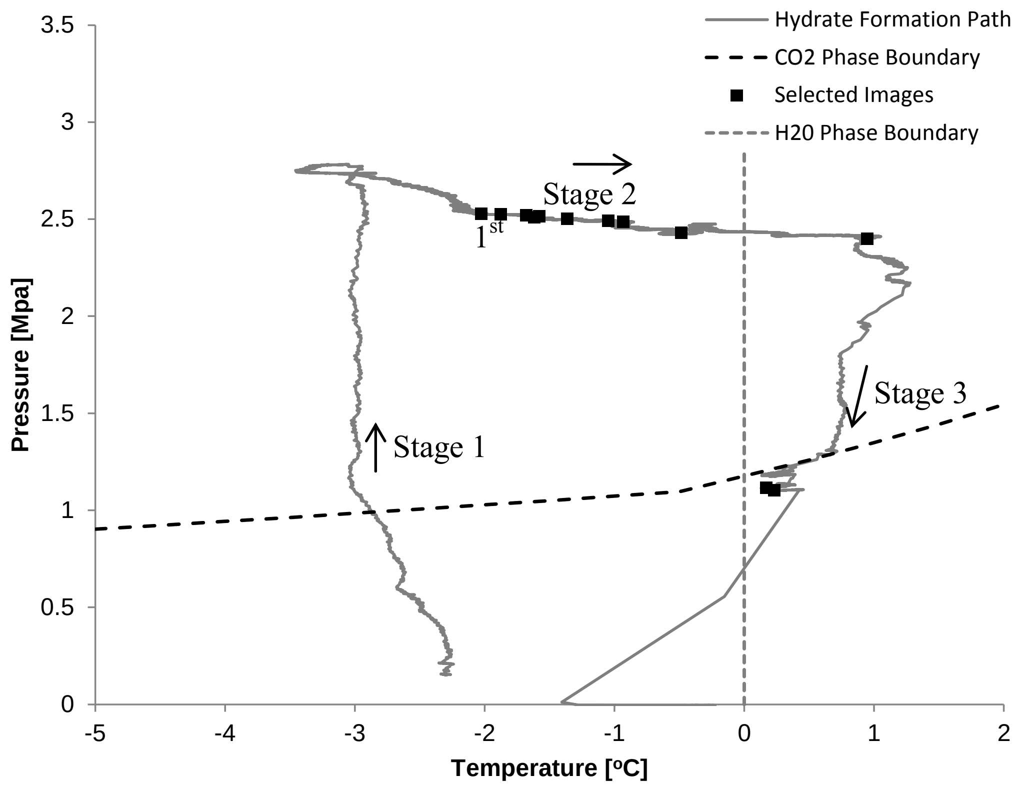


Figure 3. Pressure-Temperature path of hydrate formation and dissociation in clay specimens with segregated ice lenses. The twelve points correspond to the selected images shown in Figures 4 and 5, where the first image point is labeled on the figure and proceeds in a clockwise fashion.

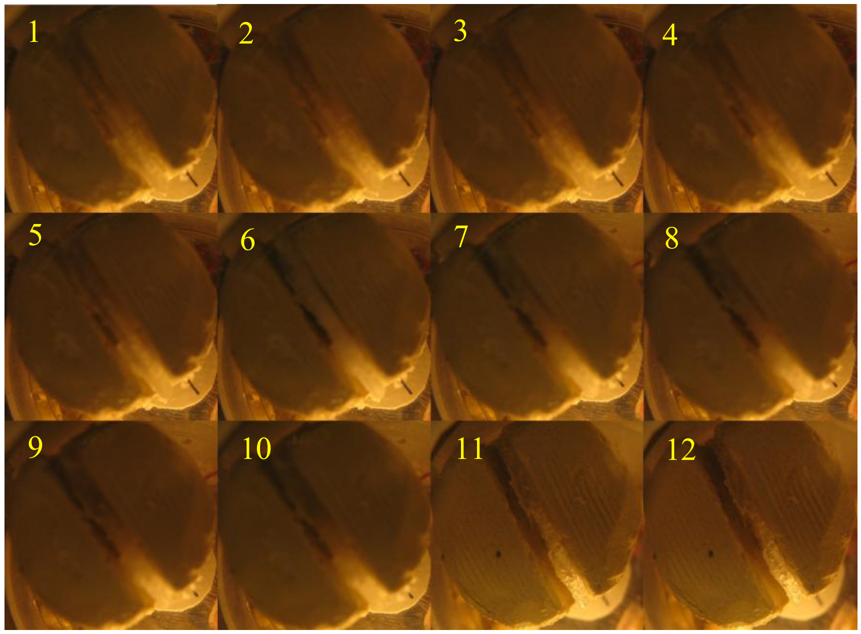


Figure 4. Unsaturated clay with ice lens in between. No obvious changes occur before the first image. The 2nd-10th images show the evolution of the lens during hydrate formation. In the 2nd-5th images, the gap on the right ride of the lens is gradually filled with hydrate, and in the 6th-10th images, hydrate formation at the expense of ice melting or possible Ostwald Ripening. Contact point/surface between lens and unsaturated soil changes, both the position and shape. The last two images show the shape of hydrate lens during the dissociation process.

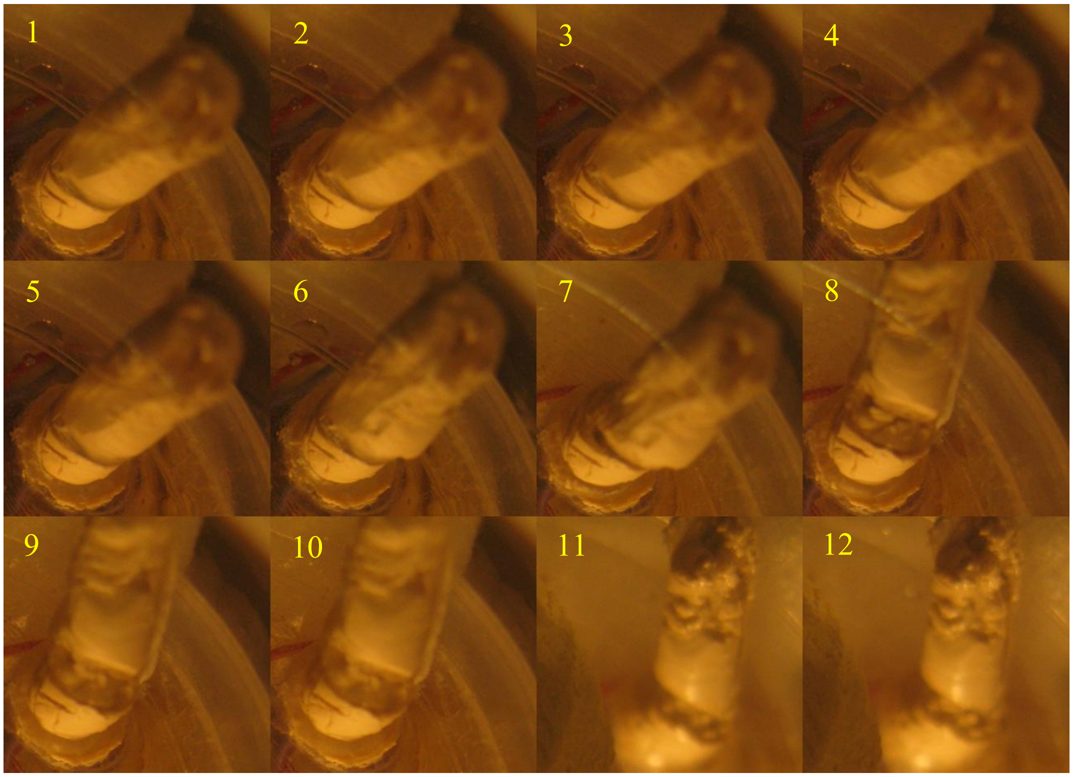


Figure 5. Saturated clay column (water content 125%), subjected to freezing before pressurization with CO_2. No obvious changes occur before the first image. The 2^{nd}-10^{th} images show sample deformation during the hydrate formation. Hydrate forms by using the available water trapped in ice lenses in the column at -1.7 °C (the upper part of the column rotates due to volumetric changes in ice lenses). The sample remains standing through the first two stages. The 11^{th} and 12^{th} images show the deformation during hydrate dissociation, where the shiny surface indicates the presence of a water film; the sample gradually collapses hydrate dissociation.

THF Hydrate Formation in Clay

Tetrahydrofuran (THF) is commonly used as substitute for CH_4 when studying hydrate systems since THF is completely miscible in water and forms Structure II hydrates at ~4°C at standard atmospheric pressure. The stoichiometric ratio of THF hydrate formation is 1THF:17H_2O, or 19% weight THF of the total solution.

Experimental Procedure. Kaolinite clay was mixed with a 1:17 molar ratio THF-water solution to form a clay paste with a "fluid mass content" of 120%. The paste was placed in a controlled cooling bath where the temperature was steadily decreased from 5°C to 1°C over 12 hours.

X-ray CT Imaging. The specimen within a thin, steel walled container was then imaged using the microCT scanner. Horizontal and vertical slices are show in the figure below. For comparison, images on the right correspond to a frozen clay specimen (at similar water content). Results show hydrate formation biased by thermal boundary conditions (bottom cooling followed by side cooling). Both ice and hydrate formation show segregation into lenses, and the consequences of "cryogenic suction" during hydrate formation on successive hydrate or ice-lens formation.

While topological differences between hydrate and ice lens formation are under investigation, it is important to highlight that crystallization leads to segregation in both cases. Implications on the physical properties of hydrate bearing clays measured at GT during the last decade will be explored next.

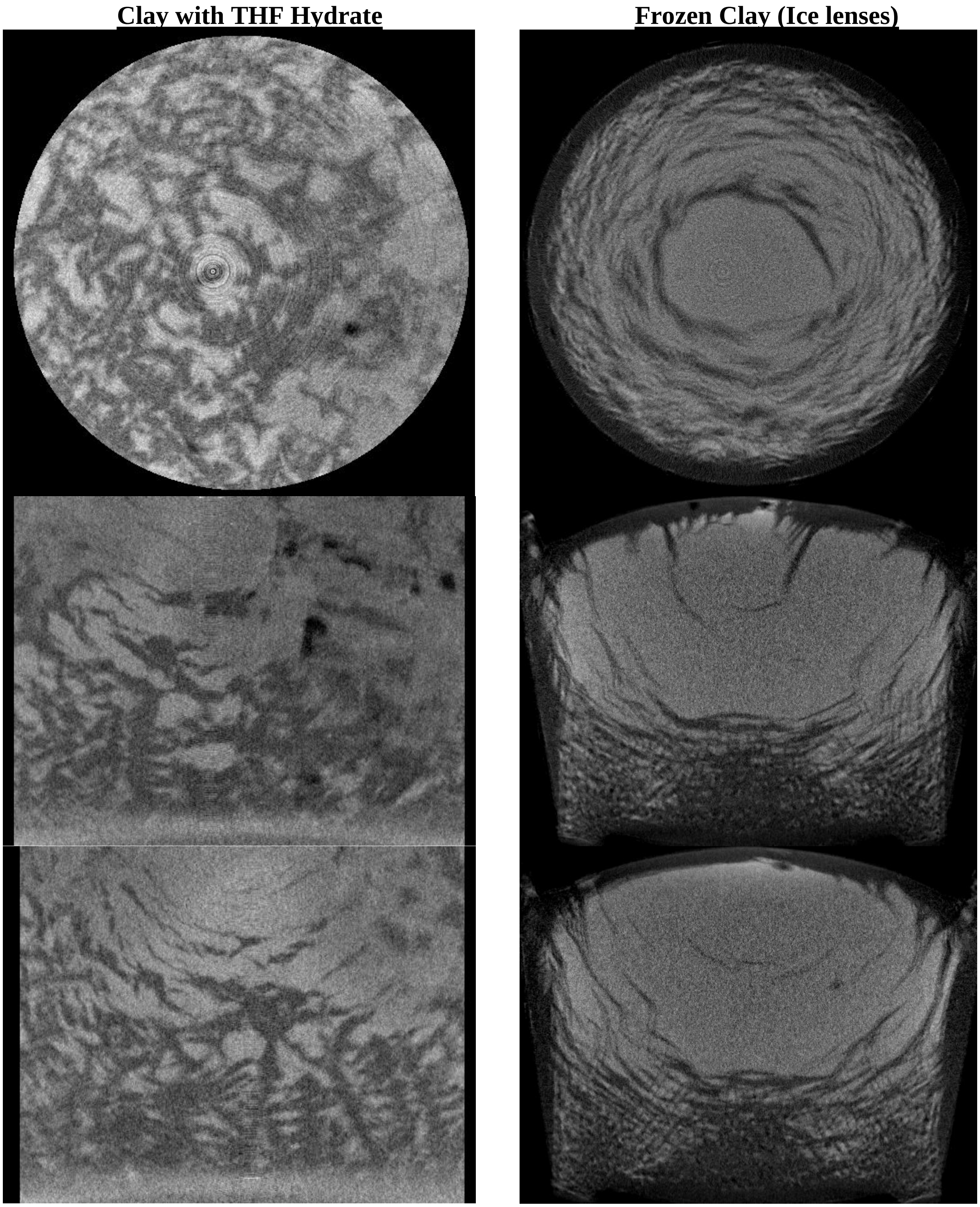


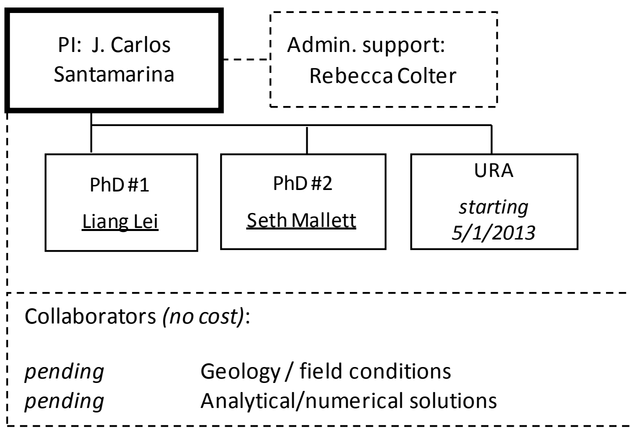
Figure 6. Clayey sediment during (left) THF hydrate formation and (right) freezing and ice lense formation

PRODUCTS

- **Publications – Presentations:** None at this point
- **Website:** Publications (for academic purposes only) and key presentations are included in http://pmrl.ce.gatech.edu/.
- **Technologies or techniques:** None at this point.
- **Inventions, patent applications, and/or licenses:** None at this point.
- **Other products:** None at this point.

PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

Research Team: The current team is shown next. We anticipate including external collaborators as the project advances



IMPACT

While it is still too early to assess impact, we can already highlight preliminary success of exploring hydrate lenses morphology in real systems, and analogue studies using a high resolution tomographer.

CHANGES/PROBLEMS:

None so far.

SPECIAL REPORTING REQUIREMENTS:

We are progressing towards the required check point on the ability to obtain high resolution images of hydrate bearing clayey sediments.

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

13131 Dairy Ashford Road, Suite 225
Sugar Land, TX 77478

1450 Queen Avenue SW
Albany, OR 97321-2198

Arctic Energy Office
420 L Street, Suite 305
Anchorage, AK 99501

Visit the NETL website at:
www.netl.doe.gov

Customer Service Line:
1-800-553-7681