

## GAS HYDRATES UP CLOSE WITH SCANNING ELECTRON MICROSCOPY

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One of the challenges of investigating natural and lab-made gas hydrates has been to examine the grain and pore structures of these materials, characteristics that are revealing guides to the physics and chemistry of hydrate growth and the effects of changes in environmental conditions. Yuri Makogan of Texas A&M and Dendy Sloan at the Colorado School of Mines are leaders among those groups who have used pressurized optical cells to investigate the growth of gas clathrate hydrates in the laboratory (1, 2). Scanning Electron Microscopy (SEM) also offers significant potential for providing additional information due to its greater resolution capabilities and large depth of focus. Kuhs et al. (3) have reported success in using cryo-SEM techniques to image and identify grain structures in CH<sub>4</sub>, CO<sub>2</sub>, and Ar hydrates prepared from reaction of ice with gases or liquids.

Technical hurdles of gas hydrate imaging involve avoiding condensation on samples during cold transfer, coating the samples without introducing heat or damage to the sample surface, maintaining the sample material at conditions that avoid spontaneous decomposition or significant sublimation under vacuum, and avoiding electron beam damage of the imaging area. In February of this year we took delivery of a Gatan Alto 2100 crysystem that was installed on our LEO 982 field emission SEM at the USGS in Menlo Park, California. Gatan has largely circumvented the problems listed above by creating a sample preparation chamber that allows for cold transfer of samples to the vacuum system, maintenance of cold temperatures while samples are cleaved to reveal fresh surface material, and cold coating with gold-palladium to prevent electrical discharge under the beam. Samples are then vacuum transferred to an auxiliary cold stage installed in the SEM chamber. Purchased using NASA funds to look at planetary ices, we have also used this attachment to image a suite of gas hydrate samples made in our laboratory for physical property testing (4). This work was supported by the National Methane Hydrate R&D Program and the USGS Gas Hydrate Project. While our findings are preliminary, the SEM images are remarkable and very revealing of the fundamental grain and pore characteristics of our sample material after synthesis, compaction, pressure-temperature processing, and/or deformation. We find that distinguishing hydrate from ice can be quite challenging in some instances, although the use of sublimation and/or surface decomposition techniques can aid in identification of the material under investigation. We also find that extreme care must be taken to avoid producing sample surface artifacts, and to distinguish them from intrinsic sample surface morphology.

Several SEM micrographs of our lab-synthesized gas hydrates made from heating granular ice with pressurized gas are shown below. Their captions indicate our preliminary interpretations of the grain and pore morphology. These micrographs reveal fairly uniform sample textures of well-crystallized hydrate material with crystal-face development exposed along pore walls. Our initial success with this system persuades us that it will be an extremely useful tool in resolving the surface morphology of both lab-made and natural gas hydrates. Such comparisons should help us decide how close to the mark our efforts are to emulate gas hydrates in nature, and should also greatly aid in the interpretation of physical property measurements made on these materials.

<sup>1</sup> Makogan, Y. F. Hydrates of Hydrocarbons. Pennwell Publishing, Tulsa, 1997.

<sup>2</sup> Sloan, E. D. Jr., Clathrate Hydrates of Natural Gases, 2<sup>nd</sup> Ed., Marcel Dekker, New York, 1998.

<sup>3</sup> Kuhs, W.F., Klapproth, A., Gotthardt, F., Techmer, K. & Heinrichs, T. The formation of meso- and macroporous gas hydrates. *Geophysical Research Letters*, vol. 27 (18), p. 2929-2932, 2000.

<sup>4</sup> Stern, L., Kirby, S., Durham, W., Circone, S., and Waite, W. Synthesis of pure methane hydrate suitable for measurement of physical properties and decomposition behavior. Chapter 25, in: *Natural Gas Hydrate: In Oceanic and Polar Subaerial Environments*; Max, M.D., Ed., Kluwer: Dordrecht, p. 323-349, 2000.

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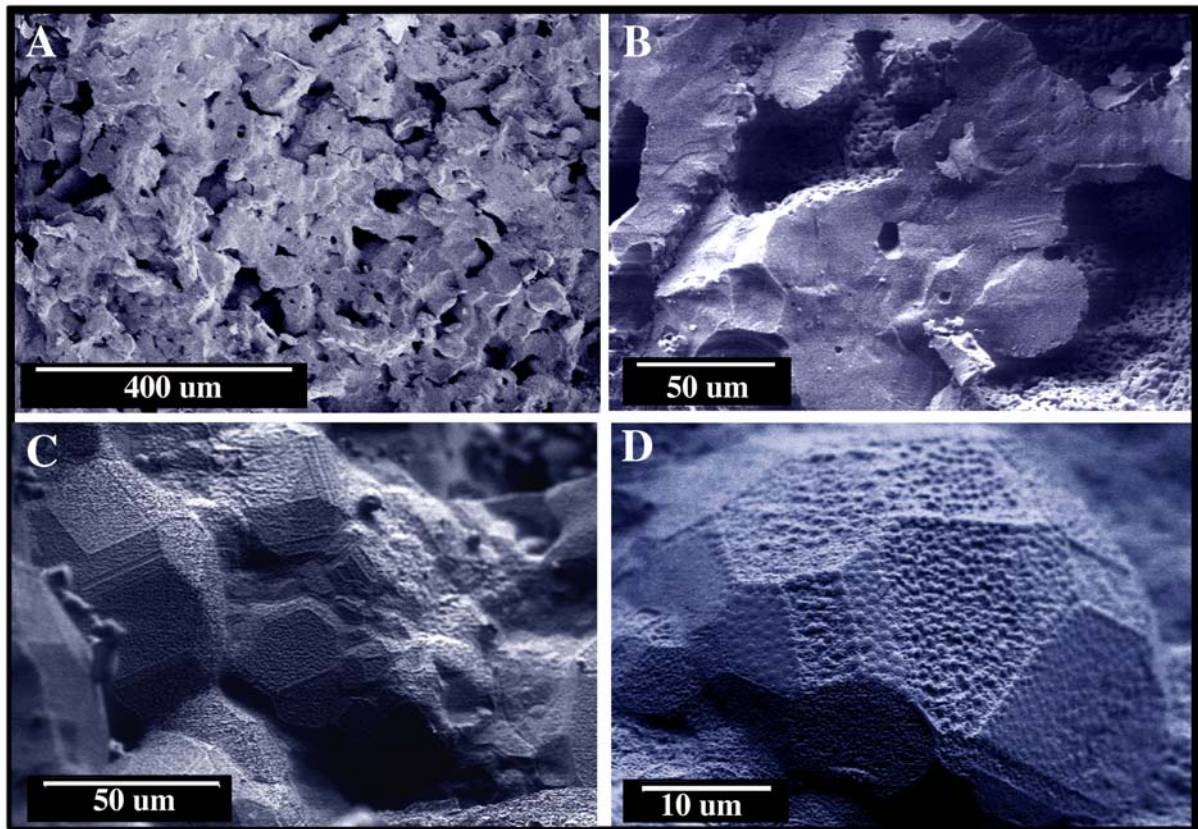


Figure caption: SEM images of pure, polycrystalline methane hydrate made by reacting granular ice with cold, pressurized methane while heating through the ice melting point: (A) Low magnification. This granular-but-cohesive texture is quite different from the simple spherical grain shapes, average grain size (200 micron) and geometrically-simple pore shapes of the granular ice from which it was made. This comparison indicates that fundamental changes take place in the grain and pore textures during conversion to hydrate. (B) Higher magnification reveals considerable recrystallization in forming the hydrate and more complex pore geometry than in the granular ice reactant. The “bumpy” surface texture of the pore walls is also different. (C) Features imaged along pore walls vary from sample to sample, but many of the “bumps” on the pore walls are small hydrate crystals with characteristic cubic-crystal faceting. (D) The highest magnification reveals tiny dome-shaped structures on these crystal facets that may be hydrate crystal growth structures. All samples were prepared, cleaved, coated, and imaged under high vacuum conditions at a temperature of about 110 K.