

Scanning Electron Microscopy investigations of laboratory-grown gas clathrate hydrates formed from melting ice, and comparison to natural hydrates

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ABSTRACT

Scanning electron microscopy (SEM) was used to investigate grain texture and pore structure development within various compositions of pure sI and sII gas hydrates synthesized in the laboratory, as well as in natural samples retrieved from marine (Gulf of Mexico) and permafrost (NW Canada) settings. Several samples of methane hydrate were also quenched after various extents of partial reaction for assessment of mid-synthesis textural progression. All laboratory-synthesized hydrates were grown under relatively high-temperature and high-pressure conditions from rounded ice grains with geometrically simple pore shapes, yet all resulting samples displayed extensive recrystallization with complex pore geometry. Growth fronts of mesoporous methane hydrate advancing into dense ice reactant were prevalent in those samples quenched after limited reaction below and at the ice point. As temperatures transgress the ice point, grain surfaces continue to develop a discrete “rind” of hydrate, typically 5 to 30 μm thick. The cores then commonly melt, with rind microfracturing allowing migration of the melt to adjacent grain boundaries where it also forms hydrate. As the reaction continues under progressively warmer conditions, the hydrate product anneals to form dense and relatively pore-free regions of hydrate grains, in which grain size is typically several tens of micrometers. The prevalence of hollow, spheroidal shells of hydrate, coupled with extensive redistribution of reactant and product phases throughout reaction, implies that a diffusion-controlled shrinking-core model is an inappropriate description of sustained hydrate growth from melting ice. Completion of reaction at peak synthesis conditions then produces exceptional faceting and euhedral crystal growth along exposed pore walls. Further recrystallization or regrowth can then accompany even short-term exposure of synthetic hydrates to natural ocean-floor conditions, such that the final textures may closely mimic those observed in natural samples of marine origin. Of particular note, both the mesoporous and highly faceted textures seen at different stages during synthetic hydrate growth were notably absent from all examined hydrates recovered from a natural marine-environment setting.