Methane hydrates are present in marine seep systems and occur within the gas hydrate stability zone. Very little is known about their crystallite sizes and size distributions as they are notoriously difficult to measure. Crystal size distributions are usually considered as one of the key petrophysical parameters as they influence mechanical properties and possible compositional changes, which may occur with changing environmental conditions. Variations in grain size are relevant for gas substitution in natural hydrates by replacing CH\textsubscript{4} with CO\textsubscript{2} for the purpose of carbon dioxide sequestration. Our investigations show that crystallite sizes of gas hydrates from some locations in the Indian Ocean, Gulf of Mexico and Black Sea are in the range of 200-400 µm; larger values were obtained for deeper-buried samples from ODP Leg 204. The crystallite sizes show generally a (log-) normal distribution and appear to vary sometimes rapidly with location.

Scientific and economic interest, however, is large to better understand the replacement kinetics in particular in the context of carbon dioxide sequestration projects achieved by gas replacement in hydrates. The mean crystal sizes of gas hydrates and the crystallite size distributions are of particular interest here, as the exchange rates will be contingent on the extent of the grain boundary networks. Likewise, the mechanical properties, in particular the deformation of gas hydrate aggregates depend on the distributions of crystallite sizes. It turns out that synthetic samples often have smaller crystallites sizes than natural samples and mechanical laboratory tests may not reproduce faithfully the situation in natural settings [1].

Gas hydrate crystallite size distributions are also important for our understanding of hydrate formation and evolution processes. The crystal size evolution is mainly governed by the free energy differences between grains, that is, the grain boundary surface energy and the contribution of deformational work to the free energy [2]. The data measured in December 2008 at the beam-line BW5 corroborate and extend information of crystallite size distributions of gas hydrates. Bragg tomography is at present the only tool to investigate gas hydrate crystallite size distributions systematically using the Moving Area Detector Method [3, 4].

It turns out that there is an order-of-magnitude difference in crystallite size of natural and most synthetic gas hydrate samples, although larger synthetic samples have been produced [5]. Shallow-buried, seepage associated marine gas hydrates from the Black Sea and Gulf of Mexico are 190-400 µm in size. Comparing the latter to deeper buried, larger hydrates from the Hydrate Ridge, suggests that hydrate crystals in marine environments may well be continuously growing. If the initial crystallite size distributions for a given p-T-x condition can be established, crystallite size information should give access to the formation ages of gas hydrates. Other factors that may influence the crystal size evolution are inhibitors such as salts/brines, particles or impurities in the grain boundary networks, or the crystal structure. What is needed to proceed further is a broader crystallite size distribution data base for various settings differing in their thermodynamic regime as well as the determination of the crystallite size distributions of freshly grown marine gas hydrates in designated sea-floor experiments and/or more realistic studies of gas hydrate crystal growth in laboratory work. The results of this work are submitted to "Geochemistry, Geophysics, Geosystems".
Figure 1. Crystal size distributions from hydrates sampled in eastern Black Sea seeps, measured with the Moving Area Detector Method. (A) Batumi Seep, GeoB 11927-7; (B) Batumi Seep GeoB 11956.

References


