

## The Impact of Porous Microstructures of Gas Hydrates on Their Macroscopic Properties

Werner F. Kuhs, Georgi Genov, Evgeny Goreschnik, Andreas Zeller and Kirsten S. Techmer  
GZG Abt. Kristallographie, Georg-August-Universität Göttingen, Göttingen, Germany

Gerhard Bohrmann  
Research Center Ocean Margins, Universität Bremen, Bremen, Germany

### ABSTRACT

Methane hydrates from both sub-permafrost and seafloor occurrences show a very particular microstructure as evidenced by scanning electron microscopy. These hydrates are frequently porous, with typical pore sizes ranging from 100 nm to 500 nm and occasionally reaching 1  $\mu\text{m}$ . The pores are predominantly closed with only occasional openings between them, and they are filled with methane gas. The gas-filling will affect the physical properties of gas hydrates. In particular, an increase in the attenuation of elastic waves can be expected. We suggest that the repeatedly observed combination of high seismic velocities and high attenuation in gas hydrate-bearing sediments may well be attributed to the presence of gas in the porous microstructures.

### INTRODUCTION

The general picture of a gas hydrate is that of a dense ice-like substance acting as a cement in sedimentary material, although very little is known about the actual microstructures in geological settings. Laboratory-grown gas hydrates of methane, carbon dioxide and nitrogen have been found to be mesoporous to macroporous (Kuks, Klapproth, Gotthardt, Techmer and Heinrichs, 2000). Meanwhile there is accumulated evidence that natural gas hydrates from both continental and seafloor occurrences show identical microstructures. In fact, all natural samples investigated so far by means of cryo-scanning electron microscopy show a very pronounced sub-micron porosity. In particular, samples from Hydrate Ridge (Suess, Bohrmann, Rickert, Kuhs, Torres, Trehu and Linke, 2002) as well as samples from the continental Mallik site, NWT, Canada (Techmer, Heinrichs and Kuhs, 2004) exhibit such porous microstructures together with denser parts. The occurrence of porous microstructures may be indicative for the occurrence of excess free gas during the formation (Staykova, Kuhs, Salamatin and Hansen, 2003). Here, we present the results of microstructural investigations of several marine and continental gas hydrates, comparing the observed structures with laboratory-made material. The comparison should enable us to draw preliminary conclusions on the formation processes of gas hydrates. The analysis of the pore structure by image analysis as well as by specific surface area measurements should provide a first appreciation of porosity's role for the macroscopic properties of gas hydrates. Some of these properties are relevant to a number of geophysical and engineering problems. In particular, the frequently observed anomalous features of seismic signals in gas hydrate horizons, notably the strong attenuation combined with high wave speeds

(e.g. Guerin and Goldberg, 2002), should be considered in the light of the unusual microstructures found in gas hydrates.

We first present the experimental techniques for a microstructural analysis of gas hydrates and show the appearance of marine gas hydrates from a number of different locations as well as continental sub-permafrost hydrates. Based on these observations, we will attempt to quantify the porosity in these hydrates and relate it to the observed macroscopic properties.

### EXPERIMENTAL TECHNIQUES

#### Cryo Electron Microscopy

Gas hydrates need high pressures and/or low temperatures to be stable. Electron microscopic investigations under high vacuum conditions must then be carried out at temperatures below  $-150^{\circ}\text{C}$  to avoid sample decomposition. The SEM laboratory at GZG Göttingen features a Field-Emission Scanning Electron Microscope (FE-SEM) combined with an EDX-detector (energy dispersive X-ray detector) for major chemical element analyses. The FE-SEM (LEO Gemini 1530) is a dedicated low-keV system that achieves high resolution even at primary electron energies below 1 keV. It is then possible to run surface studies of samples at low accelerating voltages, thus minimizing beam damage. Additionally, the microscope is equipped with a nitrogen-cooled preparation stage as well as a nitrogen-cooled sample stage in the main chamber, allowing for studies of materials at temperatures down to  $-185^{\circ}\text{C}$ . Further treatments, such as fresh cuts of surfaces and/or an additional conductive coating of the surface, may be undertaken in the cryo preparation chamber. However, at the low acceleration voltages  $<2$  keV, the charging of the gas hydrate samples is nearly negligible, making it feasible to look at surfaces without any coating. This also circumvents ambiguities that may arise from the possible generation of artifacts in the coating process. In order to get qualitative elemental analyses by EDX, it was found that the accelerating voltage could be increased for short intervals without significantly modifying the microstructures observed. Thus, beam-sensitive surfaces of ice or gas hydrates can readily be investigated (Kuks,

---

Received March 12, 2004; revised manuscript received by the editors October 13, 2004. The original version (prior to the final revised manuscript) was presented at the 14th International Offshore and Polar Engineering Conference (ISOPE-2004), Toulon, France, May 23–28, 2004.

KEY WORDS: Gas hydrate, porosity, seismic attenuation, electron microscopy.