

Appearance and preservation of natural gas hydrate from Hydrate Ridge sampled during ODP Leg 204 drilling

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Abstract

The state of preservation of natural gas hydrate samples, recovered from 6 sites drilled during ODP Leg 204 at southern summit of Hydrate Ridge, Oregon Margin, has been investigated by X-ray diffraction (XRD) and cryo-scanning-electron-microscopy (cryo-SEM) techniques. A detailed characterization of the state of decomposition of gas hydrates is necessary since no pressurized autoclave tools were used for sampling and partial dissociation must have occurred during recovery prior to the quench and storage in liquid nitrogen. Samples from 16 distinct horizons have been investigated by synchrotron X-ray diffraction measurements at HASYLAB/ Hamburg. A full profile fitting analysis (“Rietveld method”) of synchrotron XRD data provides quantitative phase determinations of the major sample constituents such as gas hydrate structure I (sI), hexagonal ice (Ih) and quartz. The ice content (Ih) in each sample is related to frozen water composed of both original existing pore water and the water from decomposed hydrates. Hydrate contents as measured by diffraction vary between 0 and 68 wt.% in the samples we measured. Samples with low hydrate content usually show micro-structural features in cryo-SEM ascribed to extensive decomposition. Comparing the appearance of hydrates at different scales, the grade of preservation seems to be primarily correlated with the contiguous volume of the original existing hydrate; the dissociation front appears to be indicated by micrometer-sized pores in a dense ice matrix.

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1. Introduction

Natural gas hydrate occurs worldwide in oceanic sediments and polar areas, where temperature and pressure conditions of the gas hydrate stability field are reached and sufficient gas is available (Matsumoto et al., 2000; Kvenvolden and Lorenson, 2001; Bohrmann and Torres,

2006). Based on global estimates, although still uncertain, gas hydrates in ocean and permafrost areas are considered as significant reservoirs for natural gases (in particular methane) along with societal and economic points of view. Natural gas hydrates might therefore become a major hydrocarbon source which may help to meet the increasing demand due to global consumption of hydrocarbons (Max et al., 2006). Natural gas hydrates have also captured the attention of geologists as slope stability around continents seems to be influenced by the presence of hydrates in the pore space of margin deposits (Paull et al., 2003).

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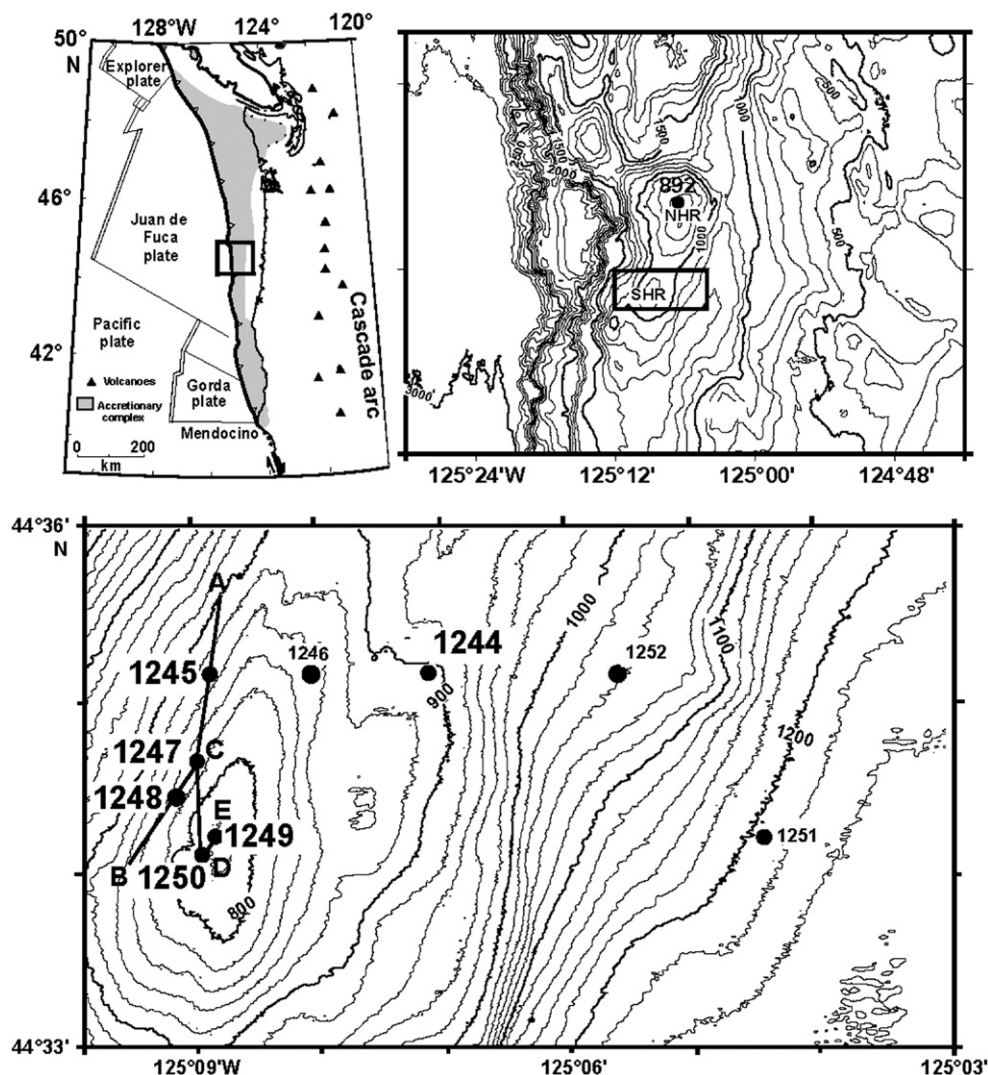


Fig. 1. Tectonic setting of the Cascadia subduction zone at the western margin of the Northamerican Plate (above left); location of the map (right) is indicated by the box. Bathymetric map of Hydrate Ridge and vicinity (above right) showing the area of a 3-D seismic survey at southern Hydrate Ridge (black box). Detailed bathymetric map (lower map) of the area of southern summit Hydrate Ridge indicating locations of ODP Leg 204 drill sites. Tracks of seismic profiles are shown and traced by letters A–E (from Tréhu et al., 2003).

Furthermore, the release of methane hydrates from large reservoirs could impact the atmospheric composition and thereby the global climate (Kennett et al., 2002).

Gas hydrates are ice-like crystalline compounds in which gases (carbon dioxide, methane, ethane etc.) are trapped within cages formed by water molecules (Sloan, 1998). From the pioneering X-ray crystallography work of von Stackelberg and Müller (1954), cubic hydrate structures I and II (sI and sII) were determined which both occur in natural marine deposits. A hexagonal clathrate hydrate designated as structure H was introduced by Ripmeester et al. (1987). Besides Nuclear Magnetic

Resonance (NMR) and Raman spectroscopy, X-ray diffraction can be used to identify the structure and determine the lattice parameters of hydrates. X-ray diffraction is the only method which can deliver absolute occupancies of the cages with gas molecules (Klapproth et al., 2003). In addition, XRD may be used to establish the relative amounts of ice, hydrate and other minerals in the gas hydrate samples to elucidate the degree of preservation.

This manuscript describes the use of synchrotron X-ray diffraction for the quantitative phase analysis of natural gas hydrate samples, from ODP drill sites at Hydrate Ridge, Oregon margin.

Quantitative phase analysis of gas hydrate samples is important, because without the use of proper autoclave tools, dissociation starts when gas hydrates are outside their p – T stability field resulting in the formation of ice or water. On the other hand, any seawater attached to the gas hydrate sample immediately converts into ice when liquid nitrogen is used for sample preservation. Ice from frozen seawater or as the end-product of dissociation and preserved hydrate cannot be easily distinguished through visual inspection and other methods must be used to differentiate between ice and hydrate. High-energy synchrotron X-ray diffraction offers both qualitative and quantitative analyses of all mineral phases present in a natural bulk sample. Due to its high spatial resolution and high penetration power it is far superior to conventional X-ray sources. Instead of a 1-dimensional detection as in most conventional X-ray diffractometers complete 2-D projections of the Debye–Scherrer cones are recorded in our synchrotron work. This is of crucial importance when larger crystallites occur in the sample (e.g. large ice crystallites as in our case), which frequently bias the conventionally recorded diffraction patterns leading to grossly erroneous phase fractions.

As an additional tool, cryo-scanning-electron-microscopy (cryo-SEM) explores the micro-structural and micro-chemical composition of the samples. The Energy Dispersive X-ray (EDX) detector, coupled with the cryo-SEM, detects constituents by their elemental composition with a spatial resolution of a few micro-

meters. By revealing details of the microstructure, cryo-SEM may also provide new insights into the dissociation processes taking place in recovered natural gas hydrate samples (Kuhns et al., 2004a). In addition, cryo-SEM helps to differentiate between ice originating from frozen seawater and from hydrate decomposition.

The determination of chemical composition, fabric, and grain size characteristics of gas hydrates in natural environments is still quite difficult due to the unknown extent of partial decomposition and ice formation that occurs during the recovery procedure. Assessing what is original and what is recovery-induced is important in order to interpret other geochemical and geophysical properties measured on recovered natural gas hydrate samples.

2. Gas hydrate on Hydrate Ridge

The gas hydrates investigated here were recovered during drilling on the southern Hydrate Ridge, a 30-km-long and 15-km-broad topographic high in the accretionary complex of the Cascadia subduction zone, located approximately 80 km west of the Oregon coast (Fig. 1). Ocean Drilling Program Leg 204 sampled the gas hydrate stability zone (GHSZ) from the seafloor to its base, which was indicated by a bottom-simulating reflector (BSR) in contrasting geological settings defined by a 3D seismic survey (Tréhu et al., 2003). By integrating results from pressure core sampler (PCS) measurements, chloride anomalies in the pore water, IR temperature logging on

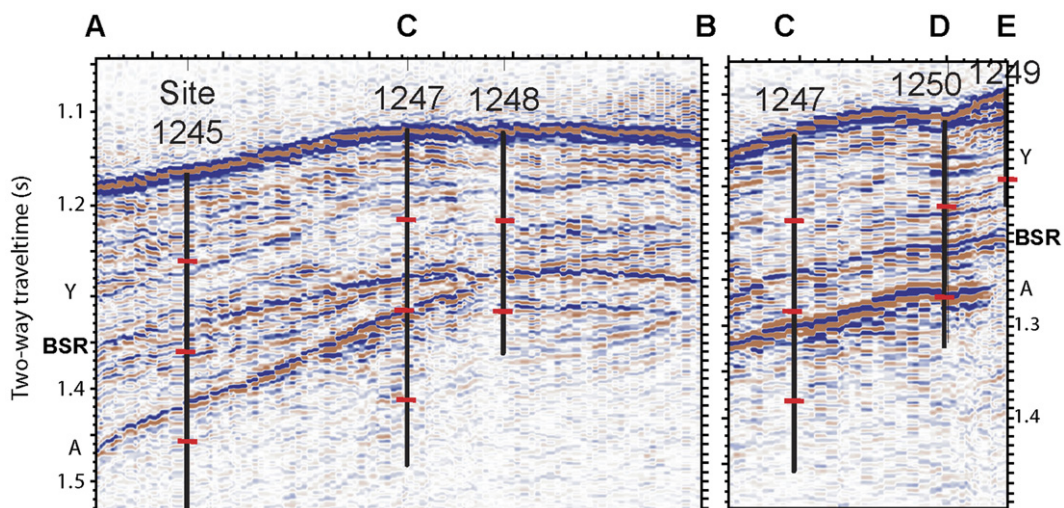


Fig. 2. North–south-trending slices from the 3-D seismic data that extend from the western flank to the summit of southern Hydrate Ridge (track lines are shown in the map of Fig. 1; from Tréhu et al., 2003). ODP drill sites are indicated. The position of the BSR marks the lower boundary of the gas hydrate stability field.

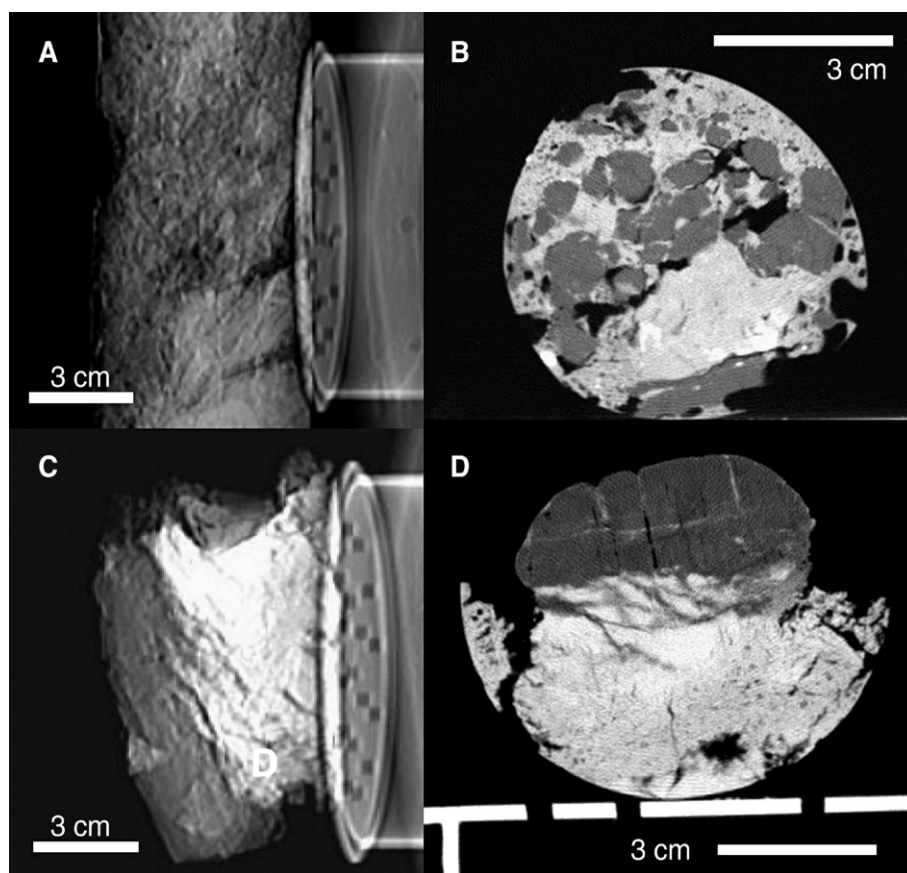


Fig. 3. CT images from both samples 1248C-8H-6, 68–67 cm (A and B) and 1247B-12H-2, 41–51 cm (C and D). CT images show dense material in white and less dense phases by darker color. Gas hydrate is represented by dark grey. Overview images of the entire core sections are shown left (A and C). CT slices are shown on the right side (B and D).

the catwalk and electrical resistivity data from logging-while-drilling, the problem of a very heterogeneous spatial distribution of gas hydrates within the GHSZ was overcome and quantitative estimates of the total amount and its spatial distribution on southern Hydrate Ridge were deduced (Tréhu et al., 2004). On average the gas hydrate content of the GHSZ between the BSR and the seafloor is generally 2% or less of the pore space, whereas some patchy zones of locally higher gas hydrate concentrations occur (Tréhu et al., 2004). High gas hydrate content of 30–40% of the pore space is restricted to the upper 30–40 m below the seafloor (mbsf) near the summit of southern Hydrate Ridge, where vigorous gas seepage occurs and gas hydrate is outcropping on the seafloor (Bohrmann et al., 1998; Suess et al., 1999, 2001). Based on a model that integrates gas hydrate growth, gaseous methane transport from below and chloride enrichment, Torres et al. (2004) calculated that a methane amount of 10^4 moles per day has to be supplied to the base

of the GHSZ. This supply of free gas is thought to occur preferentially at seismically imaged Horizon A, which is a high permeability gas-saturated sediment layer (Tréhu et al., 2004) that gets shallower towards the summit (Fig. 2).

A variety of gas hydrate textures were observed and sampled during the leg, providing new insight into the spatial distribution of gas hydrates on southern Hydrate Ridge. Based on their macroscopic geometry, samples were described as layers, massive (layers <10 cm in thickness) lenses, veins or veinlets, nodular features and disseminated hydrate grains that are distributed throughout the sediment matrix (Tréhu et al., 2003). A large collection of samples was investigated by X-ray computed tomography (CT) analyses of frozen whole-round samples, which showed that all hydrates had been present in layers with a variety of dip directions and angles within the sediment. Shallow hydrate layers parallel or sub-parallel to bedding are formed by gas injections parallel to stratification. Below 40 mbsf, hydrate layers are characterized by steeper dip angles of

Table 1

List of samples from ODP Leg 204 sites investigated in this study

ODP samples	Depth (mbsf)	No of measurements	Hydrate (%)	Ice (%)	Quartz (%)
1244C-8H-1, 47–52 cm	62.97	4	2.59±0.27	97.33±0.33	0.08±0.11
1244C-8H-1, 47–52 cm	62.97	3	1.33±0.09	98.43±0.05	0.24±0.11
1245B-6H-5, 60–78 cm	54.10	4	2.40±1.43	93.62±1.07	3.98±1.13
1247B-12H-2, 41–51 cm	93.01	4	43.88±3.71	54.53±3.82	1.60±0.29
1248C-1-CC, 0–14 cm	2.24	4	3.01±0.72	91.54±1.70	5.46±1.10
1248C-3X-3, 0–3 cm	21.83	4	1.34±0.58	96.88±0.61	1.80±0.49
1248C-8H-6, 68–87 cm	74.46	3	66.03±6.38	31.95±6.00	2.01±0.43
1248C-10H-1, 100–119 cm	87.00	2	6.64±1.33	92.89±1.19	0.47±0.14
1248C-10H-1, 100–119 cm	87.00	3	2.93±0.49	96.55±0.64	0.52±0.17
1248C 11H-5, 38–75 cm*	100.89	2	33.30±21.78	66.70±21.78	
1249C 1H-1, 0–25 cm*	0.12	2	0.00	100.00	
1249C-1H-CC, 0–10 cm	1.50	4	19.38±1.34	80.16±1.15	0.47±0.27
1249C-3H-1, 106–131 cm	5.89	3	7.48±1.73	84.58±2.31	7.94±0.57
1249F-5H-1, 64–70 cm	16.14	1	18.09	81.71	0.20
1250D-1H-3, 30–63 cm	1.66	4	2.89±1.00	96.71±1.71	0.61±0.49
1250D-1H-3, 30–63 cm*	1.66	3	1.35±0.09	97.90±0.03	0.75±0.10
1250D 1H-3, 30–63 cm	1.66	2	3.60±0.14	96.40±0.14	0.00
1250D-11H-3, 53–84 cm	78.01	4	34.45±3.87	64.60±3.58	0.97±0.36
1250D-11H-3, 53–84 cm	78.01	4	36.88±1.62	62.76±1.69	0.37±0.12
1250C 2H-CC, 0–1 cm*	5.06	2	27.50±38.89	72.50±38.89	
1250C-11H-3, 94–95 cm	86.35	4	7.09±1.01	92.78±1.08	0.14±0.06

Compositions (in weight %) of the samples are based on the synchrotron XRD data Rietveld analyses. Deviations given for the composition represent the spread from the average for different measured positions of the sample. Four samples marked by an asterisk correspond to uncrushed samples with very low quartz content, which, consequently, was not included in the Rietveld analysis.

30–90° and are interpreted as hydrate precipitates in open fractures or joints (Abegg et al., 2007).

3. Methods

During Leg 204 numerous gas hydrate samples were recovered as whole-rounds instantly after they were detected by IR imaging in the cores on the catwalk

(Tréhu et al., 2004) and preserved in liquid nitrogen for detailed shore-based studies. More than 60 whole-round samples were collected from 8 of 9 drill sites. Whole-round sections with variable sizes, around 5–20 cm in length, were first investigated by CT analyses (Fig. 3) which imaged the fabric and the appearance of the gas hydrate within the host sediment (Abegg et al., 2006). Based on the CT-image information we selected 16

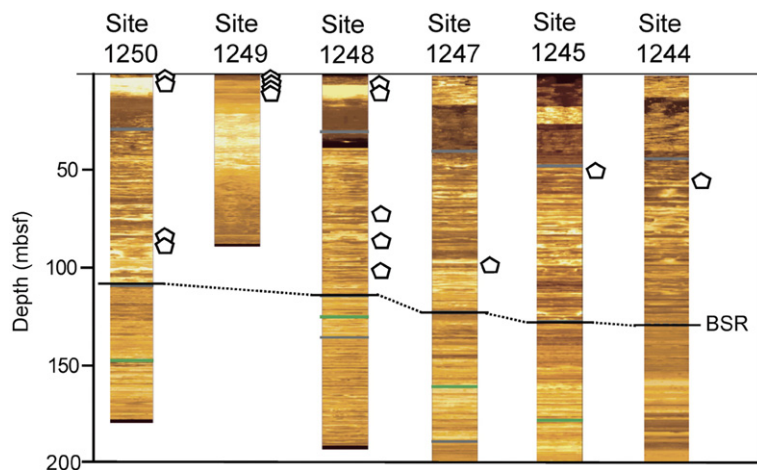


Fig. 4. ODP Leg 204 drill sites represented by logging-while-drilling electrical resistivity records from the uppermost 200 m below seafloor (light shades represent higher resistivity). Gas hydrate samples presented in this paper are shown by pentagon symbols.

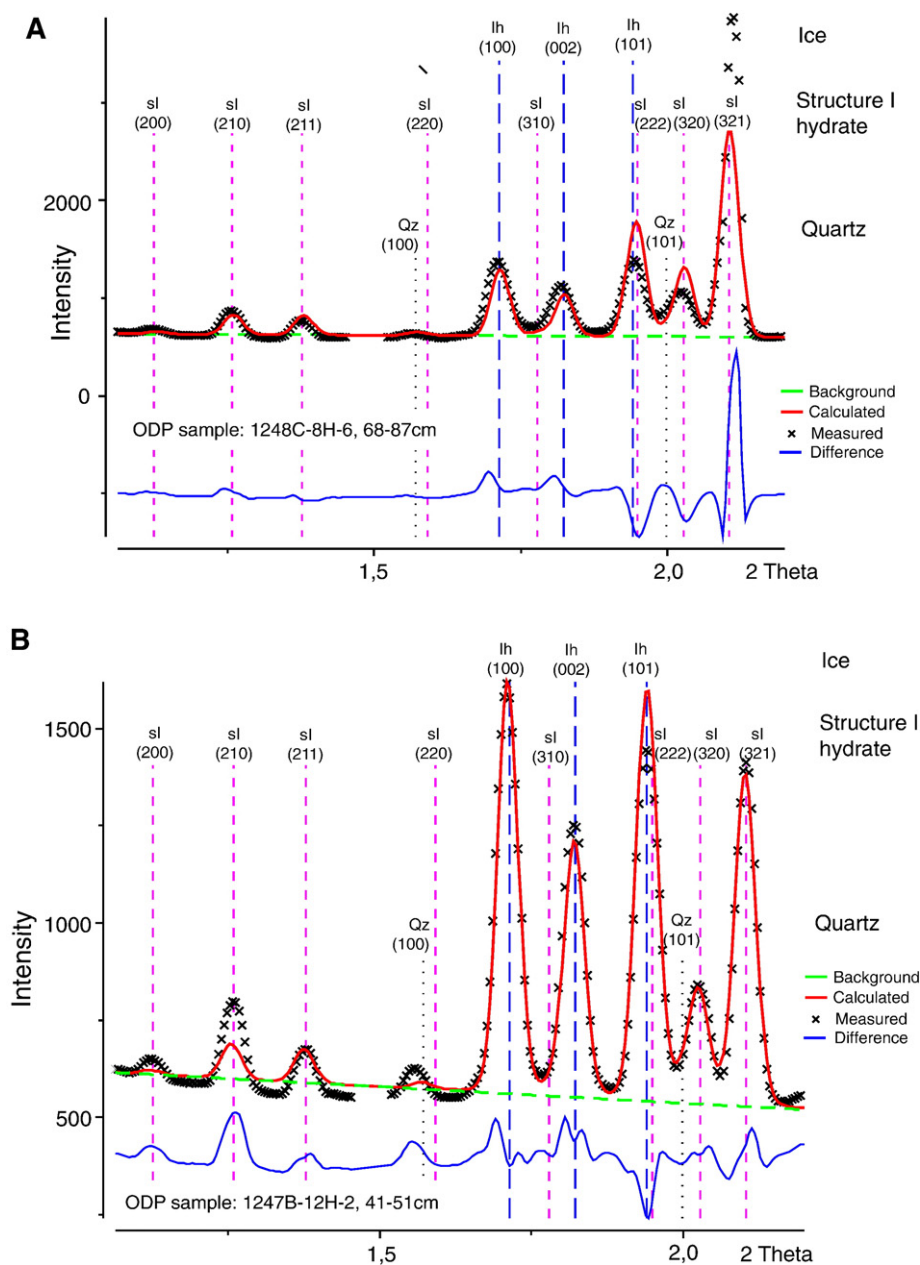


Fig. 5. XRD records from high-energy synchrotron radiation measured at HASYLAB/Hamburg and calculated models based on Rietveld analyses. Major peaks of hydrate, ice and quartz are shown from samples documenting distinct differences in gas hydrate amounts. From sample 1248C-8H-6, 68–67 cm (panel A) 68% structure I hydrate was calculated whereas sample 1247B-12H-2, 41–51 cm yields 45% gas hydrate (panel B).

samples from different horizons, all with some promise for containing gas hydrates (Table 1, Fig. 4). Working under liquid nitrogen in a cold laboratory at $-20\text{ }^{\circ}\text{C}$ (to avoid the condensation of water vapour from the atmosphere) we dissected pure hydrate/ice parts and cleaned the samples from attached sediment particles. Of these 16 cleaned sub-samples 13 were crushed to sub-millimeter size and filled into aluminium vials of

7 mm diameter and 40 mm length. Samples from four depth horizons were split into two sub-samples each (see Table 1). One set of sub-samples from each horizon was left intact and placed in aluminium vials of 7 mm diameter filling most of the vial's cross-section.

For XRD analysis we used high-energy synchrotron radiation at the beamline BW5 at DESY-HASYLAB in Hamburg. In contrast to in-house X-ray techniques,

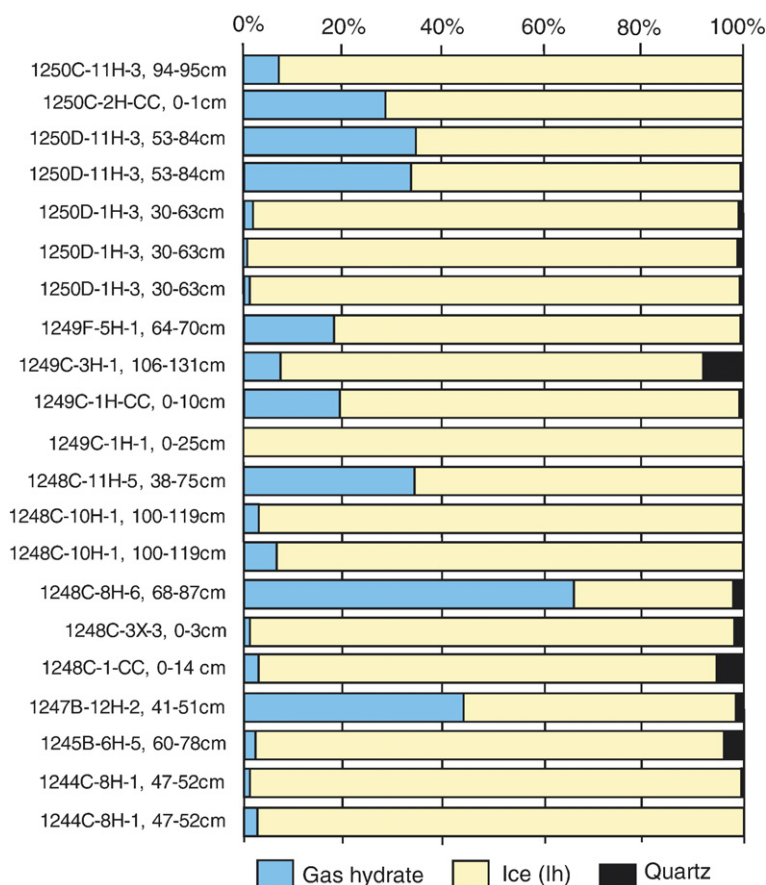


Fig. 6. Bar chart of gas hydrate, ice and quartz amounts calculated in 21 samples from 16 depth levels of frozen ODP samples which have been identified as gas hydrate samples onboard the JOIDES Resolution.

synchrotron X-ray diffraction provides better resolution, because of high radiation flux (5×10^{10} photons/s/mm² at 100 keV), high collimation, i.e. small angular divergence of the beam, and wide tunability in energy/wavelength (sub eV to hundreds of keV). A monochromatized and collimated photon beam of about 100 keV (wavelength ~ 0.124 Å) was used as an incident X-ray beam with a size of 1 mm² at the sample position. For the X-ray measurements, samples were placed in the cylindrical aluminium vials described above. The sample was held at a temperature of 70 K at ambient pressure. The small beam size allows for spatially resolved measurements to obtain information on internal sample variability. Consequently, one has to measure at several positions, or move the sample during data collection. Here, usually 2–4 areas within each sample were investigated without translating (but rotating) the sample during data collection (Table 1). The typical distance between two measured positions was 10 mm.

A two-dimensional (2-D) image plate detector (mar345) placed 120 cm away from the sample was used permitting interception of the X-ray powder diffraction cones as

complete Debye–Scherrer rings. Using the FIT2D program (Hammersley et al., 1996) these rings were integrated to yield a conventional one-dimensional (1-D) 2-theta pattern. In the 2-D images, some Debye–Scherrer rings show individual Bragg spots scattered within the ring width. These spots are distinct due to their high peak intensity compared to any other point (~ 10 times higher) within the ring width. Clearly, they represent the Bragg reflections of large crystallites of a particular phase (ice Ih or sl hydrate). The resulting 1-D powder pattern shows spikes sitting on an otherwise smooth integrated Bragg peak. Moreover, as other lattice planes of these large crystallites are not necessarily in reflection position, the Rietveld method will tend to produce a lower quality of fit. In certain cases it may hamper a reasonable refinement altogether. The problem can be addressed by masking outliers before integration. The resulting peaks in the 2-theta patterns will then not show any abrupt change in intensity. The “MASK” tool of the FIT2D program was used for this purpose, which allowed manually selected outlying points to be ignored in further treatments enabling a more meaningful profile fit.

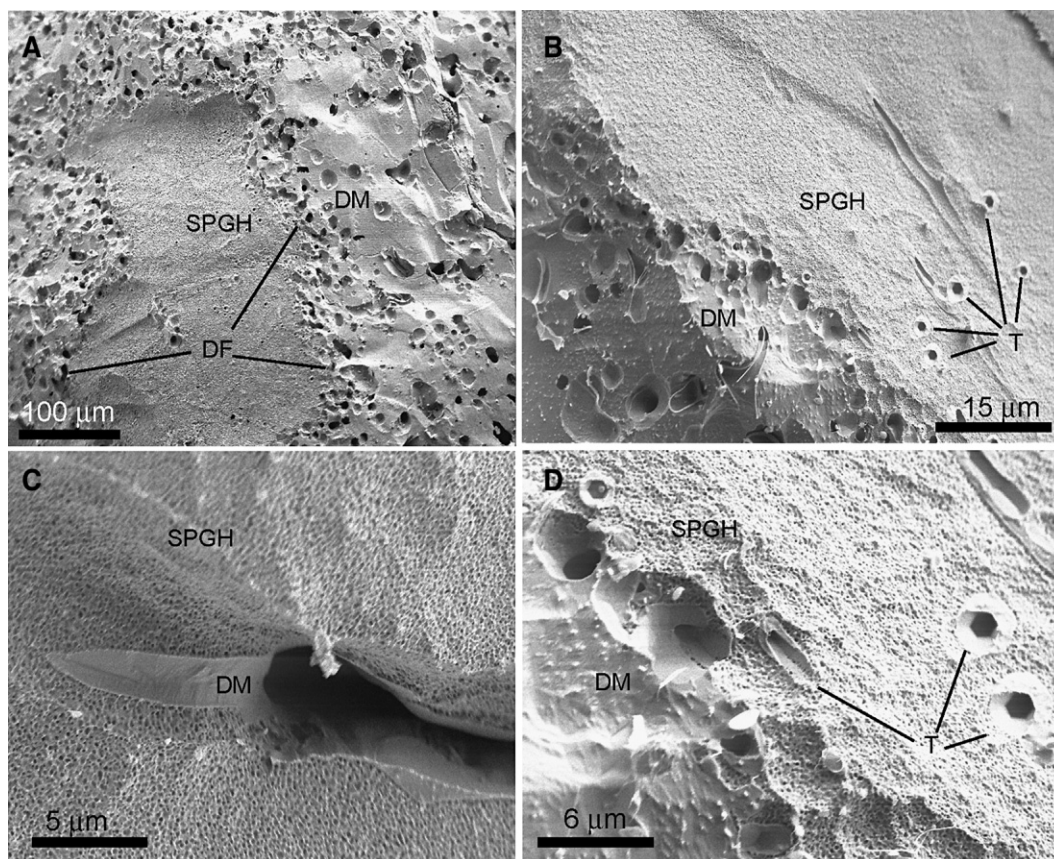


Fig. 7. FE-SEM images from ODP Leg 204 gas hydrate samples. A. Overview of an area characterized by sub-micrometer-sized porosity (SPGH) surrounded by dense material (DM) that contains pores 5–20 μm in size. Those pores are concentrated in certain areas and seem to be more frequent near the contact to sub-micrometer-porous patches (Sample 1249C-1H-CC). B. Image of the transition from a sub-micrometer-sized porosity (SPGH) area to the dense material (DM) is shown. Single tube pores (T) with hexagonal shape are typical for SPGH parts. C. Large pore in sub-micrometer-porous gas hydrate (SPGH). Note that the contact is lined by dense material (DM). D. Detail of higher magnification of image B. B–D are from sample 1247B-12H-2, 41–51 cm. Decomposition front (DF).

Phase fractions of the samples are then obtained from a full-pattern profile fitting (Rietveld refinement) using the GSAS software (Larson and Von Dreele, 2000) and are summarized in Table 1. The starting parameters for the sl hydrate (space group Pm-3n) refinements are taken from Klapproth (2002). During refinements, general parameters such as the scale factor, background parameters, the zero point and the profile parameters are optimized. The cell parameters of ice Ih and quartz are kept fixed, while the cell parameter of sl hydrate slightly varies around a value of ~ 11.88 (1) $\text{\AA}$.

In addition to XRD analyses, few samples were investigated by cryo-SEM. We used a Field-Emission SEM (FE-SEM; LEO Gemini 1530), which is dedicated to work at low acceleration voltages. The FE-SEM is equipped with a nitrogen-cooled sample stage in the vacuum chamber, which allows a study of samples at temperatures as low as -185 $^{\circ}\text{C}$. Samples were moved onto the liquid nitrogen cooled sample holder within a liquid nitrogen bath and then

transferred through a cryo-preparation chamber (without receiving a metal coating) into the vacuum chamber (10^{-5} mbar) of the SEM. A low acceleration voltage (<2 keV) was used during imaging to minimize sample alteration or beam damage. This allowed us to investigate the surface of the samples in detail down to several tens of nm resolution. In order to obtain qualitative elemental analyses the instrument is equipped with an energy dispersive X-ray sensor (EDX). Images were stored in digital format. Further details of the FE-SEM used for studies of gas hydrates were described in earlier publications (Kuhns et al., 2004a; Techmer et al., 2005).

4. Results

4.1. Synchrotron X-ray diffraction

X-ray diffraction analyses of all samples (Table 1) revealed that the gas hydrate phase in each sample is cubic

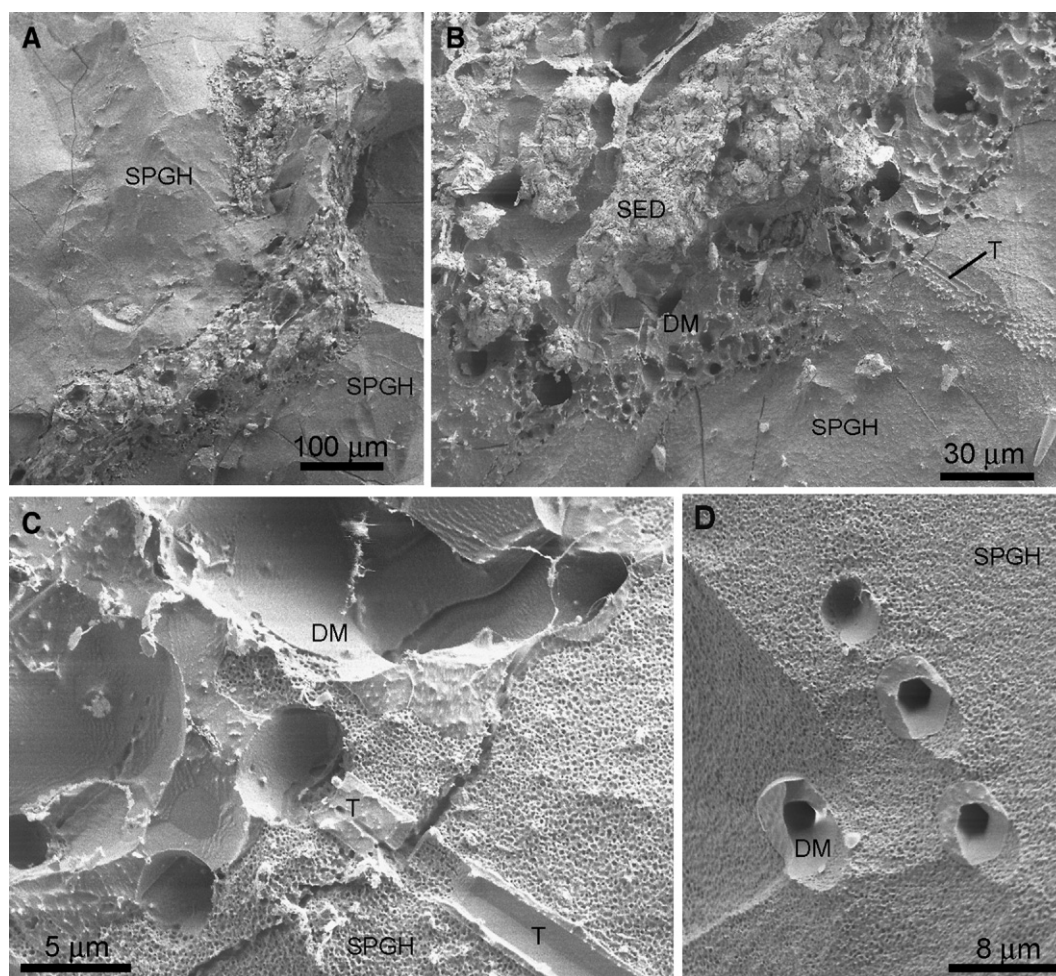


Fig. 8. FE-SEM images from ODP Leg 204 gas hydrate samples. A. Image of dominantly sub-micrometer-porous gas hydrate (SPGH) containing domains of sediment (SED). The sub-micrometer-sized porosity is not visible under low magnification. B. Transition between a sub-micrometer-porous area (SPGH) and sediment-dominated region (SED). Dense material (DM) yielding pores of a few micrometer in diameter are intercalated. C. Detail from B shows the distinct transition from sub-micrometer-porous gas hydrate (SPGH) to dense material (DM). The single tube pore (T) from the gas hydrate is ending in a pore within the dense material. D. Four single tubes of dense material with clear hexagonal shapes within the inner vug. Images A–C are from sample 1248C-8H-6, 68–67 cm; image D is taken from sample 1247B-12H-2, 41–51 cm.

sI hydrate. This is demonstrated by the presence of the three most intense sI-peaks (222), (320), (321) in the 2θ scans (Fig. 5). The hexagonal ice Ih phase in this example is by far the major fraction, which is clearly indicated by the dominant intensities of the three major ice Ih peaks (100), (002), (101) (Fig. 5). A third mineral phase is identified as quartz as documented by its (101) and (100) reflections (Fig. 5). In total, we performed 66 analyses from 16 gas hydrate samples of various depths at Sites 1244, 1245 and 1247–1250. In most cases we ran 3–4 measurements for each sub-sample. In some particular cases, i.e. from 4 samples, we measured a second set of uncrushed sub-samples in order to check the local compositional variations (Table 1).

The synchrotron XRD data Rietveld analysis provides quantitative phase fractions of the constituents present in each sample, which are listed in Table 1 and shown in Fig. 6. For the crushed samples, the amount of Ih ice varies between 32 and 98% in each sample, with 83% as a nominal average for the measured samples. It is therefore clear that ice Ih is the most abundant phase in the collected samples, despite the fact that the samples were selected for their high gas hydrate content. The sI hydrate phase fraction varies between 0 and 66% with a nominal averaged value of 15%. Eight of thirteen crushed samples contain a low amount (between 1 and 7%) of gas hydrate and only five samples showed gas hydrate contents of 20–68% along with a lower

concentration of ice Ih (30–75%). As expected based on the sample preparation procedure, quartz is only a minor constituent (the nominal average content of the samples is around 1.6%) and varies between 1.1 and 7.9% (Fig. 6). Results from the four measurements with uncrushed samples revealed an inhomogeneous distribution of gas hydrate and ice within the sample. In particular, samples with higher gas hydrate contents (about 30 wt.%) show significant local differences in the gas hydrate and ice proportions.

4.2. FE-SEM observations

Optical studies on microstructures have been carried out on a few samples with different gas hydrate concentrations (Figs. 7 and 8). From these samples the highest amount of gas hydrate (68%) was analyzed in sample 1248C-8H-6, 68–67 cm and the lowest concentration of 3.1% was found in sample 1248C-1-CC, 0–14 cm. Sample 1247B-12H-2, 41–51 cm reaches gas hydrate concentration of 43.8%, which is a medium value between the other two samples. As it was shown in other natural and synthetic gas hydrate samples, the samples studied here show a characteristic sub-micrometer-sized porosity, which can be used as a rapid visual aid in identifying gas hydrates (Kuhns et al., 2000, 2004a; Klapproth et al., 2007).

Pore sizes typically vary between 100 and 400 nm in diameter (Figs. 7C, D, and 8C, D), and are homogeneously distributed over large areas in samples of high gas hydrate concentration. The porosity is about 15% with pores that show no preferred orientation and are rarely inter-

connected as evidenced by specific surface area measurements (Kuhns et al., 2004a). In the sample of low gas hydrate concentration just two very small areas of sub-micrometer-sized porosity were found and in the sample of medium gas hydrate concentration, sub-micrometer-sized porous patches are repeatedly observed. Next to sub-micrometer-sized porous areas, dense material was observed with few larger pores of tens of micrometers in diameter. Those pores are often concentrated in certain domains and are particularly frequent in dense material that surrounds patches of sub-micrometer-sized porosity. As shown in Fig. 7A the size distribution of the pores in this area is fairly homogenous, whereas farther away the pores reveal more variable, mostly larger pore sizes. The dense material containing some micrometer-sized pores was repeatedly identified as ice by EDX. From synthetic gas hydrate samples we know that the sub-micrometer-porous material is representative for gas hydrates (Kuhns et al., 2000, 2004a). This permits us to retrace the decomposition front between gas hydrate and the (now frozen) water at the moment of quenching in liquid nitrogen and allows us to visually estimate the size of patches of un-decomposed hydrates in the SEM samples as discussed below.

Within areas of sub-micrometer-sized porosity, tubes of 2–4 μm in diameter with dense walls occur, which in all cases show a hexagonal cross-section (Figs. 7A, D and 8D). Most of the neighbouring long tubes appear to be aligned parallel to each other. Investigations of the change from areas of sub-micrometer porosity to dense areas revealed that some of the tubes end in larger pores within the dense material (Fig. 8). Contacts to sediment

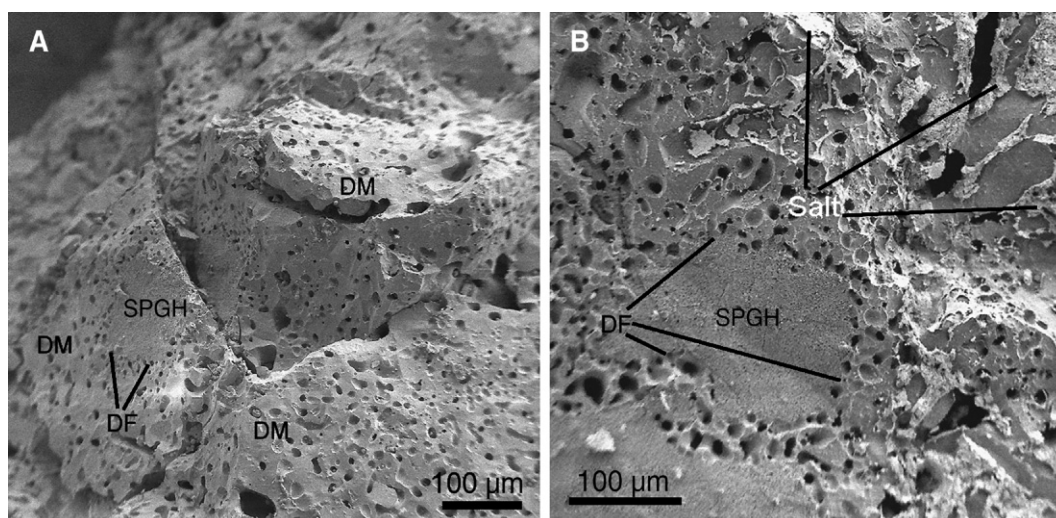


Fig. 9. FE-SEM images from ODP Leg 204 gas hydrate samples. A. Large-scale image of a small patch of sub-micrometer-porous gas hydrate (SPGH), surrounded by dense material (DM) with fewer and larger pores (tens of micrometers). The decomposition front (DF) of the gas hydrate is marked (sample 1249C-1H-CC, 0–10 cm). B. Sub-micrometer-porous gas hydrate (SPGH) with direct contact to a matrix of dense material (DM) on a decomposition front (DF). Salt crusts in the right hand side of the picture are labeled (sample 1248C-8H-6, 68–87 cm).

domains are mostly represented by dense material containing some micrometer-sized pores (Fig. 8A and B).

Figs. 7A and 9A and B show patches of sub-micrometer-sized pores which are surrounded by dense material. Fig. 9A depicts a small, single patch which is entirely encircled by a large area of dense material. The dense material is directly connected to the sub-micrometer-sized porous patch; also, no crusts of any kind are visible which might help retracing the origin of the dense material to external sources such as seawater. In Fig. 9B crusts are visible in the image which was identified as salt crusts from, presumably, seawater, by EDX-measurements. On the other hand, sub-micrometer-sized porous areas are embedded within dense material with fewer and larger pores. No sub-micrometer-sized porous patches were found with areas of salt crusts.

5. Discussion

Kim et al. (2005) observed sI hydrate in one sample collected from the Site 1249 on ODP Leg 204. Structure I hydrate was also postulated by gas analyses of distinct hydrate samples during the work onboard the JOIDES Resolution (Tréhu et al., 2003). The adopted cell parameter of 11.88(1) Å, measured at 70 K, is comparable to the earlier reports on natural gas hydrates as well as synthetic ones. For instance, Kim et al. (2005) obtained the cell parameter as 11.8615 ± 0.015 Å, measured at 123 K, while Kirchner et al. (2004) reported 11.877(3) Å for pure synthetic methane hydrate from a single crystal XRD measurement. Measurements at different locations (10 mm apart) of the same sub-sample do not show any substantial differences in cell parameter, but yield slightly different phase fractions (Table 1). Thus it appears, that all recovered gas hydrate here is of structure I, but that it occurs in different proportions relative to other phases such as ice (Table 1), indicating sample heterogeneity at a mm scale.

5.1. Distinction between gas hydrate and ice

SEM imaging within the matrix of gas hydrates shows areas of sub-micrometer-sized pores that represent the hydrate phase, which is therefore distinguishable from the ice (Kuhs et al., 2000, 2004a; Stern et al., 2004; Techmer et al., 2005; Stern et al., 2005). The gas hydrates studied here show comparable pore structures with pore diameters less than 1 µm. Such sub-micrometer-sized pores were reported from natural gas hydrate samples from the Black Sea, from the SW African Margin and from near-surface gas hydrates from Hydrate Ridge and from the Mallik drill site (Kuhs et al., 2004a; Techmer et al., 2005). The porosity is also known from laboratory-synthesized gas hydrates, specifi-

cally from those that formed from gas reacted with water/ice to form hydrates (Staykova et al., 2003; Genov et al., 2004; Kuhs et al., 2006). Straight tubiform pores with the dense walls were exclusively found within the sub-micrometer-scale porous gas hydrate domains. However, the hexagonal shape of the tubes in cross-sections indicates that the dense material of the wall represents frozen water since normal ice crystallizes in hexagonal lattice. Accordingly, using the EDX detector we were unable to detect any carbon in the material of the dense walls, which suggests that the dense material probably does not consist of gas hydrate, as was shown for samples from the Mallik drill site (Techmer et al., 2005).

Large patches of sub-micrometer-sized pores are particularly well preserved in samples with high amounts of gas hydrate. On the other hand a large proportion of ice coincides with a widespread occurrence of dense material. The appearance of gas hydrates under the SEM shows the typical feature: the sub-micrometer-sized porous material is always surrounded by dense material (Fig. 7A). This includes large pores several tens of micrometers in size, which are always surrounded by dense material (Fig. 8C). This was observed in all samples and is a good argument, that the dense material is dominantly frozen water. Local variations of the ice and gas hydrate fractions from XRD measurements of uncrushed samples agree well with SEM observations. Consequently, we can assume that by and large the dense material is mostly composed of ice. The possibility that some of the hydrates investigated here also show dense surface areas cannot be excluded, however. Dense hydrates were described in other investigations (Stern et al., 2004; Techmer et al., 2005). In the samples from the Hydrate Ridge, no dense gas hydrate as indicated by carbon signals from the EDX detector could be found. In addition, the arrangements of micrometer-sized pores (Figs. 7 and 8) and the distribution of the pores within the dense material most probably represent former gas bubbles in water that froze during the rapid quench in liquid nitrogen. Those bubbles were potentially frozen with the surrounding water. They are recognizable as cavities covered by thin ice layers.

5.2. Decomposition of gas hydrate and its detection

Decomposition of gas hydrate starts on free surfaces or interfaces of gas hydrates with sediment or along the surface of large pores that originally exist between sediment grains. Discrete rounded patches of sub-micrometer-sized porous gas hydrate are consequently decomposed around their periphery. The boundary between porous and dense material represents most probably the active decomposition surface, just immediately before the sample was frozen in

liquid nitrogen. Consequently, only large and massive pieces of gas hydrate will be preserved as gas hydrates patches whereas similar amounts of gas hydrate which occur disseminated in the sediment will decompose during retrieval within the drill string. This is indicated by small gas hydrate patches which are situated within large areas of ice originating from hydrate decomposition. Ice originating from quenched seawater can be identified by the presence of salt crusts. Micro-structurally identical salt crusts were obtained by us in laboratory experiments for rapidly quenched sea water. Such salt precipitates cannot be observed in frozen hydrate water, because hydrate is composed of pure water and contains no salt. The patchy distribution of ice and gas hydrates seen in SEM is confirmed by the varying proportions of gas hydrate and ice at different locations in uncrushed samples.

Hydrate dissociation itself is an endothermic reaction consuming a considerable amount of heat, which could lead to a simultaneous freezing of the water released by the dissociation process. In addition to gas hydrate decomposition, gas expansion and gas exsolution are further processes that can cause a temperature decrease in sediment cores during their ascent from seabed to the surface. Consequently, decreasing temperatures induced by any process could probably lead to the formation of ice in the ascending sediments. Temperature measurements taken by the Temperature, Pressure and Conductivity (TPC) tool during the ascent of cores revealed at least sharply-defined cooling anomalies with ΔT up to $\sim 4^\circ\text{C}$ measured on top of the TPC tool (Ussler et al., 2006). This may indicate even lower cooling temperatures in small areas around gas hydrates inside such cores. The spot-like temperature decreases could induce local ice formation and contribute to the self-preservation effect of hydrates which is observed at temperatures below 0°C (Yakushev and Iomin, 1992; Stern et al., 2003). This effect allows gas hydrates to exist for some time outside its normal p-T conditions of stability. The thermal limits of the preservation window and the effects of pressure variations were investigated on many pure samples of structure I as well as on mixed hydrate samples (sI and sII) by Stern et al. (2003; Kuhs et al., 2004b; Circone et al., 2005). This effect was first observed in laboratory experiments on both natural and laboratory-made gas hydrate (Davidson et al., 1986), and is suggested as a basis for a commercial scheme for methane hydrate storage and transport (Gudmundson and Borrehaug, 1996).

6. Conclusion

Preservation of gas hydrates from ODP samples from conventional APC cores, without using autoclave coring

systems, seems to be unsatisfactory due to widespread and advanced dissociation of the hydrate. Typically, samples we investigated from ODP drill sites are decomposed up to 85% and are converted to hexagonal ice. Only a few samples revealed gas hydrate concentrations more than 15% going up in rare cases to 70% of the selected sample. High gas hydrate contents can only be expected when the starting material consists of massive gas hydrates which are considerably more resistant to decomposition than thin hydrate layers, veinlets or disseminated hydrate crystals. The distribution of gas hydrates in partially decomposed samples was found to vary at scales of mm to cm.

Gas hydrate samples frozen in liquid nitrogen show many features of hydrate decomposition. Results from FE-SEM studies are in agreement with XRD conclusions. Gas hydrate domains seem to be represented by sub-micrometer-sized porosity, whereas on this scale the frozen water appears dense in FE-SEM images containing, however, many pores of larger size. These pores are probably caused by methane bubbles discharged from outer surfaces of decomposing hydrates which were frozen during quenching in liquid nitrogen. Hydrate decomposition was obviously ongoing before the process was stopped in the liquid nitrogen bath. We cannot exclude that some of the ice was formed directly by the cooling effect of hydrate decomposition during the ascent of the core to the surface within the drill hole and above, before the sample was quenched in liquid nitrogen.

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References

- Abegg, F., Bohrmann, G., Kuhs, W., 2006. Data report: shapes and structures of gas hydrates imaged by computed tomographic-analyses, ODP Leg 204, Hydrate Ridge. In: Tréhu, A., Bohrmann, G., Colwell, F.S., Torres, M. (Eds.), Results, vol. 204, pp. 1–8. [Online]. Available from World Wide Web.: http://www-odp.tamu.edu/publications/204_SR/122/122.htm.
- Abegg, F., Bohrmann, G., Freitag, J., Kuhs, W., 2007. Fabric of gas hydrate in sediments from the Hydrate Ridge — results from ODP 204 samples. *Geo Mar. Lett.* 27, 269–277.
- Bohrmann, G., Torres, M., 2006. Gas hydrates in marine sediments. In: Schulz, H.D., Zabel, M. (Eds.), *Marine Geochemistry*. Springer, pp. 481–512.
- Bohrmann, G., Greinert, J., Suess, E., Torres, M., 1998. Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability. *Geology* 26, 647–650.
- Circone, S., Kirby, S.H., Stern, L.A., 2005. Thermal regulation of methane hydrate dissociation: implications for gas production models. *Energy Fuels* 19, 2357–2363.
- Davidson, D.W., Garg, S.K., Gough, S.R., Handa, Y.P., Ratcliffe, C.I., Ripmeester, J.A., Tse, J.S., 1986. Laboratory analysis of a naturally occurring gas hydrate from sediment of the Gulf of Mexico. *Geochim. Cosmochim. Acta* 50, 619–623.
- Genov, G., Kuhs, W.F., Staykova, D.K., Goreshnik, E., Salamatina, A.N., 2004. Experimental studies on the formation of porous gas hydrates. *Am. Mineral.* 89, 1228–1239.
- Gudmundson, J., Borrehaug, A., 1996. Frozen hydrate for transport of natural gas. *Proc. 2nd Int. Conf. on Natural Gas Hydrates*, Toulouse, pp. 415–422.
- Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N., Häusermann, D., 1996. Two-dimensional detector software: from real detector to idealised image or two-theta scan. *High Press. Res.* 14, 235–248.
- Kennett, J.P., Cannariato, K.G., Hendy, I.L., Behl, R.J., 2002. Methane Hydrates in Quaternary Climate Change: The Clathrate Gun Hypothesis. American Geophysical Union, Washington D.C.
- Kim, D., Uhm, T., Lee, H., Lee, Y., Ryu, B., Kim, J., 2005. Compositional and structural identification of natural gas hydrates collected at Sites 1249 on Ocean Drilling Program Leg 204. *Korea J. Chem. Eng.* 22 (4), 569–572.
- Kirchner, M.T., Boese, R., Billups, W.E., Norman, L.R., 2004. Gas hydrate single-crystal structure analyses. *J. Am. Chem. Soc.* 126, 9407–9412.
- Klapproth, A., 2002. Strukturuntersuchungen an Methan- und Kohlenstoffdioxid-Clathrat-Hydraten. Ph.D. dissertation, Georg-August-Universität Göttingen.
- Klapproth, A., Goreshnik, E., Staykova, D., Klein, H., Kuhs, W.F., 2003. Structural studies of gas hydrates. *Can. J. Phys.* 81, 503–518.
- Klapproth, A., Techmer, K.S., Klapp, S.A., Murshed, M.M., Kuhs, W.F., 2007. Microstructures of gas hydrates in porous media. *Proc. Int. Conf. Physics and Chemistry of Ice*, Bremerhaven, July 23–28, 2006. Royal Society of Chemistry. RSC Publishing, pp. 321–328.
- Kuhs, W.F., Klapproth, A., Gotthardt, F., Techmer, K., Heinrichs, T., 2000. The formation of micro- and macroporous gas hydrates. *Geophys. Res. Lett.* 27, 2929–2932.
- Kuhs, W.F., Genov, G.Y., Goreshnik, E., Zeller, A., Techmer, K., Bohrmann, G., 2004a. The impact of porous microstructures of gas hydrates on their macroscopic properties. *Int. J. Offshore Polar Eng.* 14, 305–309.
- Kuhs, W.F., Genov, G., Staykova, D.K., Hansen, T.C., 2004b. Ice perfection and onset of anomalous preservation of gas hydrates. *Phys. Chem. Chem. Phys.* 6, 4917–4920.
- Kuhs, W.F., Staykova, D.K., Salamatina, A.N., 2006. Formation of methane hydrate from polydisperse ice powders. *J. Phys. Chem., B* 110, 13283–13295.
- Kvenvolden, K.A., Lorenson, T.D., 2001. The global occurrence of natural gas hydrates. In: Paull, C. (Ed.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Geophysical Monograph, vol. 124. American Geophysical Union, pp. 3–18.
- Larson, A.C., Von Dreele, R.B., 2000. General Structure Analysis System (GSAS). Los Alamos National Laboratory Report LAUR, pp. 86–748.
- Matsumoto, R., Uchida, T., Waseda, A., Uchida, T., Takeya, S., Hirano, T., Yamada, K., Maeda, Y., Okui, T., 2000. Occurrence, structure, and composition of natural gas hydrate recovered from the Blake Ridge, northwest Atlantic. *Proc. Ocean Drill. Program Sci. Results* 164, 13–28.
- Max, M.D., Johnsen, H.K., Dillon, W.P., 2006. Economic geology of natural gas hydrate. *Coastal Systems and Continental Margins*. Springer, 340 p.
- Paull, C.K., Ussler III, W., Dillon, W.P., 2003. Potential role of gas hydrate decomposition in generating submarine slope failures. In: Max, M.D. (Ed.), *Natural Gas Hydrate in Oceanic and Permafrost Environments*, pp. 149–156.
- Ripmeester, J.A., Tse, J.A., Ratcliffe, C.I., Powell, B.M., 1987. A new clathrate hydrate structure. *Nature* 325, 135–136.
- Sloan, E.D.J., 1998. *Clathrate Hydrate of Natural Gases*, (second edition). Marcel Dekker Inc., Publisher, New York, 705 pp.
- Staykova, D.K., Kuhs, W.F., Salamatina, A.N., Hansen, T., 2003. Formation of porous gas hydrates from ice powders: diffraction experiments and multistage model. *J. Phys. Chem., B* 107, 10299–10311.
- Stern, L., Cicerone, S., Kirby, S., Durham, W., 2003. Temperature, pressure, and compositional effects on anomalous or “self” preservation of gas hydrate. *Can. J. Phys.* 81 (1–2), 271–283.
- Stern, L., Kirby, S.H., Circone, S., Durham, W.B., 2004. Scanning electron microscopy investigations of laboratory-grown gas clathrate hydrates formed from melting ice and comparison to natural hydrates. *Am. Mineral.* 89, 1162–1175.
- Stern, L.A., Kirby, S.H., Durham, W.B., 2005. Scanning electron microscope imaging of grain structure and phase distribution within gas-hydrate-bearing intervals from JAPEX/JNOC/GSC et al. Mallik 5L-38: what can we learn from comparisons with laboratory-synthesized samples? In: Dallimore, S.R., Collett, T.S. (Eds.), *Scientific Results from the Mallik 2002 Gas Hydrate Production Research Well Program*, Mackenzie Delta, Northwest Territories, Canada. Geological Survey of Canada, Bulletin, vol. 585, 19 p.
- Suess, E., Torres, M.E., Bohrmann, G., Collier, R.W., Greinert, J., Linke, L., Rehder, G., Tréhu, A., Wallmann, K., Winckler, G., Zuleger, E., 1999. Gas hydrate destabilization: enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin. *Earth Planet. Sci. Lett.* 170, 1–15.
- Suess, E., Torres, M.E., Bohrmann, G., Collier, R.W., Rickert, D., Goldfinger, C., Linke, P., Heuser, A., Sahling, H., Heeschen, K., Jung, C., Nakamura, K., Greinert, J., Pfannkuche, O., Tréhu, A., Klinkhammer, G., Whiticar, M.C., Eisenhauer, A., Teichert, B., Elvert, E., 2001. Sea floor methane hydrates at Hydrate Ridge, Cascadia Margin. In: Paull, C., Dillon, W.P. (Eds.), *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. Geophysical Monograph, vol. 124. American Geophysical Union, pp. 87–98.
- Techmer, K.S., Heinrichs, T., Kuhs, W.F., 2005. Cryo-electron microscopic studies of structures and composition of Mallik gas-hydrate-bearing samples. In: Dallimore, S.R., Collett, T.S. (Eds.), *Scientific Results from the Mallik 2002 Gas Hydrate Production*

- Research Well Program, Mackenzie Delta, Northwest Territories, Canada. Geological Survey of Canada, Bulletin, vol. 585. 12 p.
- Torres, M.E., Wallmann, K., Tréhu, A.M., Bohrmann, G., Borowski, W.S., Tomaru, H., 2004. Gas hydrate growth, methane transport, and chloride enrichment at the southern summit of Hydrate Ridge, Cascadia margin off Oregon. *Earth Planet. Sci. Lett.* 226, 225–241.
- Tréhu, A.M., Bohrmann, G., Rack, F.R., Torres, M.E., et al., 2003. Proc. ODP, Init. Repts., 204 [CD-ROM]. Available from: Ocean Drilling Program, Texas A&M University, College Station TX 77845-9547, USA.
- Tréhu, A.M., Long, P.E., Torres, M.E., Bohrmann, G., R., R.F., Collett, T.S., Goldberg, D.S., Milkov, A.V., Riedel, M., Schultheiss, P., Bangs, N.L., Barr, S.R., Borowski, W.S., Claypool, G.E., Delwiche, M.E., Dickens, G.R., Gracia, E., Guerin, G., Holland, M., Johnson, J.E., Lee, Y.-J., Liu, C.-S., Su, X., Teichert, B., Tomaru, H., Vanneste, M., Watanabe, M., Weinberger, J.L., 2004. Three-dimensional distribution of gas hydrate beneath southern Hydrate Ridge: constraints from ODP Leg 204. *Earth Planet. Sci. Lett.* 222, 845–862.
- Ussler III, W., Paull, C.K., McGill, P., Schroeder, D., Ferrell, D., 2006. Data report: a test of the temperature, pressure, and conductivity tool prototype at Hydrate Ridge. In: Tréhu, A.M., Bohrmann, G., Torres, M.E., Colwell, F.S. (Eds.), *Proc. ODP, Sci. Results*, vol. 204, pp. 1–41. doi:10.2973/odp.proc.sr.204.112.2006. College Station, TX (Ocean Drilling Program).
- von Stackelberg, M., Müller, H.R., 1954. Feste Gashydrate II: Struktur und Raumchemie. *Z. Elektrochem.* 58, 25–39.
- Yakushev, V.S., Istomin, V.A., 1992. In: Maeno, N., Hondoh, T. (Eds.), *Gas-hydrate self-preservation effect*. Hokkaido University Press, Sapporo, pp. 136–140.