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Geochemistry of gas hydrates and associated fluids in the sediments of a passive continental margin. Preliminary results of the ODP Leg 164 on the Blake Outer Ridge

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THE ODP LEG 164 SHIPBOARD SCIENTIFIC PARTY

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Abstract: Marine sediments containing gas hydrates have been drilled up to a depth of 750 m below the sea floor (mbsf) at the Blake Outer Ridge during the ODP Leg 164. Gas hydrates are present between 190 and 450 mbsf. Shipboard analyses of gases and interstitial waters are interpreted with the help of thermodynamic models for gas hydrates and aqueous solutions. Two aspects of the influence of gas hydrates on the chemistry of associated fluids are investigated here. The first one is related to the methane/ethane ratio, which exhibits a sudden change of trend at the base of the gas hydrate zone. This phenomenon could be due to gas hydrates, which act as a concentration barrier for ethane. The second aspect concerns the presence of interstitial waters less saline than sea water above and inside the gas hydrate zone. This could result from the upward expulsion of saline waters during the compaction of sediments in the gas hydrate zone.

New advances on the geochemistry of marine gas hydrates have been obtained during ODP Leg 164 on the Blake Outer Ridge near the southeast coast of North America. This region is characterized by the presence of a strong reflector on seismic profiles, which mimics the topography of the sea floor. This reflector, called the BSR (bottom simulating reflector), is believed to be caused by the high acoustic impedance contrast between a high-velocity gas hydrate-rich layer overlying a low-velocity free gas-rich layer (Minshull & White 1989; Hyndman & Spence 1992; Singh *et al.* 1993; Katzman *et al.* 1994). Three sites (994, 995 and 997) have been drilled along a transect near the crest of the Blake Ridge up to a depth of 750 m below the sea floor (mbsf). Sites 995 and 997 are characterized by the presence of a strong BSR on the seismic profiles, whereas no BSR is distinguishable at Site 994. The drillings have confirmed the presence of gas hydrates in the sediments, as demonstrated by direct sampling on the cores and numerous indirect geochemical and diagraphic evidence. Sediments are homogeneous and mainly composed of greenish nannofossil-rich clays. Thus, the Blake Ridge provides an ideal site to investigate the influence of gas hydrates on the geochemistry of fluids circulating through the sediments. The gas hydrate zone is located between 190 and 450 mbsf. Gas hydrates are finely disseminated throughout this zone. Estimations of the mean gas hydrate content, based on chloride anomalies and logging results, range from 3 to 6% of the volume of porous interstitial space. Two zones, locally richer in gas hydrates, have been observed. The first one is located at depths between 200 and 230 mbsf, whereas the second one is between 420 and 450 mbsf. Two aspects of the influence of gas hydrates on the geochemistry of fluids are described here. The first aspect is related to the methane/ethane ratio, which exhibits a change of its trend near the base of the gas hydrate zone. The second aspect concerns the low salinity of pore waters above and inside the gas hydrate zone. Measured chloride contents of interstitial waters indeed reach values which are about 10% lower than that of sea water. But, before any study of these phenomena, a good understanding of possible phase assemblages involving gas hydrates, aqueous solution and vapour phase is necessary. This will lead us to distinguish different zones in the sedimentary column.

The different zones

Gas hydrates are stable only when certain conditions of low temperature, high pressure and sufficient amount of methane are met. In the Blake Ridge, temperature and pressure are

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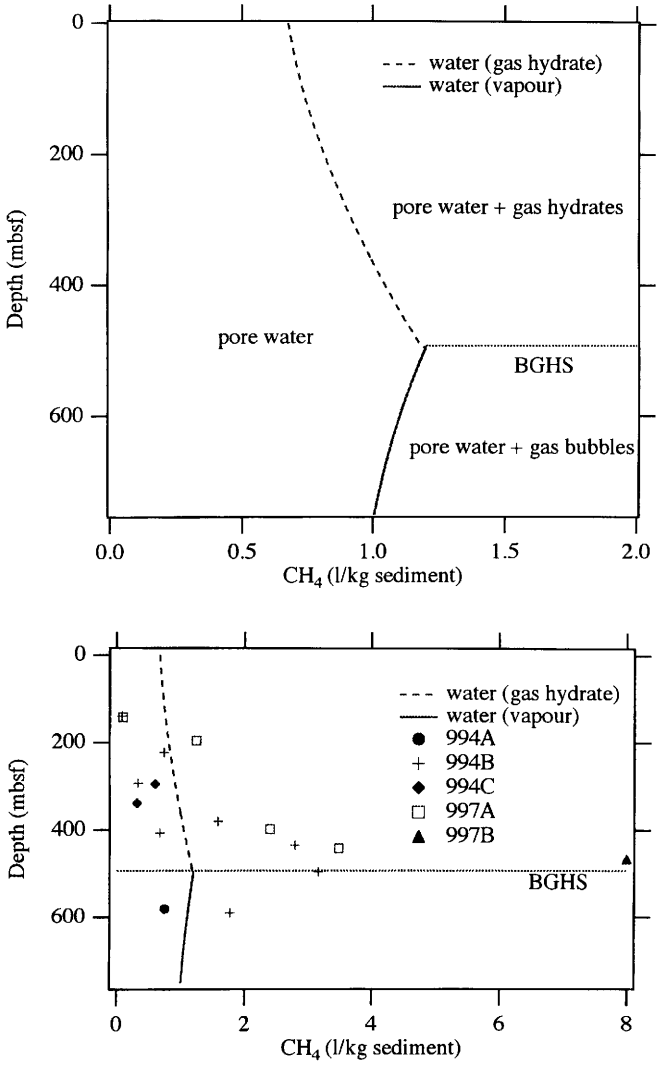

Fig. 1. (**a**) Solubility curves of methane in an aqueous phase in equilibrium either with gas hydrates (labelled as water (gas hydrates)) or with gas phase (labelled as water (vapour)). The BGHS is indicated by the dotted curve. (**b**) Comparison of the phase diagram with methane amounts measured (Dickens, pers. comm.) on PCS samples.

favourable for the formation of gas hydrates between 0 and 450 mbsf. However, no gas hydrates have been sampled or detected by geochemical methods or logging between 0 and 190 mbsf. The absence of gas hydrates in the upper layers of the sedimentary profile may be explained by insufficient quantities of methane. In order to check this hypothesis, it is necessary to quantify the minimum amount of methane for the formation of gas hydrate in a saline aqueous solution. The methane content required for forming gas hydrates depends on the temperature, pressure, water composition and quantity of water in the sediments.

In situ measurements were carried out using downhole tools, such as the WSTP (Westbrook *et al.* 1994) for temperature and the PCS (Petitgrew 1992) for pressure. The water composition was measured by ionic chromatography, and the quantity of water by weighing a piece of sediment before and after being dried in an oven. As there are no experimental data on the methane solubility in a saline aqueous phase at hydrate conditions, thermodynamic models, as

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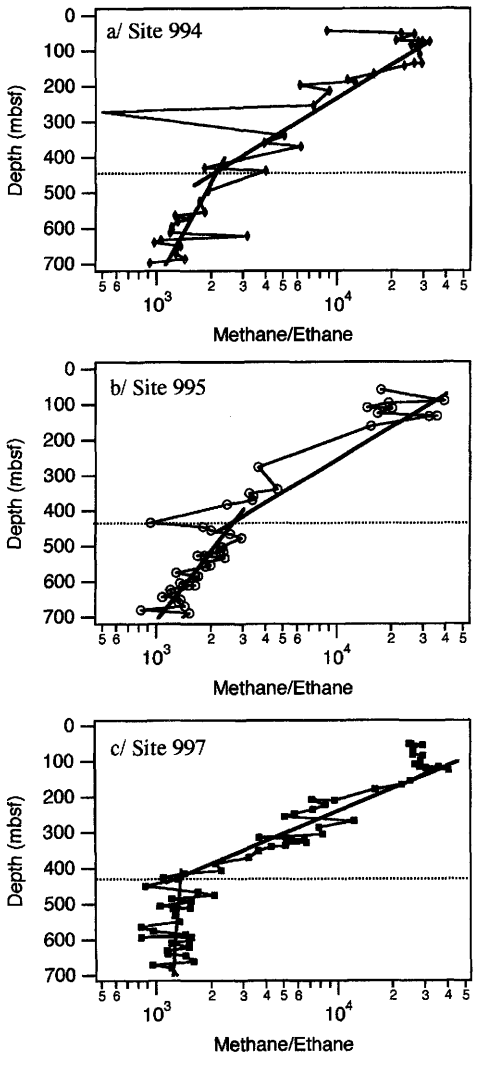

Fig. 2. The methane/ethane ratio vs depth measured in 'free gas': (**a**) Site 994, (**b**) Site 995, (**c**) Site 997.

described in Dubessy *et al.* (1992) and Bakker *et al.* (in press), have been used to estimate this parameter. The model of Duan *et al.* (1992) was applied to model the methane solubility in an aqueous saline solution in equilibrium with a vapour phase.

The result is a phase diagram, which is shown in Fig. 1a and was calculated using the conditions prevailing at Site 997 (geothermal gradient of 36.9°C km^{-1}, hydrostatic regime pressure). The diagram is composed of three fields. The first one, on the left, applies when the amount of methane is low (below 0.8–1.21 under STP (i.e. 25°C and 1 atm) conditions per kg of sediment). When the methane content is above these values, a CH_4-rich phase appears, which is either a gas hydrate (above the base of gas hydrate stability, abbreviated as the BGHZ, at 490 mbsf) or a gas phase (below the BGHZ). *In situ* measurements of the amount of methane in the sediments were made possible using the PCS (Pettigrew 1992). Comparison of the diagram with values measured by Dickens (pers. comm.) confirms that zones containing no gas hydrates are characterized by pore waters undersaturated in methane (in particular, the zone between 0 and 190 mbsf). This demonstrates that the methane availability is a key for discerning the gas hydrate-rich zones and understanding the methane distribution.

Indeed, methane, produced by the degradation of organic matter by methanogenesis bacteria, migrates upward to the sea floor. Between 0 and 30 mbsf the methane content is negligible, as it is consumed in the reduction of sulphate migrating downward from the sea. A diffusion gradient for the methane probably occur between 30 and 190 mbsf. The top of the gas hydrate zone, located at 190 mbsf, thus corresponds to the depth at which the amount of methane is just sufficient for the formation of gas hydrates (around 0.81 kg^{-1} of sediment). Between 0 and 190 mbsf, methane is the limiting factor that prevents the formation of gas hydrates. However, abundant quantities of methane are present in the gas hydrate zone and below the gas hydrate zone, as demonstrated by the PCS data (Fig. 1b). The base of the gas hydrate zone, located at 490 mbsf at Site 997, corresponds to the depth at which limiting temperature and pressure values for the stability of gas hydrates are reached. Below 490 mbsf bubbles of free gas appear.

The methane/ethane ratio

Methane/ethane ratios have been measured using the sampling technique, commonly called the 'free gas' sampling technique. A syringe, piercing the plastic around the core of sediments, is used to collect the remaining gases trapped in the sediments. Gases are then analysed on a gas chromatograph. It is important to note that these samples provide only an estimate of the bulk amount of volatile hydrocarbons (methane, ethane, etc.) that were dissolved in pore waters and either trapped in gas hydrates or in gas bubbles.

The methane/ethane ratio is plotted in Fig. 2a–c for sites 994, 995 and 997 as a function of the depth. The ratios are high, well above 1000.

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This confirms that most of the methane in these sediments have been produced biogenically. The methane/ethane ratio decreases exponentially with depth. In a logarithmic plot (Fig. 2a–c) the ratio can thus be represented by a straight line. Such a behaviour of the methane/ethane ratio has already been observed at other ODP sites of continental margins. However, at sites 994, 995 and 997, a sudden change of the slope of the methane/ethane line is observed near the base of the gas hydrate zone.

It can be noted that there is a gradation in this effect from Site 994 to Site 997. This observation might indicate that gas hydrates have an influence on the diffusion of ethane. Under the temperature conditions of the upper 750 m of the sedimentary column at the Blake Ridge (3–25°C), ethane is more soluble than methane in aqueous water, as indicated, for example, by comparing the values of the Henry constant for methane (37 600 atm) and ethane (26 300 atm) at 20°C (Perry *et al.* 1984). Gas hydrates, too, tend to preferentially incorporate ethane instead of methane when they are in equilibrium with a gas phase, as indicated by thermodynamic models describing the properties of gas hydrates (Dubessy *et al.* 1992; Bakker *et al.* in press). For example, a gas phase containing 1% of ethane and 99% of methane in mole fraction is predicted to be in equilibrium with a gas hydrate containing 3% of ethane and 97% methane in mole fraction expressed on a water-free basis at 25°C and 210 bar. However, the fractionation of methane and ethane between a gas hydrate and an aqueous solution is not known and remains to be estimated with predictive thermodynamic models. A working hypothesis for explaining the change of the trend of the methane/ethane ratio is that gas hydrates preferentially incorporate ethane, and thus act as a concentration barrier for ethane. It is interesting to note that higher concentrations of other hydrocarbons, such as isobutane, *n*-heptane, etc., are also observed at Site 997 near the BGHS (up to 500 ppm for isobutane in a PCS sample at Site 997).

The salinity of pore waters

Extensive sampling and analysis of interstitial waters have been carried out at sites 994, 995 and 997. The chloride contents vs depth at Site 994 are shown in Fig. 3. The chloride profiles of sites 994, 995 and 997 are very similar. The curve is characterized by irregular and anomalous freshening spikes in the gas hydrate zone. These spikes result from the melting of gas hydrates during the recovery, as gas hydrates do not contain any salts. In addition, the curve

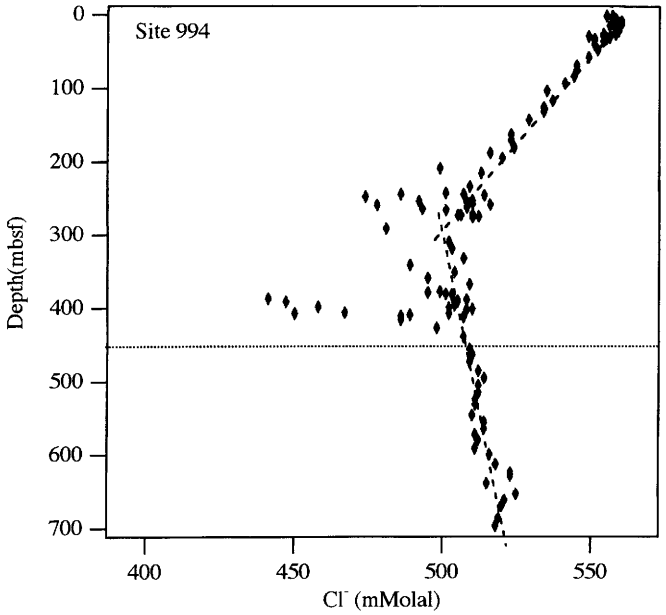

Fig. 3. Chloride content vs depth in interstitial waters at Site 994 (chloride contents are very similar at sites 995 and 997).

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exhibits a background trend towards lower salinities in the gas hydrate zone. One possible explanation for this involves gas hydrates. When sediments compact, they expel water. Such a mechanism normally has no incidence on the salinity of pore waters. However, in the gas hydrate zone, salts are excluded from gas hydrates. Thus, waters, that are expelled in the gas hydrate zone as a result of the compaction, are expected to be more saline. This should result in a preferential loss of ions in the gas hydrate zone. Moreover, because of the subsidence, sediments that were in the gas hydrate zone reach the 'free gas' zone below the BGHZ. Gas hydrates melt and release fresh waters that should also contribute to lowering the salinity of pore waters at these depths.

Conclusion

The data gathered during ODP Leg 164 allow us to better understand the influence of gas hydrates on the geochemistry of fluids. Two aspects have been described here. The first one is related to the change of trend of the methane/ethane ratio at the base of the gas hydrate zone. The second aspect concerns the presence of less saline pore waters in the gas hydrate zone. Both phenomena are tentatively explained and would be a consequence of the formation of gas hydrates in the sediments. In the first case, gas hydrates would preferentially concentrate ethane and heavier hydrocarbons with respect to methane, and thus modify the methane/ethane profile. In the second case, crystallization of gas hydrates during the compaction of sediments leads to a preferential migration of dissolved ions to the sea, and thus to a decrease in the salinity of pore waters in the gas hydrate zone. At the present stage, these are only working hypotheses that need to be developed more quantitatively and compared with other studies.

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