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# Literature Review on Physical Properties of Gas Hydrates and Implications for Sediment Stability

Coastal Geoscience and Global Change Programme
Internal Report IR/02/072

BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/02/072

# Literature Review on Physical Properties of Gas Hydrates and Implications for Sediment Stability

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*Key words*

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$CO_2$ Hydrate grown in plastic covered gravel. (Photo CA Rochelle).

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# Foreword

This report is the published product of a study by the British Geological Survey (BGS) as part of the Coastal Geoscience and Global Change Programme. It is part of ongoing work into Gas Hydrates as it is recognized that these may have significant importance as a Geohazard and as an instigator of climate change.

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# Summary

This literature review was undertaken as a preliminary study as part of an Ocean Margins Link research project, involving BGS, the University of Leicester and Geotek, into the characterisation of the physical properties of gas hydrates.

The bulk of global organic carbon is taken to be stored in methane hydrates below the ocean floor. These ice-like solids, formed within sediments, comprise 'cages' of water molecules enclosing gas that are stable at high pressures and low temperatures. Recent work suggests that destabilisation of sediment hosted hydrates could trigger catastrophic slope failures on ocean margins (Mienert et al.,1998). The liberation of 'greenhouse' gases, such as methane, within the hydrate cages, during destabilisation may have significant effects on the efficiency of global thermohaline circulation.

Current research and observations from recovered samples indicate that hydrates form a variety of fabrics within the sediment, and that such fabrics are significant in influencing hydrate stability, (Malone,1985; Ivanov et al.,1998). The influence of the pressure and temperature history on the gas-hydrate distribution in laboratory sediments is being investigated. Pressure vessels are being developed to enable laboratory quantification of the effect of hydrate fabrics. Current investigations are concentrating on developing techniques to grow significant quantities of hydrates within sediments under controlled conditions. It is intended that this will lead to the study of the physical properties of these hydrate/sediment assemblages.

The effect of hydrate on submarine slope stability is still poorly understood. Although it is possible to use standard geotechnical models to calculate Factors of Safety against slope failure, it is likely that these will be inadequate for reliable risk assessment of submarine slopes containing gas hydrate as there is huge uncertainty in physical properties of hydrate bearing sediments. The solid hydrate and the gas and water evolved from disassociating hydrate will probably change the way the sediment responds to static (e.g. weight) and dynamic (e.g. earthquake) loading and a more rigorous method of slope stability analysis will be required for more accurate risk assessment

# 1. Introduction

## 1.1 WHAT ARE GAS HYDRATES?

Natural gas hydrate is an ice-like substance that is made up of rigid cages of water molecules, with a natural gas molecule in most of the cages. Sir Humphrey Davy first discovered hydrates in 1810, but they remained largely a curiosity until they became a problem for the hydrocarbon industry, as they often form in pipelines. In most natural occurrences, this gas is predominantly methane. In recent decades their discovery in large quantities has prompted investigation into the recoverability of the contained methane. Hydrates are believed to be identifiable by their physical properties (Table 1), which are distinctly different from those of the sediments in which they form and the pore fluids that they replace.

Gas hydrates form under certain conditions. The methane concentration has to be fully or near fully saturated . Hydrates form at high pressure, such as with increasing water depth and/or low temperature (Figure 1), with geothermal heating of sediments determining the base of the hydrate stability zone (HSZ). In addition to temperature and pressure, phase conditions can alter depending on the presence of salts or other gases, such as sodium chloride or carbon dioxide, dissolved in the pore fluid (Bakker et al.,1996; Kvenvolden,1998) which alter the chemical potential of the system. In the Cascadia margin it is thought that hydrate at the sea floor is a secondary phase formed by restabilisation of gas, which has been forced up through fractures, by the addition of hydrogen sulphide from near surface sediments (Suess et al.,1999). This ties in with the known phase/ chemical relationship (Kvenvolden,1998), the presence of hydrogen sulphide increasing the temperature at which a hydrate can remain stable for a given pressure. Although possible hydrate mounds are reported in the literature, (Long et al.,1998), their formation/stability characteristics are poorly understood.

| | Water | Ice | Methane Hydrate | Sediment |
|---|---|---|---|---|
| **P-wave velocity (km/s)** | 1.47 | 3.8 | 3.3 - 3.8 | 1.5 – 1.8 |
| **S-wave velocity (km/s)** | 0 | 2.0 | 1.7 | 0.2 – 0.45 |
| **Thermal conductivity (W/mK)** | 0.59 – 0.56 | 1.5 – 2.5 | 0.5 | 1.3 – 1.8 |
| **Density (g/cm$^{-3}$)** | 1.035 | 0.917 | 0.92 | 2.4 – 2.7 |
| **Electrical resistivity (Ωm)** | 0.3 | 10 - 1000 | 150 | 1.0 |

**Table 1. Physical properties of the constituent parts of the hydrate system (after (von Huene et al.,1985; Pecher,1995)**

## 1.2 LOCATION AND DETECTION OF GAS HYDRATES

Methane hydrates are generally restricted to two world regions where the pressure and temperature conditions are suitable: polar and deep oceanic. Oceanic methane hydrates occur in water depths in excess of 300 m where the bottom sea temperatures approach 0$^{o}$C. Methane hydrates are distributed around the continental margins because the land

mass can provide large quantities of organic matter required for the generation of methane gas, (von Huene et al.,1985; Ashi,1999).The phase diagram (Figure 1) implies, theoretically, hydrates can exist in thick layers provided that they fall into specific pressure-temperature conditions.

Hydrates have been recovered from a number of locations world wide. These include the marine sites of the Blake Bahama Ridge, the Middle America Trench, the Nigerian continental slope and the Nankai Ridge and the sub polar sites of the Mackenzie delta and off the north Norwegian coast. They have also been found in the Caspian and Black Seas with a fresh water occurrence in Lake Baikal.

Hydrates were first remotely identified in the marine environment by interpretation of a Bottom Simulating Reflector (BSR) on seismic sections. This is believed to arise at the hydrate/gas and hydrate interface. The Base of the Gas Hydrate Stability Zone (BGHSZ) lies beneath this, and is the lower limit of hydrate formation. In the past, gas hydrate has been found inadvertently on a number of occasions during drilling operations, as without free gas the BSR does not occur, it is now being actively sought by a number of research programmes. Hydrate is commonly found in the sediment as shown in Figures 2a and 2b, with the position of the hydrate layer dependant on local conditions (Figure 3).

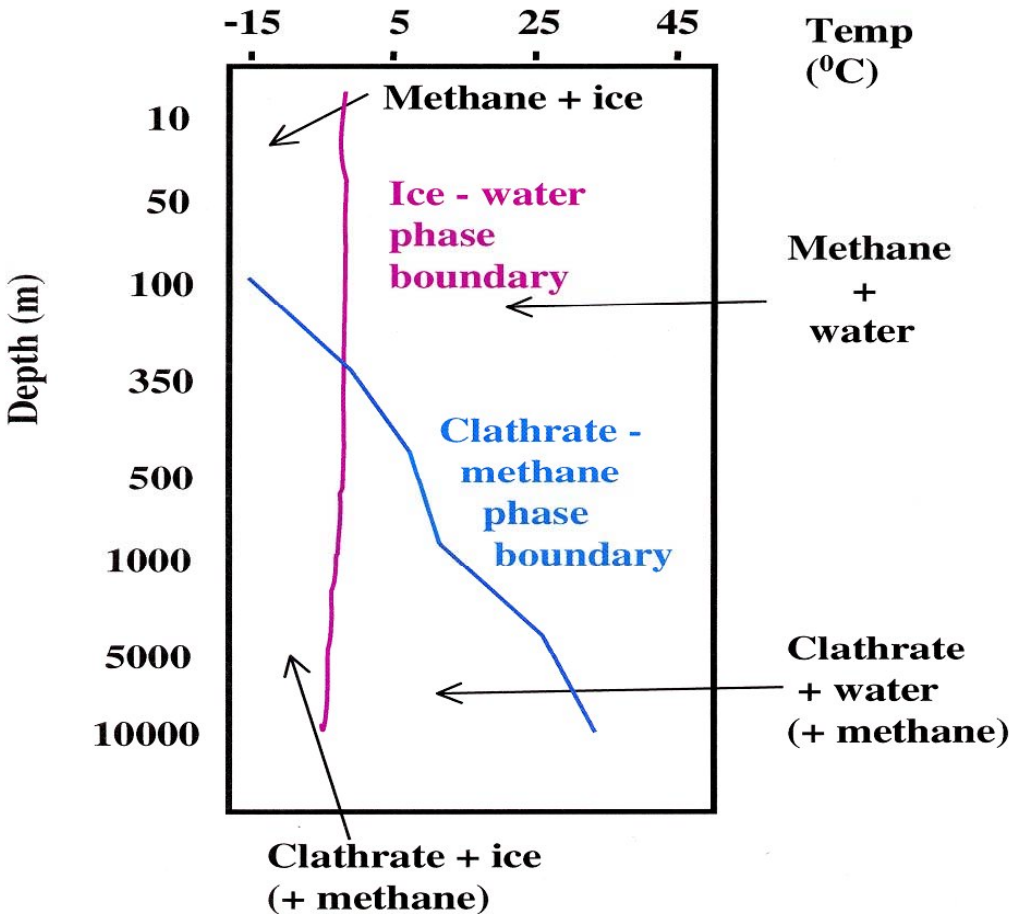



**Figure 1. Depth /Temperature phase diagram for Methane Hydrate stability (after Kvenvolden,1998)**

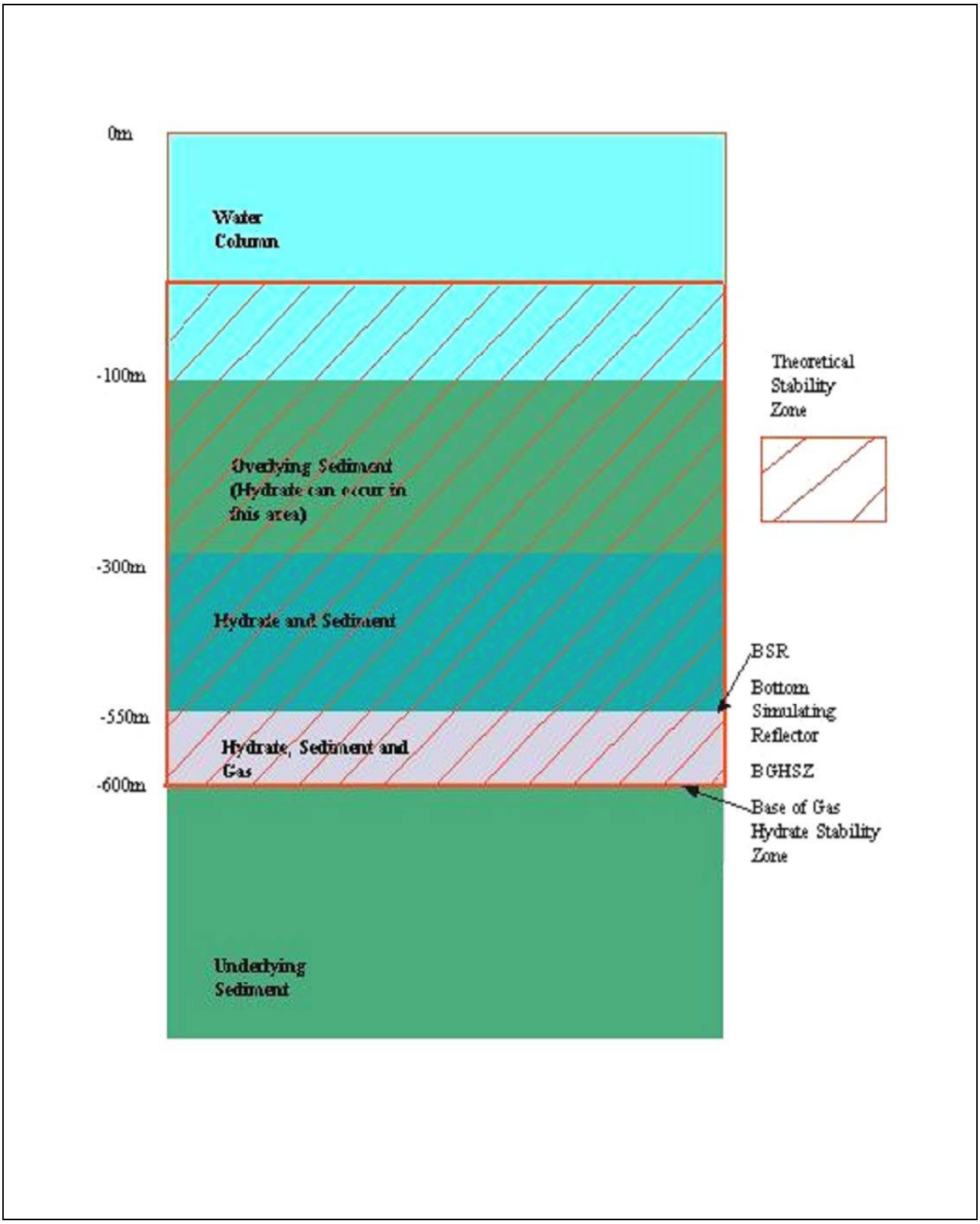



**Figure 2a. Schematic representation of hydrate emplacement within the sediment column.**

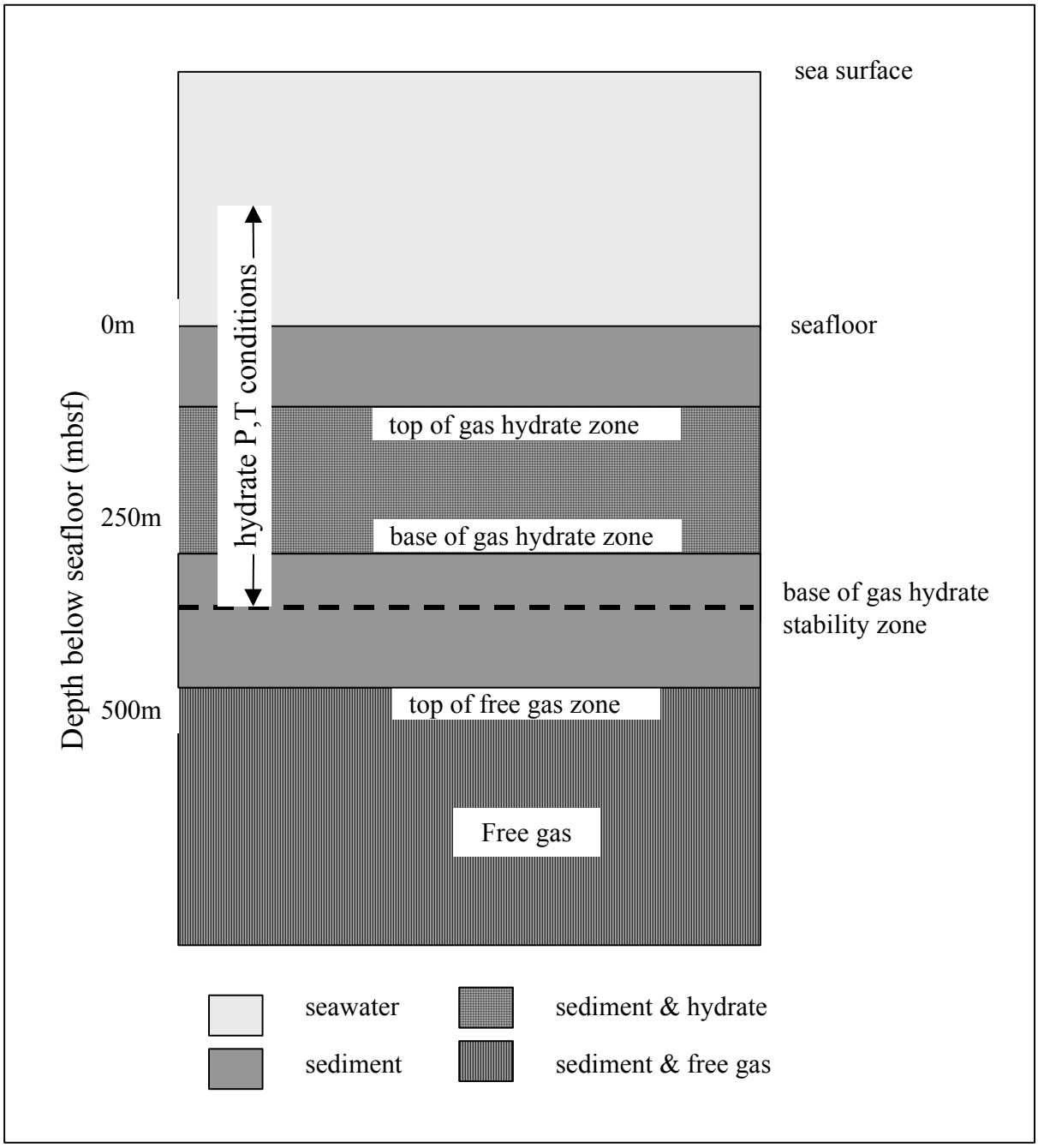



**Figure 2b. Possible distribution of hydrate on the basis of analytical modelling of methane flux, assuming low hydrate concentrations, providing an explanation of observations at Site 994 of ODP Leg 164 (Xu and Ruppel, 1999).**

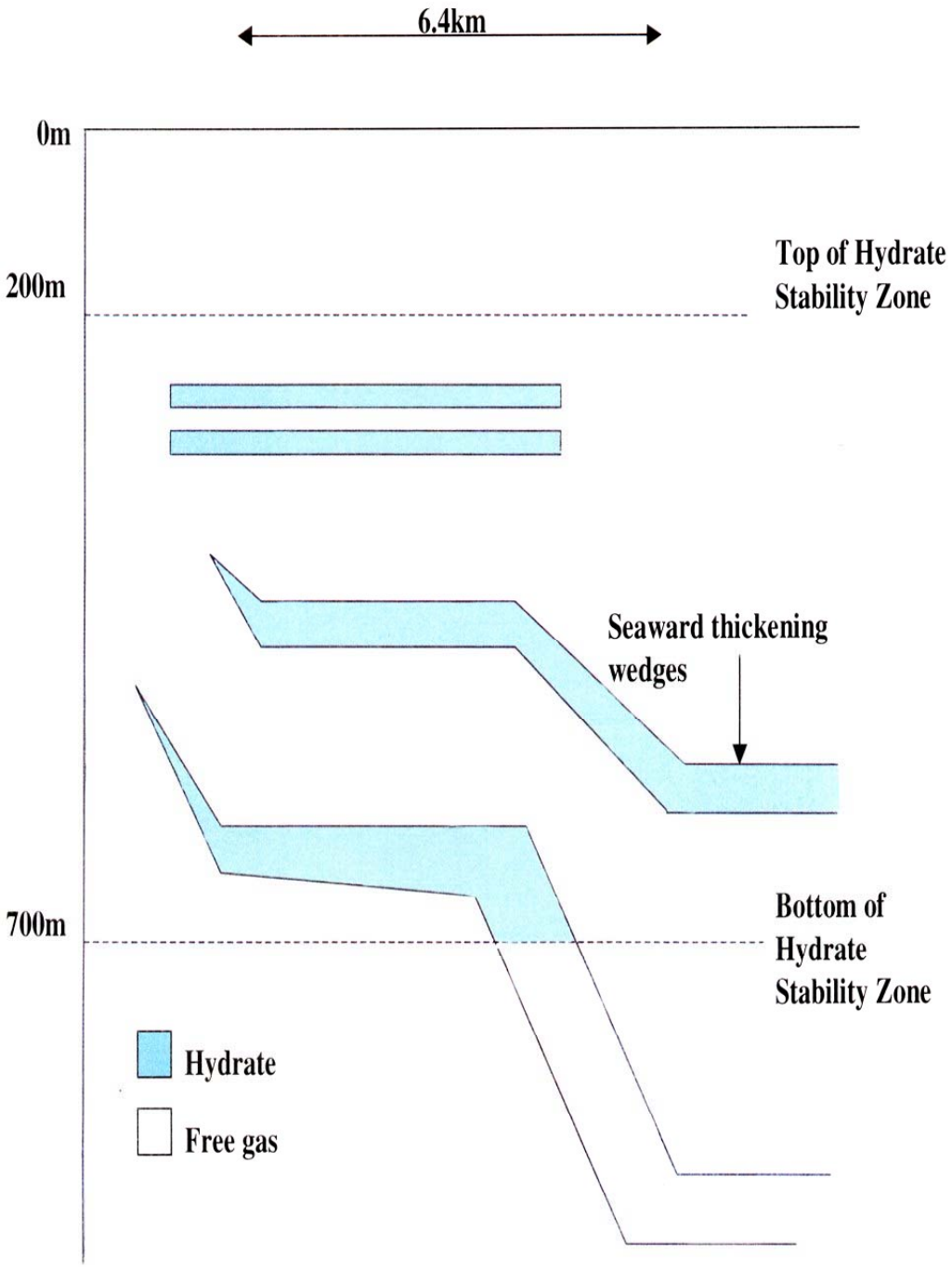



**Figure 3. Distribution of hydrate layers within a sediment in a permafrost environment (after Collet, 1993). Layers are formed due to differences and changes in local conditions**.

Figure 4 shows tomographic processing of seismic reflection data and may be a more accurate indication of the presence of hydrate within the sediment column as it shows the lateral variation of velocity profile. It is also theoretically possible for hydrate to exist in the water column, although (Milkov,2000) states that this is impossible due to low concentrations of water-dissolved gas, which, are incapable of creating the saturation level required for hydrate formation. Solid Hydrate also has a density of <1, which means detached blocks will float up through the water column and disassociate. It appears from the reported occurrences of hydrate that mass emplacements exist well within their theoretical upper boundary limits(Collett,1993; Suess et al.,1999).

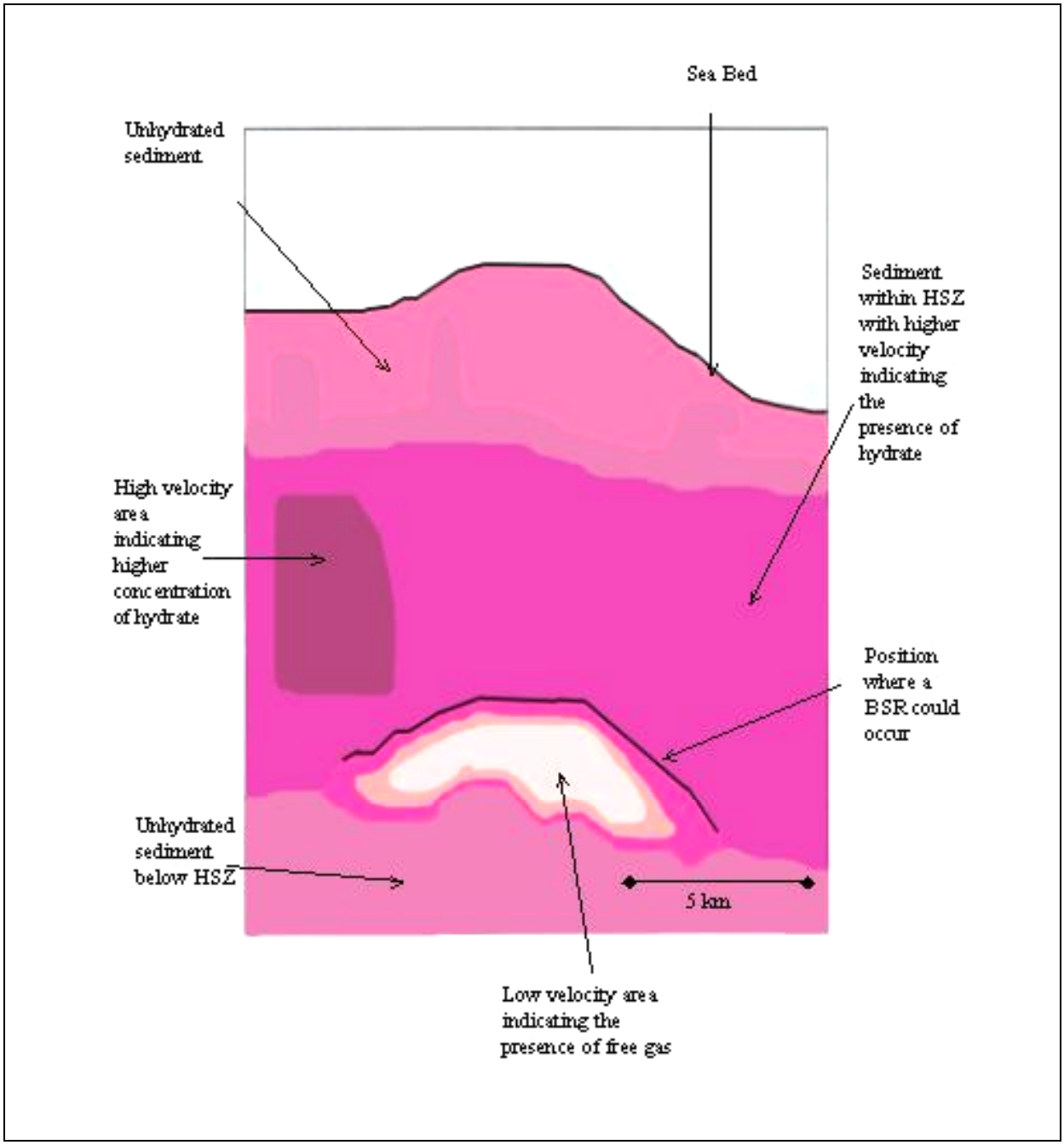



**Figure 4. Local velocity structure through sediment column derived from tomographic inversion (after (Tinivella et al.,1998)**

## 1.3 IMPORTANCE OF GAS HYDRATES TO SOCIETY

Due to their structure, hydrates can hold greater quantities of gas than an equivalent volume of gas at standard temperature and pressure. This ratio is in the region, hydrated gas: free gas 1:160. World estimates for the amount of carbon in continental gas hydrate deposits range from $7.6x10^{15}$ g (Meyer 1981) to $1.8x10^{19}$ g (Dobrynin et al.,1981). World estimates for the amount of carbon in oceanic gas hydrate deposits range from $1.7x10^{18}$ g (McIver,1982) to $4.1x10^{21}$ g (Dobrynin et al.,1981). Kvenvolden (1998) estimates the potential methane reservoir in US oceanic gas hydrates to be up to $1.0x10^{20}$ g. To provide a comparison, (Kvenvolden,1998) also suggested currently proved and recoverable reserves of conventional methane carbon in reservoirs are up to $4.1x10^{16}$ g. He also suggested that gas hydrates provide up to five times the volume of methane per volume rock than conventional natural gas. The most conservative estimates indicate gas hydrate stored in the oceans, accounts for at least half of the world organic carbon budget. Current research (Dobrynin et al.,1981; Collett,1993; Raynaud et al.,1998; Ashi,1999) indicates that this amount of potential gas is important for a number of reasons:

There is a potential for significant contribution to the hydrocarbon needs of the industrialised world.

Methane is an important greenhouse gas. Its release to the atmosphere could have severe implications for global climate change.

The dissociation of hydrate would release large amounts of gas into the surrounding sediment, possibly leading to a reduction of sediment strength with potential risk for structures located within or on them. In the case of sediment slopes this could lead to significant failures with a subsequent catastrophic release of methane into the atmosphere.

Hydrates are an important sink/source in the global carbon cycle.

Consequently, a thorough understanding of the physical properties of hydrate and surrounding sediment is needed to aid interpretation of seismic reflectors and underpin stability models, and their implications for climatic feedback mechanisms. Due to the temperatures and pressures needed to stabilise hydrates, the current state of knowledge of hydrate properties is limited to the basic observations on samples obtained from a few sites, seismic surveys and a few geophysical borehole logs. There has been a lack of direct measurement until the late 1990's as the bulk of investigation has centred on the chemical properties related to the production side of the oil industry i.e. the formation of pure hydrate within pipelines. This situation has changed in recent years with the development of pressure recovery vessels and storage containers, which allow the recovery and examination of intact samples of natural hydrate. Table 2 shows observations made on hydrate zones within sediment and in laboratory specimens, the wide ranges of values demonstrating the difficulty of assessing physical properties.

| $V_p$ km/s | | |
|---|---|---|
| **2.6** | Synthetic Hydrate in Sand (Propane) | (Stoll and Bryan,1979) |
| **2.4** | Solid Synthetic Propane Hydrate | |
| **2.2-5.3** | Solid Natural Hydrate (DSDP Leg84) | (von Huene et al.,1985) |
| **3.3-3.6** | Natural Hydrate in a Coarse Matrix (Mallick 2L-38 Research Well) | (Miyairi et al.,1999) |
| **1.6-1.8** | Natural Hydrate in a Clay Matrix (ODP Leg 164) | (Guerin et al.,1999) |
| **2.7-3.9** | | (Winters et al.,2000) |
| **2.4-2.9** | Ice and Natural Hydrate Coarse Matrix | |
| **3.8** | Water and Natural Hydrate Coarse Matrix Synthetic Hydrate in Sand | |
| **3.8** | Ice | (Pecher,1995) |

| $V_s$ km/s | | |
|---|---|---|
| **1.7-1.8** | Natural Hydrate in a Coarse Matrix (Mallick 2L-38 Research Well) | (Miyairi et al.,1999) |
| **0.4-0.7** | Natural Hydrate in a Clay Matrix (ODP Leg 164) | (Guerin et al.,1999) |
| **1.7** | Synthetic Propane Hydrate | (Pandit and King,1982) |
| **2.0** | Ice | (Pecher,1995) |

**Table 2. Velocities through Hydrate and Hydrated Sediment**

# 2. Hydrate Morphology

From the small number of samples containing hydrate that have been recovered, four contrasting morphologies have been identified, massive nodules of solid hydrate, hydrate

disseminated through the sediment pore structure, aerated near surface emplacements and layered structures, enabling some inferences to be drawn on the effects of sediment on hydrate formation.

## 2.1 MASSIVE SAMPLES

At site 570 on Leg 84, of the Deep Sea Drilling Program, off the Pacific Coast of Guatemala, a core of massive hydrate was recovered. It was 1.05m long and believed to come from a 3-4m thick massive hydrate body. The Ocean Drilling Program leg 164, off the south east seaboard of the U.S.A. also found massive samples, which were up to 35mm long (Figure 5) and thick or nodular pieces 50-80mm in the top 9m of sediment at site 996.

**Figure 5. Massive Gas Hydrate (~14x5 cm) coated with slurry. (Paull et al.,1996) Ocean Drilling Program Leg 164, section 164-997A-42X-3 (~331mbsf)**

## 2.2 DISSEMINATED STRUCTURE

In contrast, drilling on the McKenzie delta in Canada enabled large pieces to be preserved, 20mm in diameter, with the hydrate occurring as intergranular filling (Uchida et al.,1999). At this site the sediment matrix, containing the largest hydrate concentration, was described as an unconsolidated medium grained sandstone (Katsube et al.,1999). The cores were well preserved upon recovery from this environment enabling a detailed examination of the hydrate dissemination to be obtained using X-ray computerised tomography attenuation imaging (Figure 6). Such differences in distribution also showed up in laboratory tests, sands had hydrate concentrations of 15-80% in their interstices (Booth et al.,1998) and tended to form in thick zones, whereas silts showed few hydrate grains forming within them.

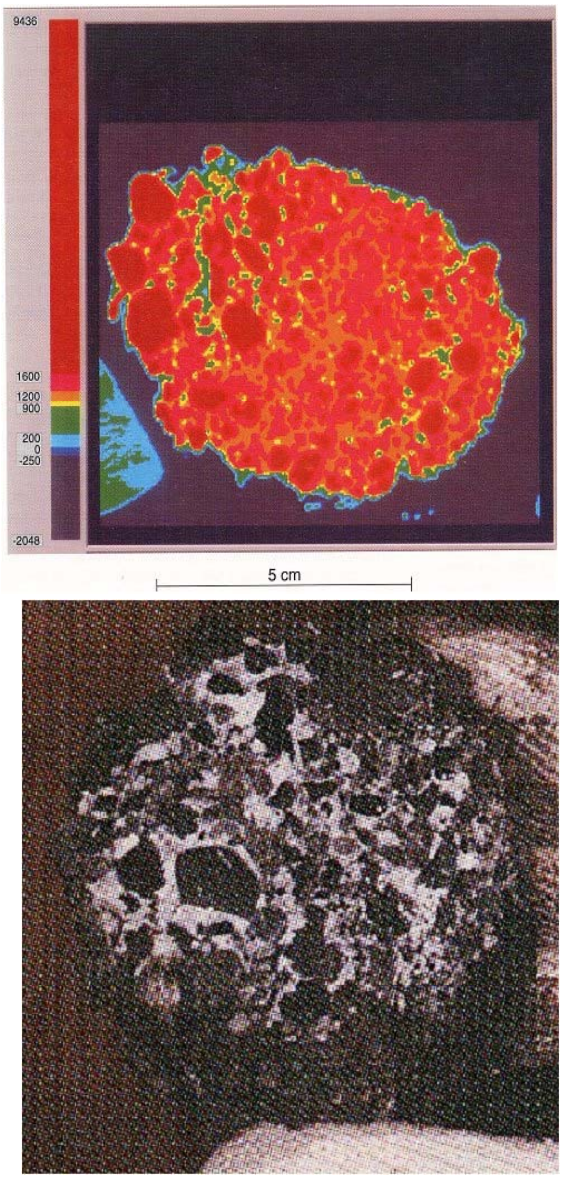



**Figure 6 Computerised tomographic image (top) of a hydrated sediment sample (bottom)Reproduced with the permission of the Minister of Works and Government Services Canada, 2002 and Courtesy of Natural Resources Canada, Geological Survey of Canada**

## 2.3 AERATED STRUCTURE

At both of the sites above samples were found, in the main, at depth or buried within the sediment. Recent surveys of the seabed in the Cascadia Margin area, off the north west seaboard of the U.S.A. have found hydrate forming at the surface or within the top 0.5m of sediment (Bohrmann et al.,1998). This has a markedly different structure to the hydrates described above suggesting a different formation mechanism (Figure 7). At this site no evidence of cementation of the sediment matrix and no occupation of sediment pore space has been found (Suess et al.,1999), despite this being recorded for hydrates situated near the BSR at this site (Bohrmann et al.,1998). The sediment at the seabed and the BSR had a similar lithology in that they were fine grained, suggesting the morphology might be controlled by the effects of the depth of burial, such as the sediment particle orientation or grain packing and their effects on pore connectivity. Other structures were also found at this site, indicating a number of formation mechanisms.

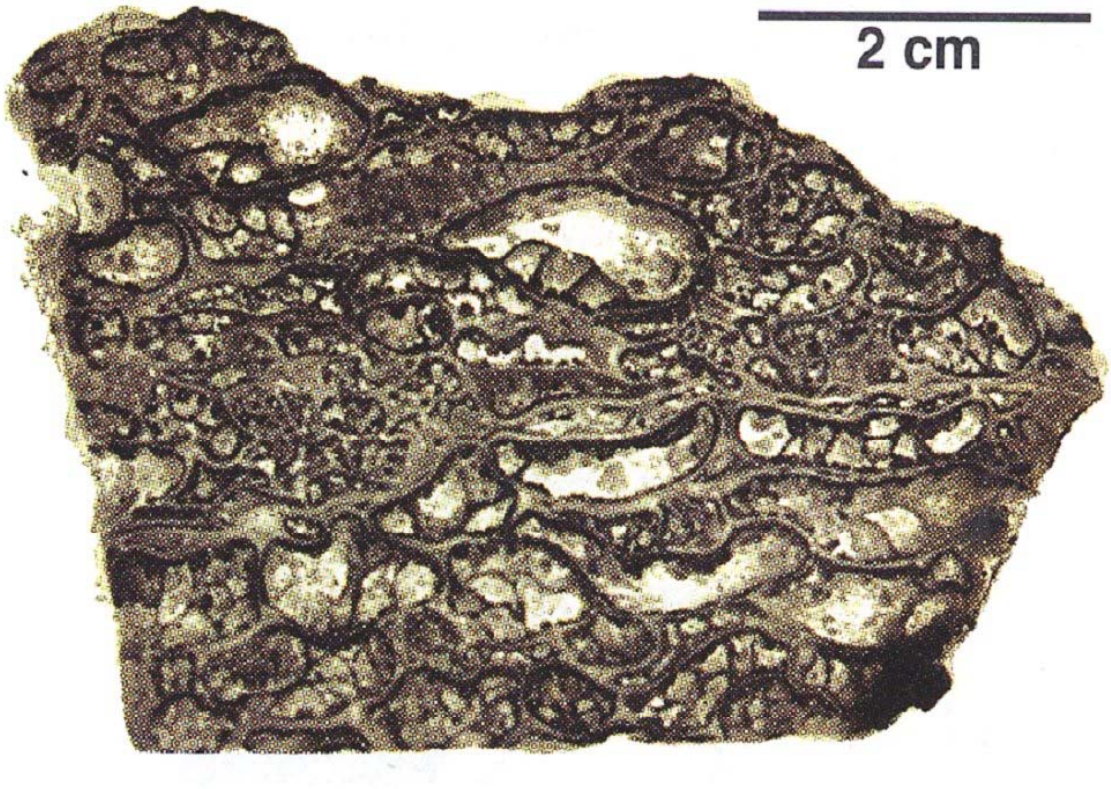



**Figure 7 Thin section of pure gas-hydrate layer showing globular structure of gas hydrate outlining former gas bubbles. From Geology 1998 Bohrmann, G. Greinert, J. Suess, E. Torres, M. Reproduced with permission of the publisher, the Geological; Society of America, Boulder, Colorado, USA. Copyright © Geological Society of America**

## 2.4 SOLID LAYER STRUCTURE

Thin friable 'plate like' veins of 1-2mm thick (Figure 8) were found on the Blake Ridge (Paull et al.,1996). They appear to fill fractures in the fine-grained (mud or clay) sediments. Thicker veins have been found in fine grained seabed sediments in the Cascadia Margin area that appear to follow the bedding planes in the sediment.

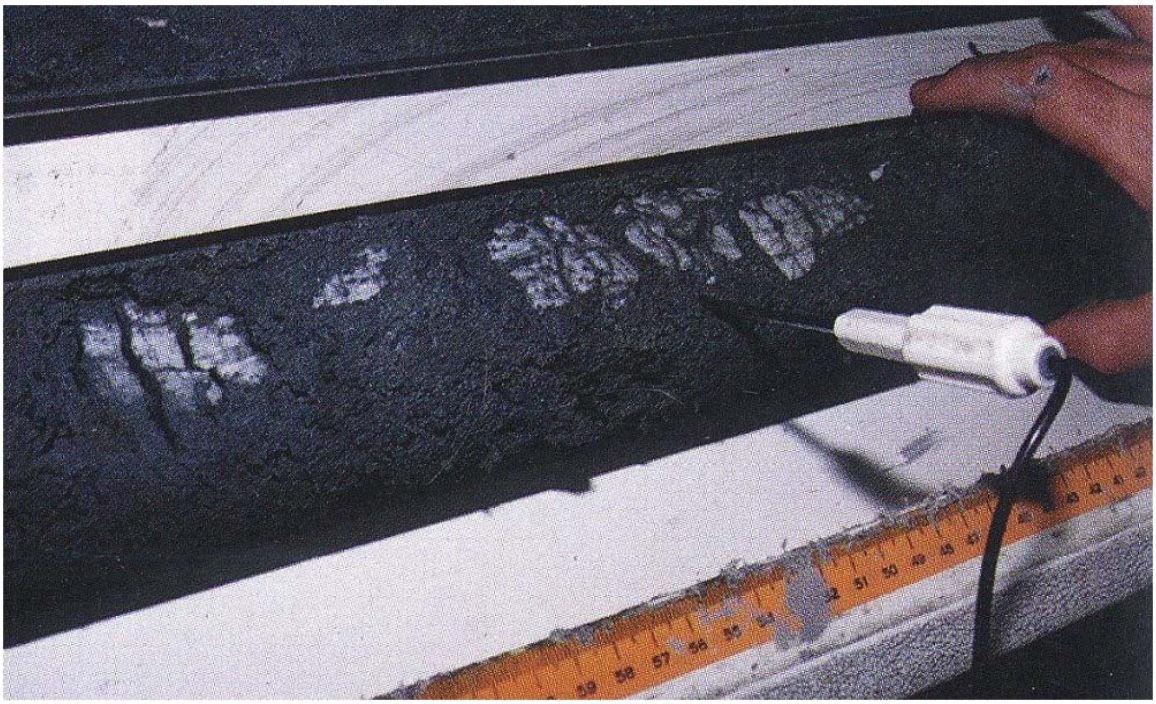


**Figure 8. Thin veins of Gas Hydrate. (Paull et al.,1996) Ocean Drilling Program Leg 164, section 164-996D-6H-1 (~42mbsf)**

## 2.5 IN SITU EMPLACEMENT AND FORMATION CONTROL

Within the seafloor hydrate stability zone it is possible for two or more distinct bands of hydrate to occur (Collett,1993) (Figure 4). The formation of these bands is not a feature apparent from seismic records. If a layer is less than $1/8^{th}$ of the length of the wavelength from the seismic source (Widess,1973), it is not always possible to see it on a seismic record. Conventional sources need to use low frequency, long wavelengths to propagate the sound energy into the deeper layers. The use of Chirp technology (Schock and Leblanc,1990) could overcome this problem. This potential for layering could have significant implications for slope stability scenarios, but this has not as yet been studied.

Published results suggest the porosity of the material alone is not related to hydrate occurrence. For instance hydrate formed in a gravel of porosity 23-29% whereas it was absent in a silty sand of porosity 24-41% (Winters et al.,1999). Mudstones, which have porosities of (24-30%) have been found to contain smaller amounts of hydrate (Katsube et al.,1999). The grain size distribution of the sediment could therefore have some bearing on the ability of the sediment to host large concentrations of hydrate. A poorly graded, uniform sediment such as a gravel will have no smaller particles in the pore spaces or in the pore connections so the available storage space and the permeability will be maximised. A well graded or gap graded sediment, typical of glacial deposits, will have smaller pore spaces and reduced pore interconnectivity. This will reduce the size of

the individual pore storage volumes and the permeability of the sediment. It is more likely that the interconnectivity and the size of the individual pores in the sediment will have a greater control over the formation of hydrate within its structure.

Diagenetic processes have also been analysed with regard to hydrate occurrence. For example in both the Mallick field and Deep Sea Drilling Program (DSDP) Site 570 dolomitic-cemented sandstone has been found adjacent to hydrate (von Huene et al.,1985);(Jenner et al.,1999). It has been suggested that this is an artefact of chemical exclusion from the hydrate formation process (Jenner et al.,1999). Authigenic carbonate intercalated with hydrate has been found (Bohrmann et al.,1998), the formation of which is believed to be as a result of hydrate dissociation. It would appear that diagenetic processes involved with hydrate occurrence could control the geophysical and geotechnical properties of sediments.

# 3. Disassociation of Hydrates and the effect on Sediment Strength

## 3.1 OVERVIEW

The dissociation of hydrates is an important factor in sediment stability and subsequent release of methane to the atmosphere and could arise from a number of hypothetical scenarios, which have yet to be tested:

1. Decrease in pressure from:
   - sea level fall
   - sea floor uplift
   - unloading of overlying sediment.

2. Increase in temperature from:
   - ocean warming
   - change in the temperature gradient

3. Dissociation could also arise from a chemical incursion of high salinity seawater into the pore fluid around the hydrate.

This could change the phase position for hydrate formation and bringing the maximum temperature for hydrate stability below the ambient temperature. The effects of a change in pore water composition on hydrate stability are well documented (Dickens and Quinby,1997) and are the subject of ongoing research (Bakker et al.,1996). It would also appear that biological factors (Cragg et al.,1996) could be significant in the control of the top of the hydrate zone. Clearly the time factor could also be of importance for any effects of dissociation on the stability of the surrounding sediments. It is thought in impermeable sediment, the elevated pressure under the hydrate would suppress further dissociation indicating that the base would remain in a stable position (Kayen and Lee,1991). Although it has yet to be tested, this logical scenario has not been questioned in subsequent literature. In a more permeable medium, allowing dissipation of excess pore pressures, the base would tend to move up through the sediment column. The effect of dissociation with time on the sediment matrix properties will almost certainly prove to be a useful tool in assessing failure scenarios in real situations.

## 3.2 EFFECTS OF GAS ON SEDIMENT BEHAVIOUR

The shear strength of a sediment can be significantly reduced by the presence of a gas in the pore space (Sills and Wheeler,1992). Upon dissociations the gas liberated from the hydrate will increase the pressure of the pore fluid if it cannot expand beyond its hydrated volume. As $1m^3$ of hydrate can liberate $160m^3$ of gas at RTP there is potential for disruption of the overlying sediment fabric and massive over pressuring of the pore fluid (Van Rensbergen et al.,2002). This increase in the pore fluid pressure will reduce the effective stress in the sediment. There is a widely accepted relationship between effective stress and shear strength for a saturated sediment (Skempton,1954; Craig,1987), so by assuming the saturated case, the decrease in shear strength can be calculated from the increase in pore pressure.

A rare direct measurement of gas pressure under the hydrate zone reported pore pressures of 25-45% above the pressure exerted by overburden from sediments and the water column on the lower and midslope areas of DSDP Leg 84 but an associated slope failure (von Huene et al.,1985) has not been reported. These pressures were measured ahead of the drill during the coring stages and indicate the potential for increased pore pressure upon dissociation.

Laboratory experiments have shown undrained shear strength could increase due to presence of gas bubbles in some circumstances, other initial controlling parameters being consolidation and initial pore pressure (Wheeler,1988). Such tests are incredibly sensitive to initial conditions e.g. saturation, over consolidation, sample disturbance and testing methods (Nelder,2000). These results fit a conceptual model previously suggested (Wheeler,1988) and clearly illustrate the complexities involved in testing the geotechnical parameters of gas charged sediment. Wheelers' work used gassy reconstituted clayey silt sediment obtained from an estuary. It is uncertain how this work will extend to the deep ocean sediment situation but it could prove useful in initial modelling work. There are as yet no values available from deep ocean situations.

The use of saturated soil mechanics in calculating slope stability might prove to be an oversimplification. As gas could be evolved into the pore fluid during hydrate dissociation it might be more useful to study the unsaturated soil mechanics of the system. In unsaturated soil mechanics the pressures of the gas and liquid components of the pore fluid can exist at different pressures at the same depth. The exact nature of the effects of evolved gas on the sediment strength needs to be investigated, as although work has been done into this problem (Sills et al.,1991; Duffy et al.,1994)it is mainly laboratory based and concerned with very shallow gas (~0.1m) depth.

Geotechnical measurements on hydrates and hydrated sediments have not been reported in any great number. (Winters et al.,1999) report an increase in shear strength of up to 800%, from 0.82 MPa to 6.69 MPa, for the samples recovered from the McKenzie delta. As yet there is little published data using standard triaxial apparatus for hydrate due to its instability and the need for specialised testing apparatus. Shear strength values using shear vanes and similar apparatus on recovered cores are often affected by sample disturbance as a result of hydrate dissociation (Figure 9). This makes an accurate assessment of the in-situ strengths impossible. As discussed earlier the hydrate may exist in many different morphologies within the sediment. These morphologies could have a direct bearing on the shear strength of that sediment and any stability characteristics of the area in which they are found, but as yet these have not been studied systematically.

**Figure 9. Fizzing piece of hydrate in a sediment core. The soupy nature of the core could be due to the dissociation of hydrate. (Paull et al.,1996) Ocean Drilling Program Leg 164, section 164-994D-4X-3; 261 mbsf**

When considering the failure mechanism, the absolute strength of hydrate is unlikely to be of importance in the majority of cases. The one possible exception to this is the situation where a cemented hydrated layer is acting as a cap over dissociated gas. In this situation the overlying sediment could act as a slab and be subjected to 3-D bending in a similar way to loading a concrete floor slab. The compressive and tensile strength characteristics will then determine whether it will fracture allowing the upward movement of free gas. If a hydrate cemented sediment matrix exists the likelihood is that it will be more resistant to fracture than a similar unhydrated sediment. The tensile properties of a hydrated zone in all its morphological forms are of particular interest for looking at fracture formation. Fractures could be a dominant method of transporting gas to the surface. This could lead to high-pressure seepage and mechanical disruption or could act as a pressure release from the hydrate base.

# 4. Slope Stability

## 4.1 HYDRATED SLOPES

Several areas believed to contain hydrate, based on the occurrence of a BSR, are coincident with apparent slope failures e.g. (Mienert et al.,1998). However, as yet proven causal links between these events as mechanisms for slope failures from hydrate activity have yet to be found. (McIver,1982) suggested a possible failure scenario shown in Figure 10, arising from the overstressing of sediments. This model is widely reported, although no geotechnical parameters for sediments have been published to substantiate an actual occurrence.

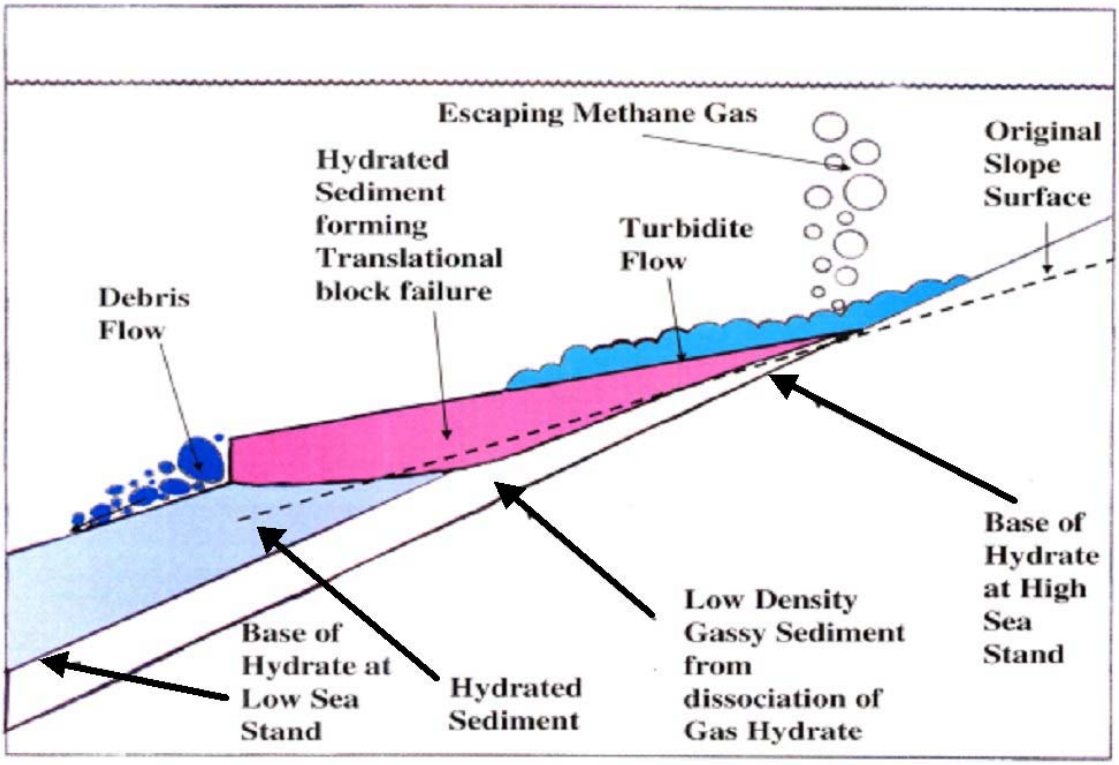



**Figure 10. Possible slope failure scenario (after McIver 1982)**

## 4.2 GENERAL SLOPE STABILITY

The basic setting for a slope failure is where the shear strength of the slope material is insufficient to resist the forces imposed on them, such as gravity and earthquake accelerations (Figure11). In areas where gas hydrates are present the slope failure scenario is believed to arise from excess pore pressure resulting from hydrate dissociation causing a large decrease in sediment shear strength. This would lead to slumping, sliding or rotational failure. There is however a distinct possibility that the free gas could cause deformation of the overlying sediment and that mechanical disruption would be the driving mechanism for failure. Some hydrate related slope failures have been attributed to earthquake-induced accelerations e.g. (Jansen et al.,1987). The factor of safety for a slope

is the ratio of the forces resisting failure to those causing failure. Resisting forces include the intergranular friction, particle cohesion and the area of the potential failure surface, the latter depending on the type of slope failure. The forces trying to cause failure are the mass of the material (W), the internal pore pressure and externally applied forces such as horizontal earthquake accelerations ($K_hW$), (Kramer,1996). A slope is said to be at limiting equilibrium when these forces are equal and the factor of safety is 1.0. In this instance the effects of increased pore pressures due to the presence of gas becomes more critical for calculating the slope stability. As the factor of safety for the slope approaches 1.0 small magnitude earthquakes, having a shorter return period, increase the possibility of a failure event occurring.

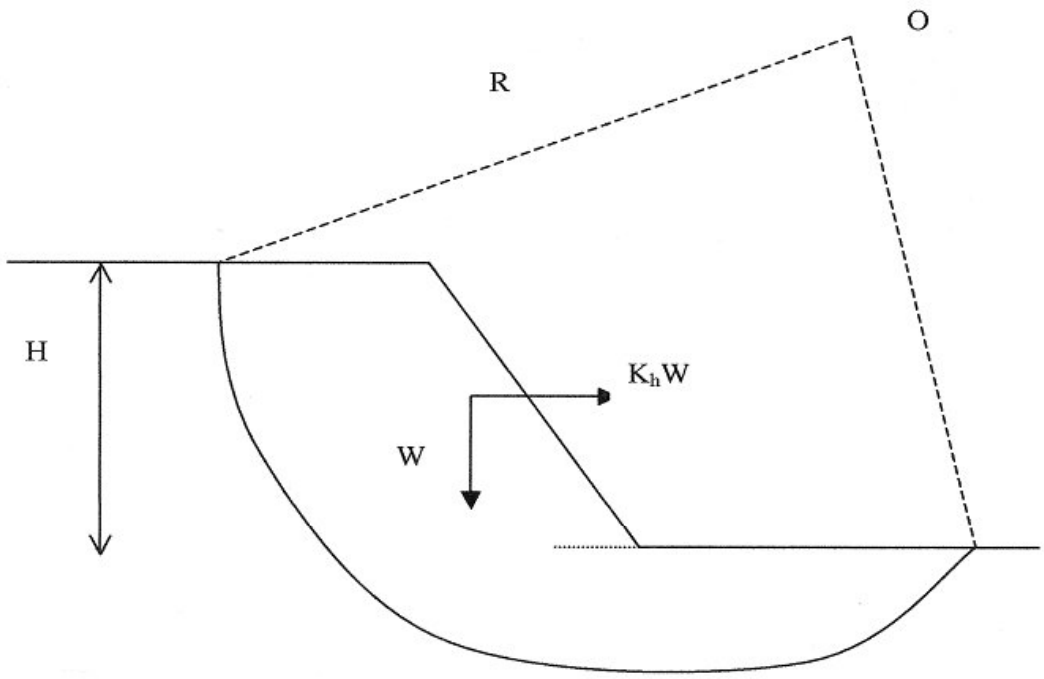



**Figure 11. Generalised slope failure scenario (Majumdar,1971)**

It appears that research is in the initial stages of understanding the complex hydrate/sediment relationship. It is probable that the different morphologies would dissociate in differing ways. As such it could be the case that different failure scenarios would apply to different hydrate morphologies. The driving mechanisms for failure cannot be determined without a thorough knowledge of the physical properties of the sediment. This would necessarily include considering the layers as shown in Figure 3 and individual hydrate layers, both separately and as an interlinked system for all realistic scenarios.

# 5. Characterising Hydrates

## 5.1 OVERVIEW

Much of the current work on hydrates is aimed primarily at hydrocarbon resource prospecting. In the main this has been focused on identifying hydrate accumulations and attempting to quantify the amount of stored gas. Although helping to identify potential risk areas, improvements are still needed to remove ambiguities and obtain the resolution and accuracy required to predict the physical properties needed for stability models.

## 5.2 IDENTIFYING HYDRATES IN SEDIMENT

The presence of hydrates within the sediment column is generally attributed to a Bottom Simulating Reflector (BSR), which can be seen on seismic sections (Figure 12). It is widely accepted that a BSR arises due to the presence of free gas under the solid hydrate, causing a strong acoustic impedance contrast. It is known that hydrate can occur in areas without a BSR (von Huene et al.,1985). Recent drilling operations through a BSR in the Faeroe-Shetland Basin found it to be indicative of a silica diagenetic boundary (Davies et al.,2001). BSR's can also be formed by other mechanisms, most notably Opal A-CT

An improved method of using deep seismics for prospecting is the use of tomography, (Tinivella et al.,1998). This method shows the vertical and horizontal variations in velocity along a survey line can be used to indicate the position of hydrated areas and the low velocity zone below the BSR (Figure 4). This method appears to offer better constraint on the thickness and position of hydrate zones. It also appears to indicate the variation in relative concentrations of hydrate within a sediment body.

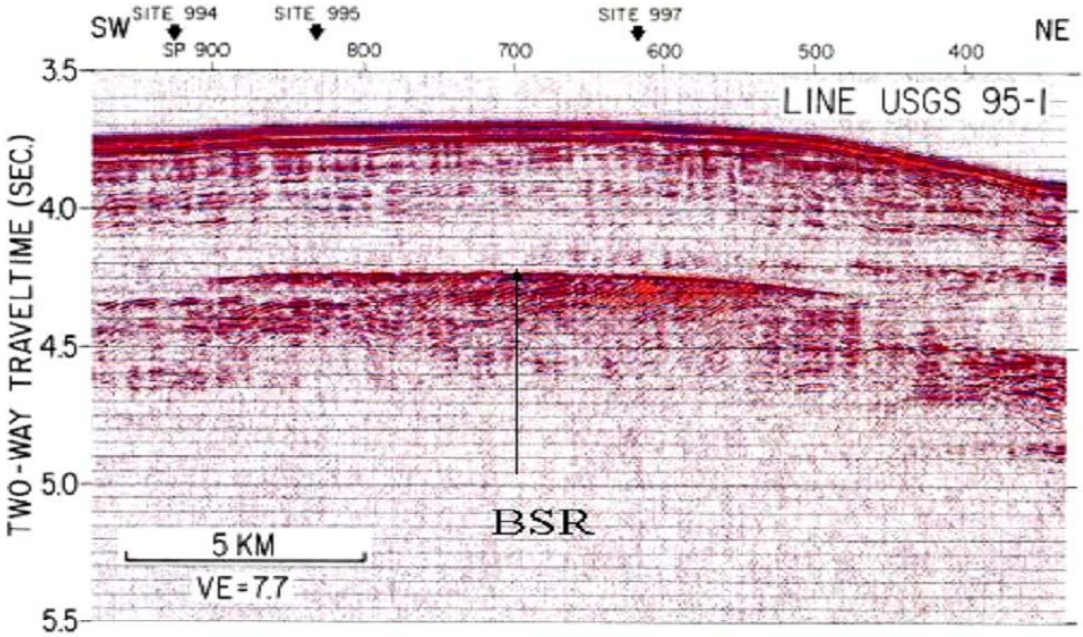



**Figure 12. Seismic reflection Profile USGS 95-1. (Paull et al.,1996) Ocean Drilling Program Leg 164.**

Vertical Seismic Profiles (Cassell,1984) are a widely used method of subsurface exploration that could utilise single boreholes bored for hydrate recovery. This method provides more accurate information than seismic traces taken from the surface as it cuts down the length of the wave travel path. Tomography could also be used to map the sediment properties between boreholes. The use of two boreholes makes it more accurate than the VSP method. One of the major stumbling blocks in current geophysical methodologies is the heterogeneous nature of hydrated sediments (Paull et al.,1996). Despite the best efforts to date, technological limitations prevent accurate assessment of conditions away from boreholes. Cross hole tomography e.g. (Leung et al.,1988) is an accepted method of subsurface visualisation in land based surveys and financial constraints permitting might provide a more accurate
insight into hydrate dissemination within the sediment fabric.

## 5.3 SEISMIC MEASUREMENTS TO QUANTIFY HYDRATE ACCUMULATIONS

Very wide ranges of values for compressional and shear wave velocities have been reported for hydrate and hydrate rich sediment (Table 2). The values obtained from ODP Leg 164 are marginally above those expected from a hydrate free sediment core. It would appear from the published results there is a link between hydrate dissemination and shear wave velocity. Equations have been derived to estimate reservoir capacity from compressional wave velocity and suggest a value of 3.8 km/s for pure hydrate (Whalley,1980). Actual measurements show distinct differences from this, which implies that the absolute measurement of P-wave velocity through sediment is not the most effective method of determining the presence of gas hydrate. P-wave velocity is also relatively insensitive to the distribution of hydrate within the pore space (Sakai,1999) and (Lee et al.,1993), believed amplitude attenuation would provide more reliable estimates of reservoir capacity. Reported shear wave velocities (Paull et al.,1996; Miyairi et al.,1999) are less numerous and also vary significantly. They are however, important in determining whether the hydrate is acting as a cement at the grain boundaries and thus increasing the rigidity of the matrix, or in the pore space modifying the solid bulk and shear moduli (Guerin et al.,1999; Sakai,1999; Walia et al.,1999).
An example of a set of geophysical logs is shown in Figure 13, taken during ODP Leg 164 at the Blake Ridge. These clearly show the problems associated with making geophysical measurements of in-situ sediments. These logs are one of the best offshore sets available. The density log shows significant variability from the physically measured density, suggesting the pads of the tool were not in contact with the sides of the borehole during measurement. As a result the other measurements are potentially affected, especially the shear wave measurements, which need a solid propagating interface in order to be made.

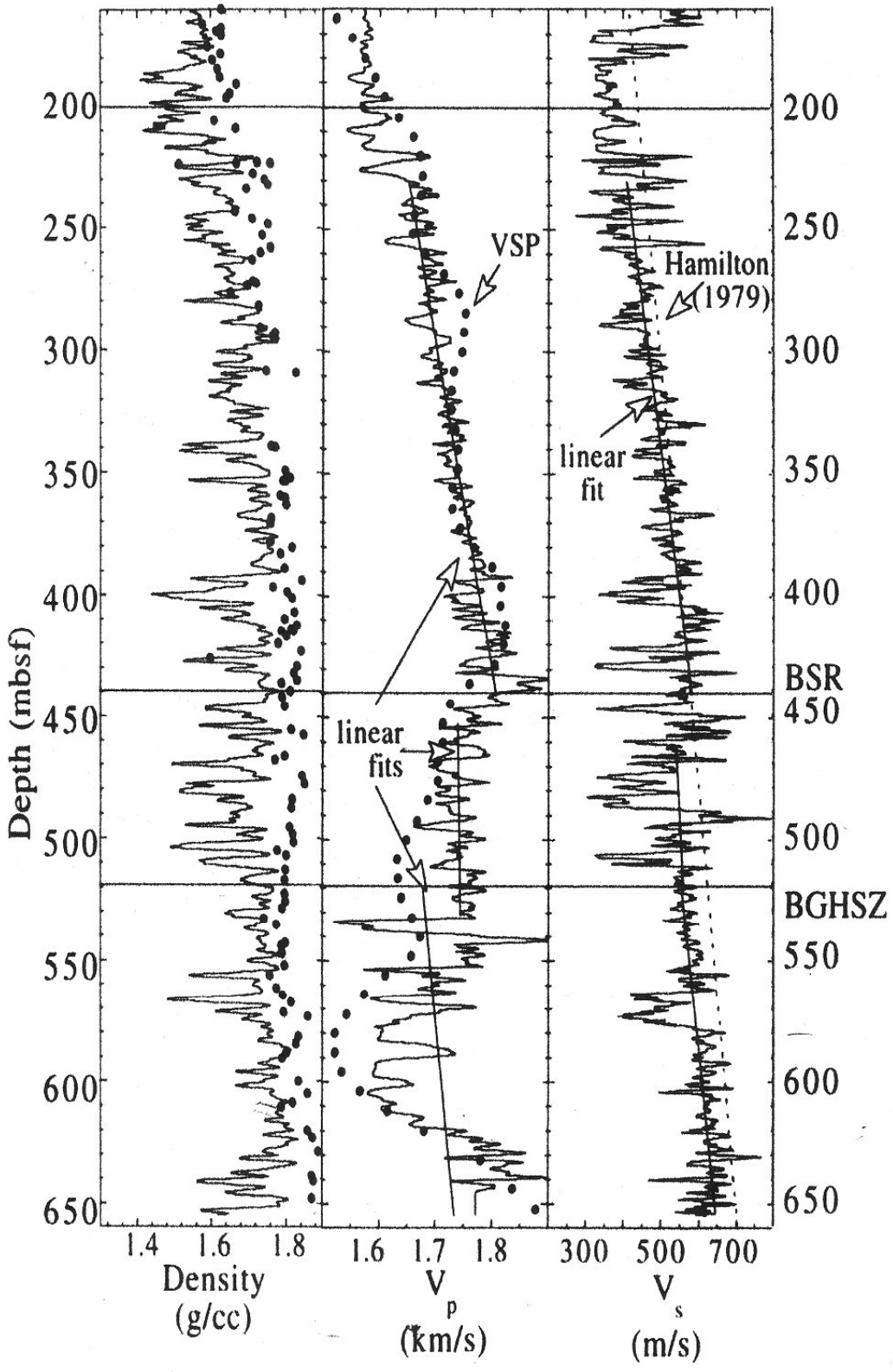



**Figure 13. Well log data from Ocean Drilling Program Leg 164, hole 995B (Paull et al.,1996)**

## 5.4 RESISTIVITY MEASUREMENTS TO QUANTIFY HYDRATE ACCUMULATIONS

Resistivity (ρ) is the resistance of a unit cube of material, given by,

$$\rho = R\frac{A}{L} \qquad \text{(Figure 14)}$$

where the resistance ( R ) is given by,

$$R = \frac{V}{I}$$

where I is the current flowing through the sample and V is the potential difference across it.

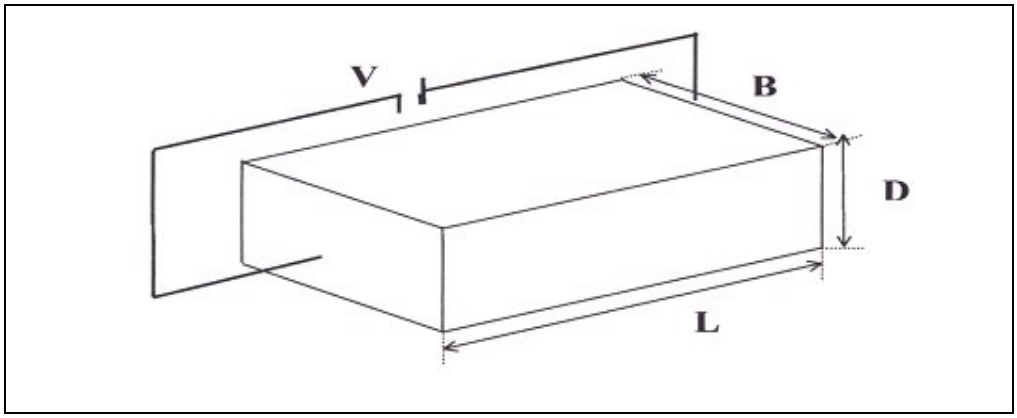



**Figure 14 The Definition of Resistivity (Griffiths and King,1981)**

The resistivity of sediment is related to its porosity by a series of equations (Archie,1942),

$$FF = \frac{\rho_{sed}}{\rho_{w}}$$

were FF is the formation factor, $\rho_{sed}$ is the resistivity of the water saturated sediment and $\rho_w$ is the resistivity of the pore fluid, and,

$$FF = \theta^{-m}$$

where θ is the porosity and Archie found ***m*** to increase relation to cementation. The saturation of the pore space is calculated from the resistivity difference.

$$S = \left(\frac{\rho_{SED}}{\rho}\right)^{-n}$$

where $\rho_{SED}$ is the resistivity when fully saturated i.e. pore space contains only water and ρ is the resistivity when the pore space contains oil and water. Archie found that ***n*** was

approximately equal to 2 for his experiments although it can change. These equations have been used successfully to model the resistivity of hydrate rich sediments (Collett et al.,1999).

Solid hydrate should, theoretically, have an extremely high resistivity, as it should not contain any free ions, which would be able to pass current electrolytically. Disseminated hydrate nodules should not affect the resistivity as current would travel around them. If the pore waters are saline rich this will increase the ion concentration of the pore fluid and decrease the resistivity, this could counter the effect of increasing resistivity due to an increase in solid hydrate phase (Lovell, pers comm. 2002). Hydrates could be distinguished from permafrost by having higher resistivities due to a lower unfrozen water content (Pearson,1983). However values of 150Ωm for hydrate compared with values of 10-1000Ωm for ice have been quoted (Pecher,1995), although it is unclear whether the ice is pure water or frozen seawater. Figure 15 shows the resistivity log from Site 995 ODP Leg164. This equates the presence of hydrate within the sediment with increased resistivity through that section. Interestingly the value only increases to 2Ωm, which is double that of the sediment. This is similar to the increase quoted for ODP Leg 146 (Hyndman et al.,1999). Both of these values are low in comparison to the values obtained by DSDP Leg 84 (von Huene et al.,1985) which showed resistivities in the log in excess of 100Ωm and the values found within the Mallick field. The doubling of resistivity to 2Ωm can be explained by solid hydrate being disseminated throughout the pore space, as suggested by (Guerin et al.,1999), filling perhaps 10 – 20% of the pore space. Values as high as 100Ωm are consistent with most of the pore space filled with hydrate. The resistivity does not reflect the morphology of the hydrate as it is an average value through the sediment. As comparatively small, high or low resistivity zones can affect the apparent resistivity, values obtained might be affected by localised anomalies.

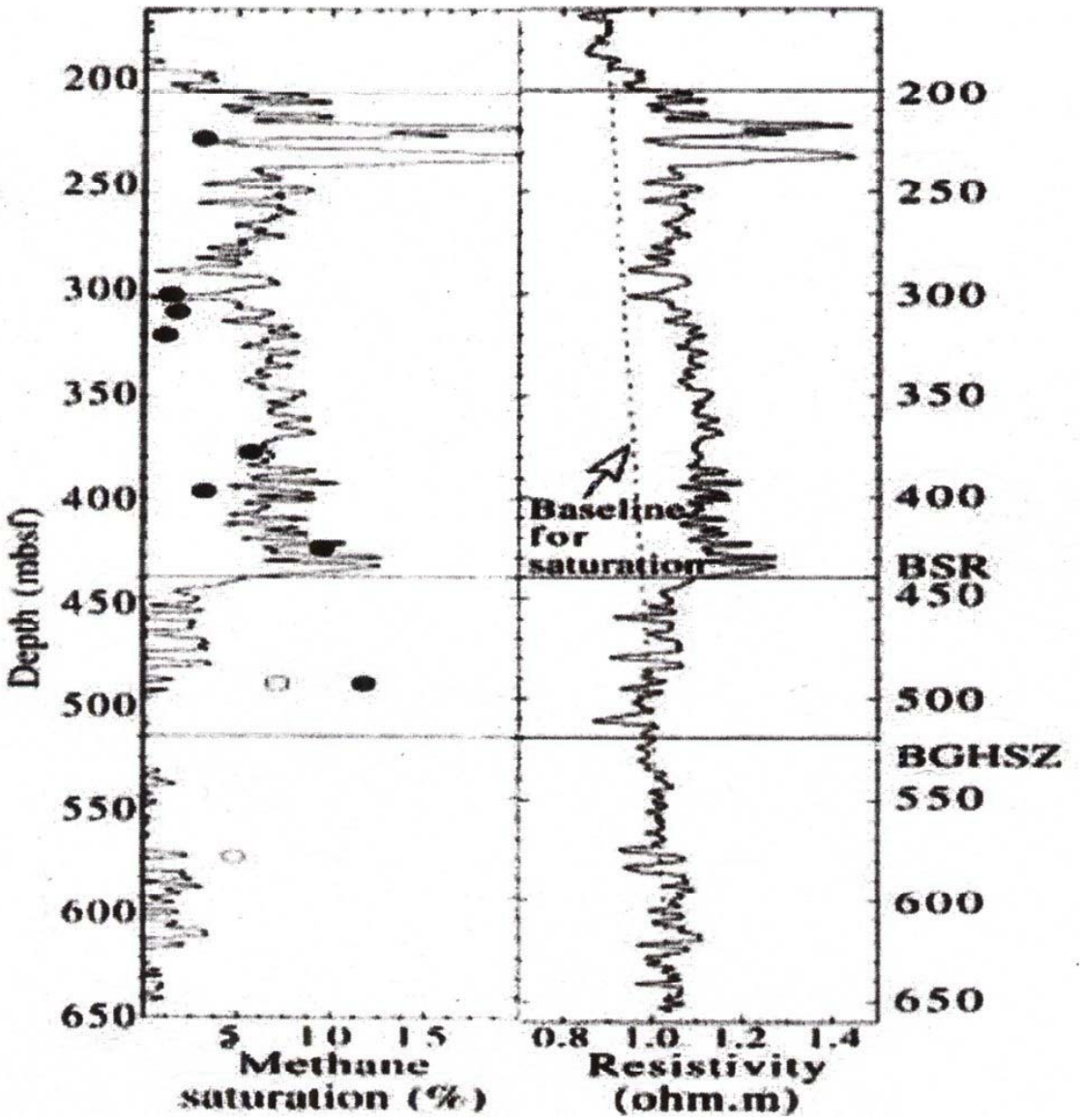


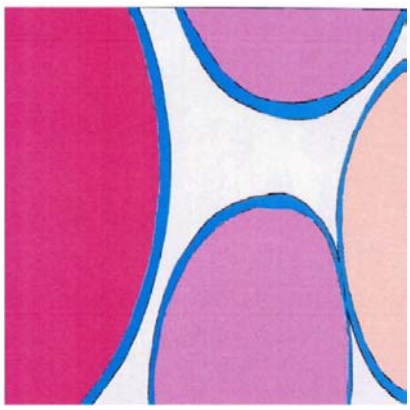

**Figure 15. Resistivity log from Ocean Drilling Program Leg 164, hole 995B (Paull et al.,1996)**

## 5.5 LIMITATIONS OF CURRENT TECHNOLOGY

Although there have been technological advances in the tools used to image resistivity variations, (Luthi and Souhaite,1990; Prensky,1999), this only allows investigations close to the immediate area of the borehole and does not give information about sediment between boreholes. It is also unclear from the literature to what extent resistivity is affected by phase changes of hydrate. Laboratory tests of synthetic hydrated sediment using the USGS (GHASTLI) system show a decrease in the resistivity upon dissociation (Winter,2000). This would be due to the presence of free ions in the solution arising from water being released. However, this scenario assumes that there is no brine phase present in the hydrated sample, which may or may not be the case in a real situation. There is no indication from this work of the effects of free gas on the resistivity of the sample. Work has been done to investigate the change in resistivity in a sample upon hydration and as the hydration increases (Pearson et al.,1982). This is very basic, and not detailed enough

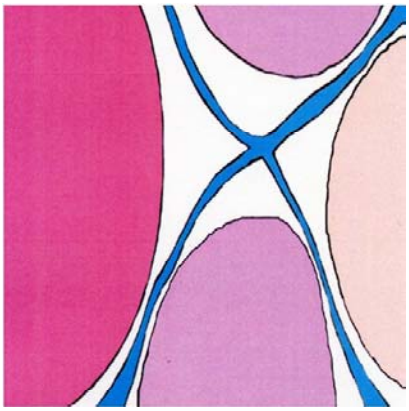
to consider the effects of sediment lithology and structure and the hydrate morphology and dissemination on the resistivity measurements themselves.

Figure 16 shows some possible hydrate emplacements at the pore size level. These variations in hydrate/sediment interaction demonstrate the variety of effects that hydrate might have on geophysical properties. However, the measured values would not be sufficient to present a unique solution to the question of hydrate distribution within a sediment as a number of these scenarios could give the same values. Dependent on the lithology, the distribution of hydrate could cause varying effects on sediment properties upon dissociation.

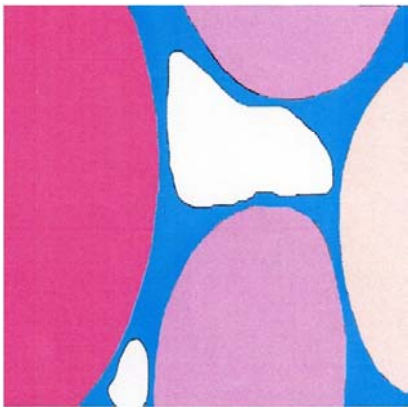


16a Observed hydrate growth around etched glass between two plates (Tohidi et al., 2001)

16b Hydrate cementing grains together. This will increase the rigidity of the sediment. (Guerrin, 2000)



16c Possible hydrate growth around grains. Free water could act as a path to carry methane into the matrix



16d Isolated hydrate within the sedimetn pore system.

**Figure 16. Possible hydrate/sediment grain configurations**

Using a pressure core sampler still under development, gas volumes of 12% of the pore volume were measured at Blake Ridge (Dickens et al.,1997), which is higher than the 1-2% inferred from the seismic records. This clearly demonstrates the limitations of velocity analysis with the current technologies for geotechnical parameter study at the resolution needed for slope stability assessment. It is difficult to quantify pore gas volumes from seismic records due to very high signal attenuation in the gassy sediments beneath the BSR. Recently effective medium theory has been used successfully to model compressional wave data in uncemented clay-rich sediments (Prasad and Dvorkin,2001). This method could be used to infer porosity and pressure using velocity data, which would enable a clearer picture of potential hydrate volumes and dissociation behaviour.

# 6. Conclusions

While pure hydrate formation has been studied extensively by the petrochemical industry, relatively little is known about hydrate-rich marine sediments as the bulk of the studies have occurred in the last 10 years. Hydrate rich sediments can exist in a wide range of morphologies. There is limited information about the way in which sediment structure and lithology affect the morphology of hydrates. Geophysical methods have identified the presence of hydrate in the sediment, but not, as yet, the fine scale hydrate structure in the hydrate stability zone. The geophysical properties of hydrate-rich sediments are varied and appear to be related to hydrate morphology. There is a need to apply better geophysical techniques with higher resolving power in order to visualise more accurately the sediment structures. The in-situ formation is highly complex and variable and has not been simulated in laboratory experiments.

The geotechnical and geophysical dissociation characteristics of the varying hydrate morphologies are generally not known and hence the change in geotechnical parameters with dissociation cannot be confidently determined. Consequently, it is impossible to constrain the slope stability models to account for the dissociation to an acceptable degree of accuracy. The amount of in-situ gas associated with hydrates is poorly quantified due to the limitations of the methods of detection available. Consequently, the increased effects of earthquakes and similar phenomena due to the presence of gas are poorly understood.

There is evidence of possible diagenesis associated with the formation of hydrates but this is poorly understood and its significance is unclear. The occurrences could however be relevant as a tool for identifying historical gas hydrate emplacements. Well-cemented formations could also have implications for fluid flow and recharging of hydrate bases.

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