"Ice" Beneath the Deep Sea: Studies of Methane Hydrate Layers Beneath the Continental Slope off Vancouver Island

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SUMMARY

Deep-sea methane hydrate "ice" layers are found a few hundred metres beneath the continental slopes of a number of areas around the world, notably in subduction zones where large accretionary sedimentary prisms are formed. The ice-like clathrate structure is stable up to temperatures of 10°-30°C beneath the sea floor at the pressures generated by water depths greater than about 800 m. The primary indicator of deep-sea hydrate is a "bottom simulating reflector" (BSR) that parallels the sea floor. These naturally occurring hydrate layers are estimated to contain a very large amount of methane, a potential clean fuel resource, but it is unlikely that recovery will be possible in the near future. Of more immediate concern is the role of such hydrate in global climate control. Because methane is a very strong greenhouse gas, release to the atmosphere of methane in hydrate resulting from a small amount of climatic warming could strongly enhance the warming trend, *i.e.*, provide positive feedback. Recent results, especially from the Vancouver Island margin, are summarized, dealing with a) the distribution and amount of such hydrate, b) the nature of the hydrate layers revealed by detailed seismic reflection analysis, and c) the hydrate formation process. A hydrate BSR is found to be widespread in a 30 km wide band beneath much of the continental slope off Vancouver Island. The hydrate layer in this area is on the order of 20 m thick, concentrated at the base of the stability field about 300 m below the sea floor. Because such deep-sea hydrate represents a very large global methane reservoir, its distribution, nature and formation warrant detailed study.

INTRODUCTION

Global climate change and the need for a clean energy source are subjects of important recent societal concern. Naturally occurring hydrates containing methane may play an important role in both subjects. Hydrates are solid ice-like substances consisting of rigid water molecule cages stabilized by enclosed gas molecules, notably those of hydrocarbons such as methane (*e.g.*, Sloan, 1990; Claypool and Kaplan, 1984). They are more properly called clathrate hydrates to distinguish them from the stoichiometric (fixed composition) hydrates found in inorganic chemistry. They contain large concentrations of gas. For ideally saturated methane hydrate with all of the water cage sites filled, the methane concentration is 7.6 moles·L [1] or a methane-water volumetric ratio of about 164:1 when dissociated. Natural hydrates are expected to have close to these methane concentrations. Except for the high melting (or dissociation) temperature at deep sea-floor pressures, most of the properties of hydrate, such as density and seismic velocity, are very similar to those of normal ice. Early studies were directed at solving the problem of hydrate formation in natural gas pipe lines that blocked flow. Subsequently, however, it has been recognized that natural hydrates occur extensively beneath the deep sea floor of continental slopes (*e.g.*, Kvenvolden and Barnard, 1983) and beneath some arctic land areas (*e.g.*, Makogon, 1981; Judge, 1982). This article summarizes some recent work on hydrates, concentrating on the continental slope off Vancouver Island. Three aspects are considered: the areal distribution of the hydrates, the nature and thickness of the hydrate layers, and mechanisms of natural hydrate formation. The work is, in part, a preparation for drill-core sampling of the hydrate by the International Ocean Drilling Program planned for 1992.

Interest in naturally occurring hydrates was first directed at a potential fuel resource and, more recently, at the role such hydrates may play in the control of global climate. Deep sea hydrate layers are estimated to contain a very large amount of methane, a potential clean fuel resource. Burning of methane produces no atmospheric pollutants except CO_2 and the lowest amount of that for any hydrocarbon. Order-of-magnitude global estimates of total methane in hydrate exceed known land hydrocarbon reserves, *i.e.*, 10^4 Gt (10^{13} tonnes) of carbon or 6×10^5 Tcf (trillion cubic feet) of methane (*e.g.*, Kvenvolden, 1988; MacDonald, 1990). However, because clathrate "ice" is very stable and difficult to dissociate on the deep sea floor, and because of the great water depth, it is unlikely that recovery will be possible in the near future (*e.g.*, Kvenvolden, 1988). Of more immediate interest is the role of such hydrate and the very large carbon reservoir that it represents in global climate con-

trol. One climate influence mechanism of specific concern is positive feedback in climate warming from other sources. Methane is a very strong greenhouse gas, and its release to the atmosphere from dissociation of hydrate, resulting from a small amount of climatic warming, could strongly enhance the warming trend. The global temperature increase from CO_2 generated by the burning of fossil fuel could be strongly enhanced. Nisbet (1990) has presented a case for such a positive feedback mechanism causing the abrupt termination of the last major glaciation about 13,500 years ago. A small triggering warming event may have initiated massive release of methane from hydrate, particularly that under arctic ice and in permafrost. Arctic hydrate is probably much more responsive to atmospheric warming than deep-sea hydrate, but the amount of the latter is very much larger, so it also may play an important role. The isolation provided by the sea and the thermal inertia of the several hundred metres of sediment over the deep-sea hydrate layers make them only slowly sensitive to a triggering atmospheric warming event in the positive feedback model (see also MacDonald, 1990).

Additional applications of data on deep-sea hydrate of scientific interest are as a heat flow mapping tool and as an indicator of upward fluid expulsion, particularly from consolidating and deforming accretionary sedimentary prisms (Davis *et al.*, 1990). Because the depth to the base of the hydrate stability field (which can be detected seismically, see below) is strongly temperature dependent, it provides a method of mapping the sea-floor thermal regime in some critical areas (*e.g.*, Yamano *et al.*, 1982; Davis *et al.*, 1990). Such thermal data are important for estimating the maximum depth extent of major thrust earthquakes in subduction zones and for modelling of metamorphic processes in accretionary sedimentary prisms. Also, the thickness of the hydrate layers formed may be proportional to the amount of methane in pore fluid brought into the hydrate stability field and, thus, to the total fluid expelled upward through the sea floor (Hyndman and Davis, 1992). In this way, the hydrate thickness, which in some circumstances can be estimated seismically, may provide a semi-quantitative measure by which fluid expulsion in accretionary sediment sections may be mapped.

Deep-sea hydrates are inferred to form almost entirely from biogenically generated methane. The methane is produced by low temperature anaerobic (oxygen free) bacterial action on the organic material in the sediments, a process sometimes called methanogenesis (*e.g.*, Claypool and Kaplan, 1984). While the organic concentrations are usually small, approximately 1%, the huge volumes of sediment on continental margins result in very large amounts of methane being produced globally. This methane

production may exceed that from all other recognized sources (*e.g.*, Fig. 1). A few occurrences of hydrates indicated to be formed from thermogenically generated hydrocarbon gas (from high temperature breakdown of organic material) have been found in petroleum producing areas such as the Gulf of Mexico and the Alaska North Slope.

The pressure–temperature (P–T) stability field of hydrate (*i.e.*, freezing temperature for a particular pressure) depends first on the composition of the enclosed gas, and second on the water salinity. Higher hydrocarbon and CO_2 contents increase the melting or dissociation temperature, and higher salinity decreases it. Almost all of the enclosed gas in hydrate samples recovered from the deep sea by the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP) has been methane (*e.g.*, Kvenvolden and Kastner, 1990) and the associated pore water has close to seawater salinity. Figure 2 shows the stability field based on extensive laboratory data for pure water and methane and limited data on the effect of CO_2 and seawater salinity (*e.g.*, compilation in Sloan (1990) and equation-of-state estimates for artificial seawater by Englezos and Bishnoi, 1988). Estimates of *in situ* P–T conditions at the base of the sea-floor hydrate stability field agree well with the laboratory data (Hyndman *et al.*, 1992). The maximum sub-bottom depth for hydrate stability, then, depends first on pressure (water depth), and second on
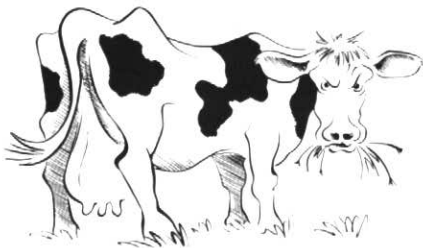
HYDRATE STABILITY FIELDS

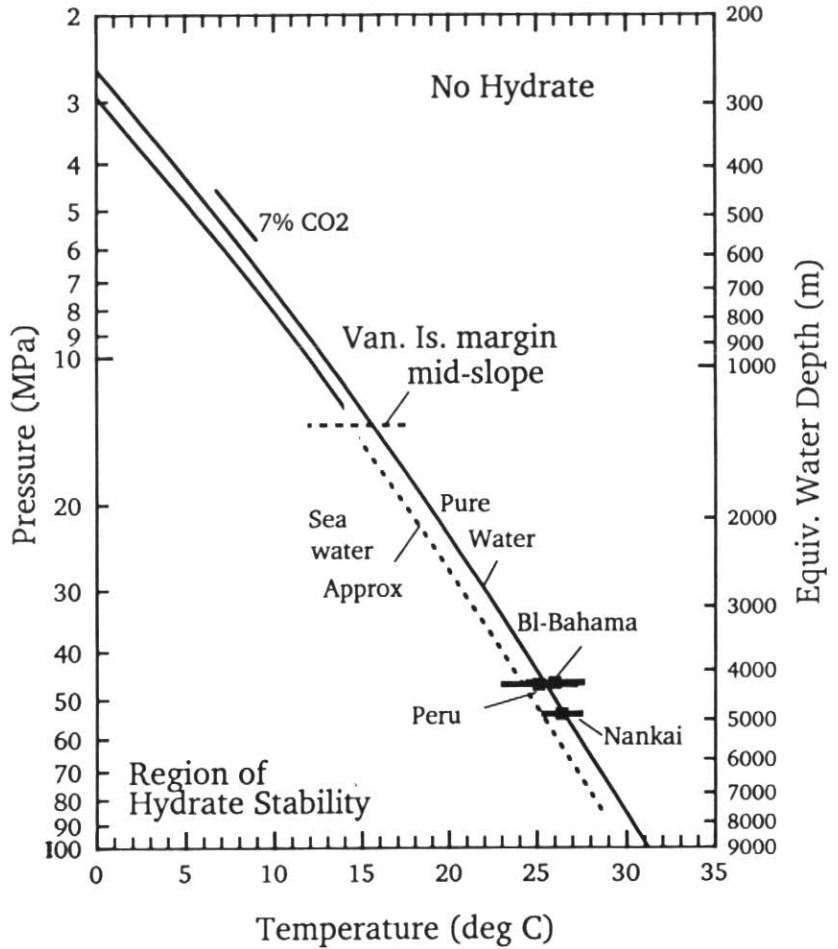Figure 1 *A big methane producer, but a poor second to deep-sea mud.*

Figure 2 *The stability field for methane hydrate in pure water. The influence of a small amount of CO_2 and of seawater salinity are illustrated. In situ calibrations of the hydrate BSR are shown along with the pressure (water depth) for the mid-slope study area off Vancouver Island.*
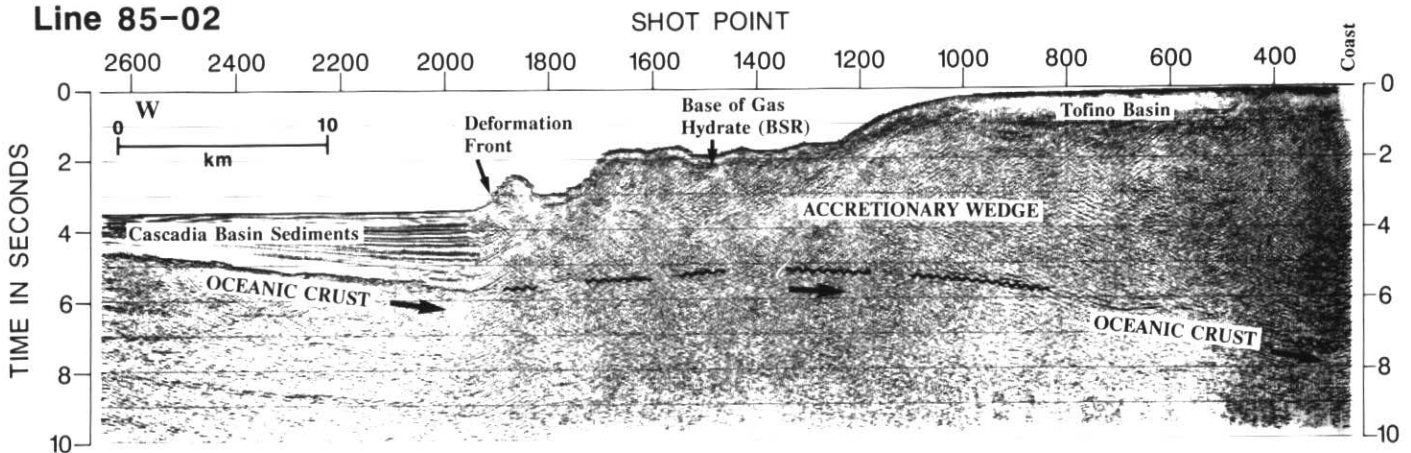
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Figure 3 *A multi-channel seismic section across the margin of Vancouver Island from the deep-sea basin to the coast, illustrating the position of the **hydrate** BSR. The incoming sediments of Cascadia Basin are about 2.5 km thick at the deformation front. The location of the section is shown in Figure 4.*
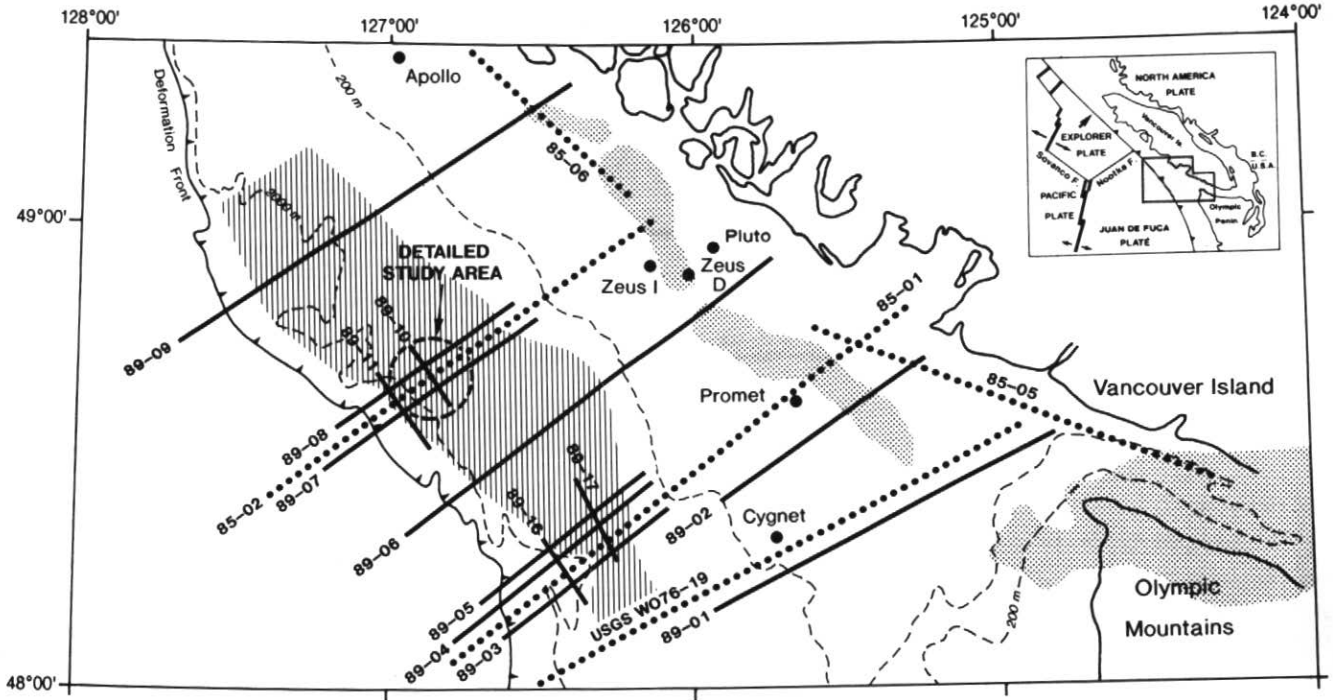
Figure 4   *The area of hydrate on the continental slope off Vancouver Island (lined area), along with the locations of the multi-channel lines defining the BSR. The light stippling is the Crescent volcanic terrane which marks the landward boundary or "backstop" of the accretionary sedimentary prism.*
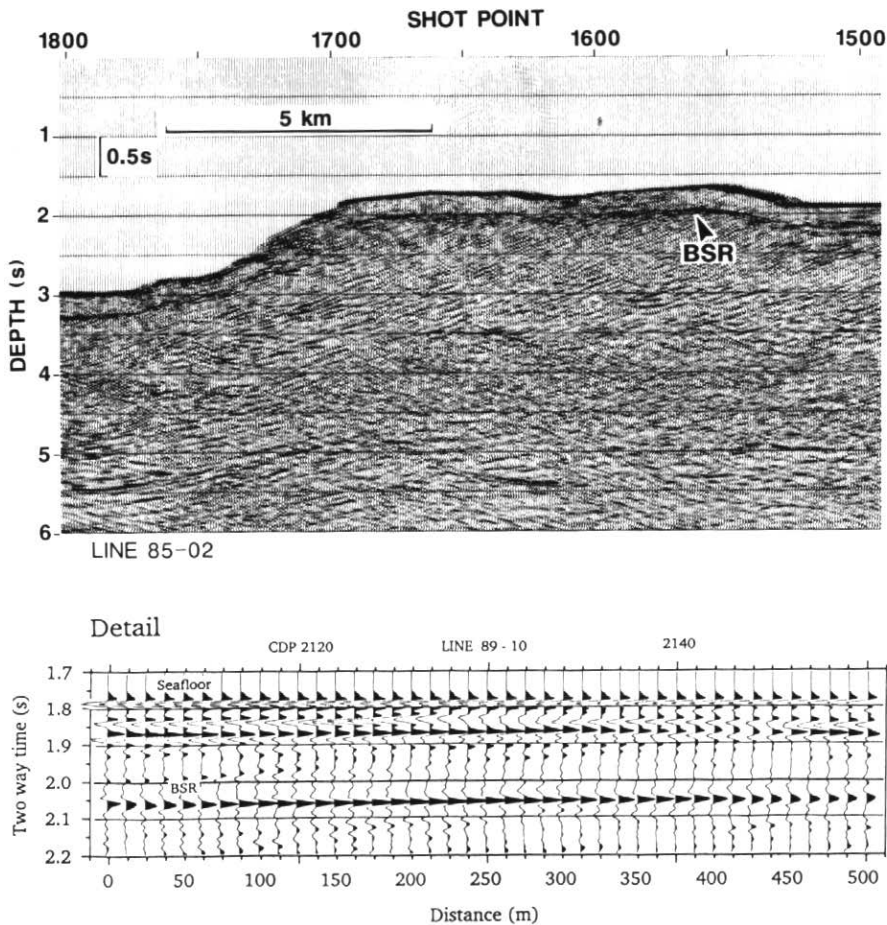

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Detail

Figure 5   *(upper) An example of a seismic section off Vancouver Island having a clear BSR. (lower) Seismic reflection waveform detail of a BSR. Note the simple pulse form and the negative polarity, opposite to that of the sea floor. The BSR is at about 2.05s. The reflectors at 1.85-1.90s are from sedimentary layering.*

the sea-floor temperature and vertical temperature gradient (heat flow and thermal conductivity). The predicted maximum depth for hydrate across the Vancouver Island continental slope, based on heat flow and other data, ranges from about 250 m to 350 m sub-bottom (Davis et al., 1990).

DISTRIBUTION OF HYDRATE BSRs OFF VANCOUVER ISLAND

The detection of hydrates beneath the deep sea floor is primarily through a strong seismic reflector called a "bottom-simulating-reflector" or BSR (Shipley et al., 1979). The BSR reflector is taken to mark the base of the hydrate stability field and to result from the velocity and density contrast between sediment containing hydrate "ice" and underlying normal sediment that could contain free gas. This boundary is roughly equivalent to the base of permafrost in arctic regions, except for the higher temperature. Sub-bottom isotherms approximately parallel the sea floor, so the base of the hydrate stability field, or melting point, approximately parallels the sea floor at a depth of several hundred metres. Although hydrates from the depth of the BSR reflector have not yet been recovered by drilling, hydrate samples from shallower sub-bottom depths in a number of areas have been obtained by the scientific DSDP and the ODP.

In Canada, hydrates have been detected off the coast of Labrador (Taylor et al., 1979) and in the Arctic (e.g., Bily and Dick, 1974; Davidson et al., 1978; Judge, 1982) as well as

off the west coast of Vancouver Island (e.g., Davis et al., 1990). Continental slope hydrate is widespread around the world (e.g., Kvenvolden, 1988), but the majority of well-defined occurrences are in subduction zones where large coarse clastic (primarily silt and sand) sedimentary wedges have been formed from the sediments scraped off the incoming and underthrusting sea floor; i.e., the environment of the Vancouver Island margin. Hydrates do not appear to occur in the sediments of deep-sea basins, and occur infrequently on stable continental margins.

Marine multi-channel seismic reflection programs were carried out across the continental margin of Vancouver Island in 1985 (Yorath et al., 1987; Hyndman et al., 1990) and in 1989 (Spence et al., 1991, 1992) (Fig. 3). These surveys have allowed mapping of the distribution of hydrate BSRs as shown in Figure 4. BSRs are also evident in some detailed single-channel seismic data carried out by K. Rohr (example shown in Davis et al., 1990). BSRs are apparent over much of a 20-50 km wide band covering the middle slope along the whole southern Vancouver Island margin. They start about 10 km landward of the sedimentary accretionary wedge deformation front at the base of the slope, and extend to the upper slope. They become indistinct at a water depth of about 1000 m. The sediment thickness predicted to be within the stability field thins to zero at about 400 m water depth as a result of increase in sea-floor temperature and decrease in pressure.

NATURE AND THICKNESS OF HYDRATE LAYERS FROM SEISMIC DATA

The primary data for defining deep sea-floor hydrate layers are multi-channel seismic reflections. An example of a section with a very clear BSR is shown in Figure 5A, with the seismic waveform detail shown in Figure 5B. Three characteristics of the BSR are evident (see Hyndman and Spence, 1992). 1) The BSR reflection has negative polarity, opposite to that of the sea floor. This means that it is generated by a downward decrease in seismic impedance (velocity × density). 2) The reflection amplitude is about 50% that of the sea floor; the estimated BSR reflection coefficient is 10-15%. 3) The BSR reflection is generally a single symmetrical pulse characteristic of a simple interface. There is no evidence for the top and bottom of a layer.

Two alternative interfaces have been suggested to explain such BSR reflections: 1) a contrast between sediment with a small amount of hydrate above the boundary and a layer containing at least several percent free gas below it (e.g., Minshull and White, 1989; Miller et al., 1991), or 2) a contrast between sediment containing a substantial amount of pore-filling hydrate above the boundary and normal sediment containing no hydrate or gas below it (Hyndman and Davis, 1992). Both contrasts can explain the required large impedance contrast. The need for free gas is based mainly on chemical arguments (see below). Much of our work has been directed at this question and, while it has not yet been completely resolved, our conclusion, based
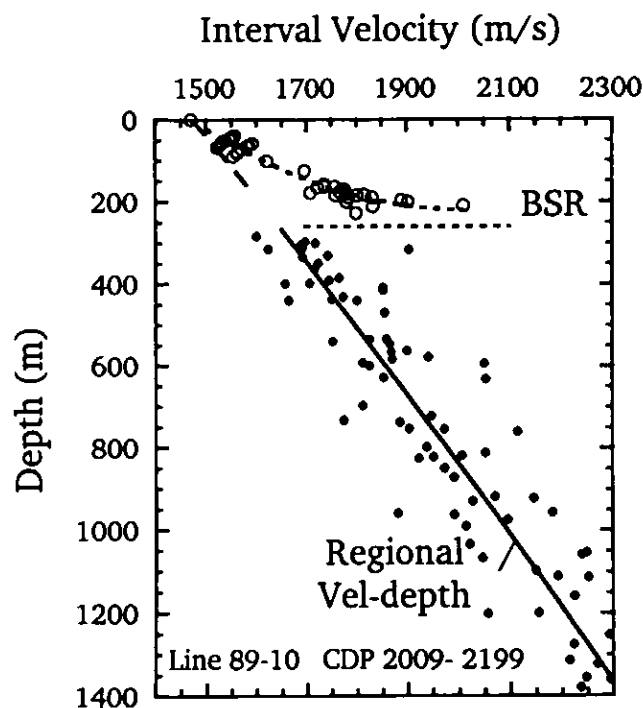

Figure 6 *Velocity versus depth from multi-channel seismic data, showing the high velocity hydrate "ice" layer above the BSR. (Unpublished data from Yuan, Spence and Hyndman, in preparation).*
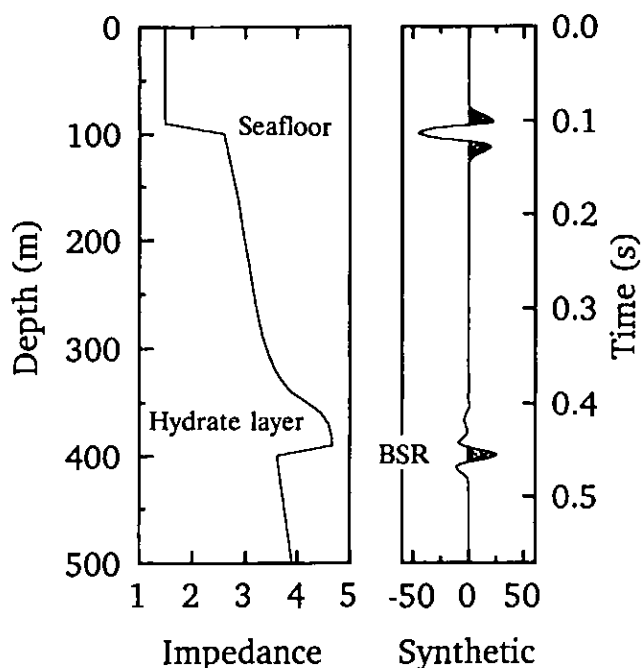

Figure 7 *A simple seismic impedance (velocity × density) model for the sea floor and for the hydrate layer that produces the BSR, along with the corresponding synthetic seismogram. The synthetic trace may be compared to the data waveform in Figure 5B.*

on the new seismic data, on drill core samples from elsewhere, and on physical arguments, is that free gas is not present.

Velocity-depth profiles from multi-channel semblance analysis do not have high resolution, but they limit the hydrate layer thicknesses to less than about 50 m in most areas, and any free gas layer to less than about 20 m. Figure 6 shows clearly the high velocity "ice" layer superimposed on the normal increase in velocity with depth from compaction. The velocities are averaged over about 100 m; the hydrate layer actually is thinner and has higher velocity than shown.

A synthetic seismogram for the simplest model of a hydrate layer with a sharp base at the BSR and a gradational top (so no reflection from the top of the layer) as predicted in our model (Hyndman and Davis, 1992) is shown in Figure 7; this synthetic BSR waveform corresponds well to the observed reflection waveform in Figure 5B. About 50% of the sediment porosity in the layer must be replaced by hydrate to give the observed BSR reflection amplitudes.

Additional seismic analyses that define the hydrate layers have included amplitude-versus-offset (AVO) analyses and waveform modelling. AVO is a very sensitive indicator of free gas layers that is widely used in petroleum exploration. The Vancouver Island AVO results do not support the free gas model. In addition to the lack of evidence for free gas, the analyses indicate that, while hydrate is stable from the BSR up to the sea floor, most hydrate is concentrated in a single layer at the base of the stability field at about 300 m sub-bottom.

MODELS FOR FORMATION OF BSR HYDRATE

The formation mechanism and the source of the large amount of methane contained in the hydrate layer are important unresolved problems. Constraints from seismic data (e.g., Hyndman and Spence, 1992) and from deep-sea drill-core geochemical data (e.g., Hesse and Harrison, 1981) indicate that at least one-fourth and probably one-half of the sediment pore spaces are filled by hydrate in a layer above strong BSRs. It appears that the large amount of methane required for such hydrate concentrations cannot be produced in the local sediments. Complete conversion of the common 0.5-1.0% organic material in continental margin sediments will produce only an order of magnitude less than the concentration estimated in the hydrate, and biogenic processes are expected to convert only a small portion of the total organic material. We have thus concluded that methane produced throughout sediment sections several kilometres thick must be concentrated in the thin hydrate layer.

We have suggested a model for concentrating the methane using the fact that hydrate BSRs are most common in subduction zone accretionary sedimentary prisms where extensive fluid expulsion from thickening and tectonic compaction is both predicted and observed. We have postulated that the methane generated in such thick sedimentary sections moves upward in expelled pore fluids, and is swept out to produce hydrate when the fluid moves into the stability field ("freezing point") several hundred metres below the sea floor (Fig. 8). The hydrate layer builds upward with progressive fluid expulsion. The major difficulty with this model is that it appears to require hydrate formation from methane dissolved in pore fluid at concentrations below saturation; the simple methane hydrate phase diagram predicts that free gas is required for hydrate formation (e.g., Kvenvolden and Barnard, 1983). Hyndman and Davis (1992) discuss several ways this problem can be resolved. In any case, we argue that the available concentrations of organic material in deep-sea sediments are usually insufficient to generate substantial free gas.

The estimated total amount of fluid expelled (m³) through an area of the sea floor (m²) as it moves landward and is incorporated in an accretionary wedge is shown in Figure 9. This semi-quantitative calculation assumes the simple approximation of equilibrium sediment consolidation with depth, i.e., that the porosity-depth function remains constant as the wedge tectonically thickens landward.
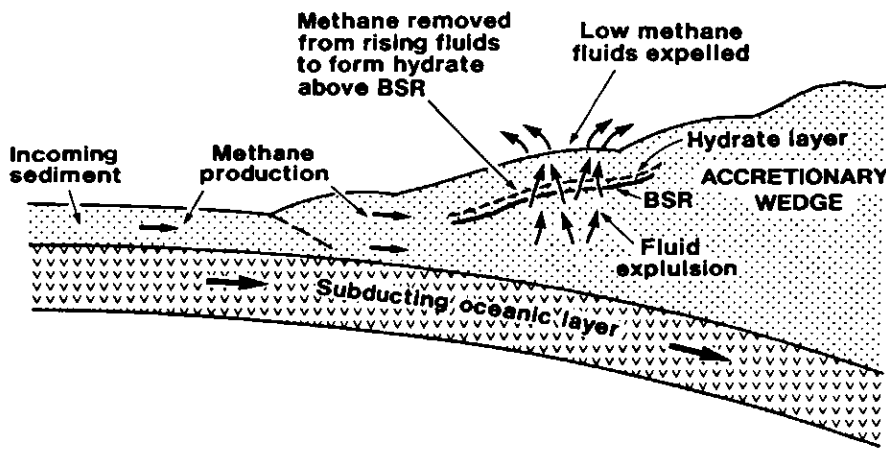

Figure 8 A schematic diagram illustrating the model of BSR hydrate formation through methane removal from rising fluids that are tectonically expelled from an accretionary sedimentary wedge.
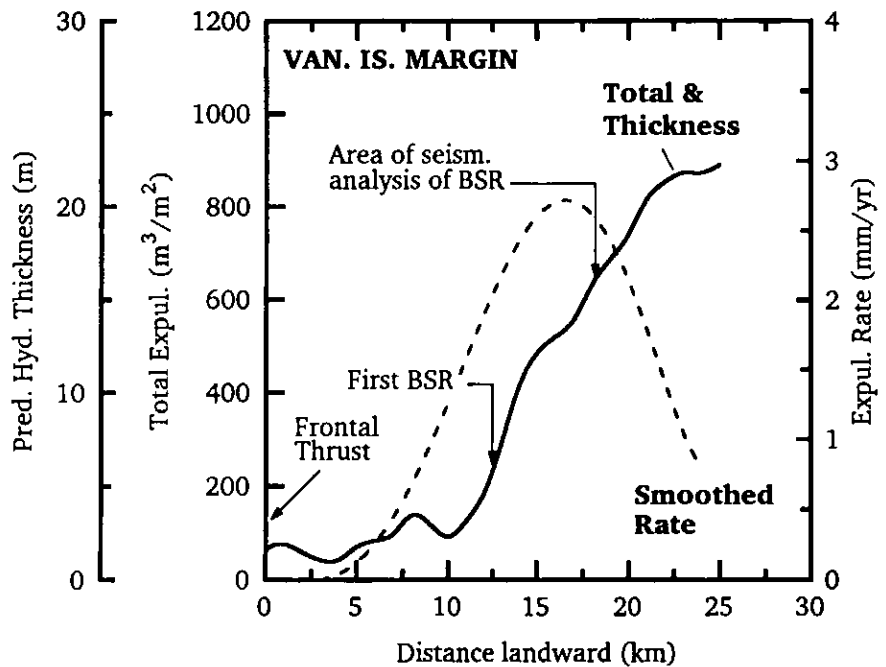

Figure 9 The estimated total amount of fluid (m³) expelled through an area of the sea floor (m²) as that area moves landward and is incorporated in an accretionary wedge. The model thickness of hydrate as a function of distance landward from the deformation front, estimated as described in the text, is also shown.

The actual consolidation may be more rapid due to tectonic compression giving larger volumes of fluid. This total expulsion is converted into the predicted hydrate layer thickness assuming that, in each parcel of pore fluid moving upward, a constant amount of methane is removed on passing into the hydrate stability field. About 50 mmole of methane must be removed per litre of rising fluid (about 20% of the saturation concentration of dissolved methane) to give the 10-30 m hydrate layer thicknesses estimated on the Vancouver Island margin from the seismic data. A continuous upward diffusion loss of methane to the sea floor is expected. Thus, on the upper continental slope where the fluid expulsion rate and therefore methane input rate become small, the hydrate layer will gradually dissociate and eventually disappear.

DISCUSSION
Methane hydrate is widespread beneath continental slopes, particularly in subduction zone accretionary sedimentary prisms such as beneath much of the continental slope of Vancouver Island. Analyses of seismic and other data for this margin indicate that the bottom-simulating-reflector or BSR can be produced by the contrast between sediments whose porosity is partially filled with hydrate and underlying sediments containing no hydrate. No free gas is required. The origin of the large amount of methane inferred to be contained in the hydrate is a critical question. A model has been developed in which methane is generated biogenically in sedimentary sequences many kilometres thick accreted in subduction zones. The methane is concentrated upward into hydrate layers a few tens of metres thick at the base of the stability field several hundreds of metres below the sea floor.

The global methane contained in deepsea hydrate layers is very large, although our new estimates of thickness of only several tens of metres are smaller than the average that has been assumed in previous global estimates. Thus, the total may be lower by a factor of 2 to 5. The conclusion that the BSR hydrate appears to be concentrated at the base of the hydrate stability field and does not generally extend to the sea floor means that its response to climate changes that affect deep seawater temperature will be relatively slow, i.e., hundreds to thousands of years.

Drill-core sampling and downhole measurements across the BSR boundary are planned for 1992 on a leg of the international scientific ODP, of which Canada is a member. It is hoped that this work will resolve some of the questions which remain on the nature and distribution of BSR hydrate.

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