

Figure 4 Scatter plot of actual summer surface water temperature versus latitude for each of the 70 Labrador lakes. The different symbols represent the different vegetation zones in which the Labrador lakes are located³². Temperature, depth, latitude and longitude of the lakes are available; see Supplementary Information.

about 6,500 yr BP, as well as decreases in the amount of summer season radiation.

The temperature gradients reconstructed for the late-glacial period in eastern North America are very strong relative to those of modern times. Under these conditions, plant species whose modern ranges are normally separated by large distances may have occurred in close proximity. These results may help explain, in some cases, the lack of modern analogues for past pollen assemblages, typified by those comprising pollen of spruce (*Picea*), sage (*Artemisia*), ragweed (*Ambrosia*), oak (*Quercus*), elm (*Ulmus*) and ash (*Fraxinus*) during the late-glacial period in Minnesota³⁴. Our results also indicate that the rapid warming and cooling phases of the Killarney Oscillation and Younger Dryas affect terrestrial ecosystems by rapidly changing the position of steep temperature gradients, to which plant and animal communities alter their geographical boundaries accordingly. This would have proved especially difficult for people inhabiting the region at that time, as they would have been subjected to a number of severe and abrupt climate changes throughout the late-glacial period. The late-glacial temperature gradients reported here will serve as a robust test for future, more refined climate models, especially because the magnitude of these gradients is dependent upon the combined effects of the Laurentide ice sheet and increased summer season radiation, the latter resulting from long-term changes of the Earth's orbit relative to the Sun. □

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Supplementary Information is available on Nature's World-Wide Web site (<http://www.nature.com>) or as paper copy from Mary Sheehan at the London editorial office of Nature.

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Direct measurement of *in situ* methane quantities in a large gas-hydrate reservoir

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Certain gases can combine with water to form solids—gas hydrates—that are stable at high pressures and low temperatures^{1,2}. Conditions appropriate for gas-hydrate formation exist in many marine sediments where there is a supply of methane. Seismic reflection profiles across continental margins indicate the frequent occurrence of gas hydrate within the upper few hundred metres of sea-floor sediments, overlying deeper zones containing bubbles of free gas^{3–9}. If large volumes of methane are stored in these reservoirs, outgassing may play an important role during climate change^{10–12}. Gas hydrates in oceanic sediments may in fact comprise the Earth's largest fossil-fuel reservoir^{2,13}. But the amount of methane stored in gas-hydrate and free-gas zones is poorly constrained^{4,9,13–18}. Here we report the direct measurement of *in situ* methane abundances stored as gas hydrate and free gas in a sediment sequence from the Blake ridge, western Atlantic Ocean. Our results indicate the presence of substantial quantities of methane (~15 GT of carbon) stored as solid gas hydrate, with an equivalent or greater amount occurring as bubbles of free gas in the sediments below the hydrate zone.

The Blake ridge is a sediment drift deposit in the Atlantic Ocean on the continental rise of North America that has strong indications for the presence of gas hydrate and free gas on the basis of seismic reflection profiles (Fig. 1)^{2,6–8,18,19}. Ocean Drilling Program (ODP)

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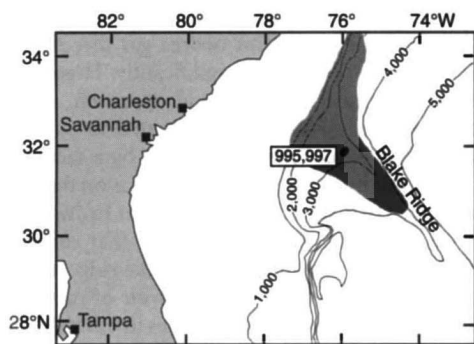


Figure 1 Location of Ocean Drilling Program (ODP) sites 995 and 997 on the Blake ridge off the southeastern coast of the United States²⁰. The region (26,000 km²) over which seismic reflection profiling indicates the presence of gas-hydrate and free-gas zones is shaded¹⁹. Bathymetric contours are in metres.

Leg 164 recently drilled locations on this ridge to investigate *in situ* characteristics and amounts of gas stored in these zones²⁰. Sites 995 and 997 were drilled from the sea floor at approximately 2,775 m below sea level (m.b.s.l.) to depths of 705 and 750 m below sea floor (m.b.s.f.), respectively.

Proxy techniques for identifying the presence of gas hydrate and free gas (seismic profiles, well-logs, porewater chemistry and core temperature) indicate that there are three general gas zones in sediment at sites 995 and 997 (Fig. 2)^{18,20}: (1) sediment is increasingly gassy but does not contain methane hydrate from 0 to 190 m.b.s.f.; (2) sediment contains intervals with methane hydrate from 190 to 450 m.b.s.f. (principally between 190 and 240 m.b.s.f. and between 380 and 450 m.b.s.f.) (3) sediment contains free methane bubbles below 450 m.b.s.f. (especially between 450 and 470 m.b.s.f.). However, as with previous indirect approaches^{3-9,14-17}, how much methane exists in each of these depth intervals is unclear.

The Pressure Core Sampler (PCS) is a tool designed to recover a 1,320 cm³ cylindrical sediment core at *in situ* pressure (Fig. 3)²¹. Thus, the quantity and composition of gas in a deep sea sediment sample at depth can be determined by releasing gas from the PCS under controlled laboratory conditions at the surface. Using the PCS, *in situ* gas quantities were determined at 17 depths at sites 995 and 997 (Fig. 2). Analyses of gas released from the PCS indicate that it is >98.5% CH₄, with the remainder consisting largely of CO₂ (ref. 20).

The downhole profile of *in situ* methane quantities (Fig. 2) is broadly consistent with shipboard interpretations concerning the distribution of gas at sites 995 and 997. Sediment from 0 to 190 m.b.s.f. and from 240 to 380 m.b.s.f. contains relatively low quantities of methane (0.04–0.14 mol dm⁻³ of pore space); sediment from 190 to 240 m.b.s.f., from 380 to 450 m.b.s.f., and from below 470 m.b.s.f. contains moderate quantities of methane (0.23–0.84 mol dm⁻³ of pore space); sediment from 450 to 470 m.b.s.f. contains an exceptional quantity of methane (2.0 mol dm⁻³ of pore space). Theoretical saturation of methane in pore water depends on whether pore space also contains methane hydrate or free methane gas^{1,22-24}. Methane saturation in sea water/methane hydrate systems increases from approximately 0.05 to 0.17 mol CH₄ per dm³ sea water at water depths from 2,775 to 3,225 m.b.s.l. (0–450 m.b.s.f.), whereas methane saturation in seawater-free methane gas systems decreases from approximately 0.17 to 0.16 mol CH₄ per dm³ sea water at water depths from 3,225 to 3,525 m.b.s.l. (450–750 m.b.s.f.)²²⁻²⁴. Thus, pore water is undersaturated with methane in sediment from 0 to 190 m.b.s.f., and saturated to greatly oversaturated in sediment beneath 190 m.b.s.f. (Fig. 2).

A volume of methane hydrate releases a quantity of methane

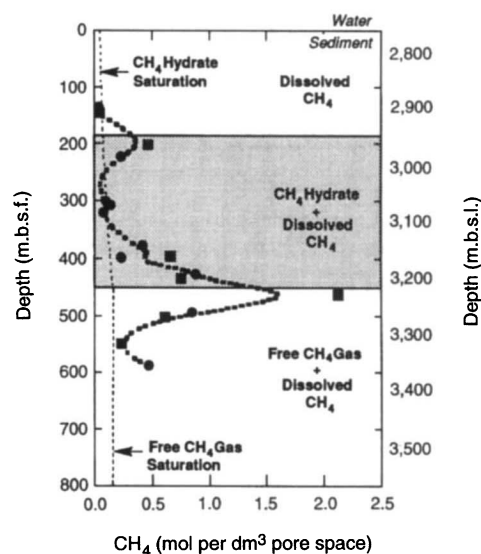


Figure 2 *In situ* methane quantities at Ocean Drilling Program (ODP) sites 995 (filled circles) and 997 (filled squares) shown with respect to water depth (m below sea level, m.b.s.l.) and sediment depth (m below sea floor, m.b.s.f.). Sites 995 and 997 are located at approximately 2,775 m.b.s.l. and extend from the sea floor to 705 and 750 m.b.s.f., respectively. Methane hydrate occurs in sediment from 190 to 450 m.b.s.f. while free methane gas occurs in sediment below 450 m.b.s.f. *In situ* methane quantities (mol per dm³ pore space) were calculated by converting the total volume of gas released from the Pressure Core Sampler (PCS) to moles (23.6 l mol⁻¹ at 1 atm and 15°C), and dividing this amount by the volume of sediment pore space inside the PCS. Sediment porosity used in this calculation was the average value measured for sediment recovered by conventional coring techniques within 10 m of each PCS core. The small volume of gas that remains in the PCS at 1 atm and 15°C cannot be determined and has not been included in these calculations. Also shown are a smoothed curve through all *in situ* methane quantities, and the saturation curves for methane in sea water with methane hydrate^{22,23} and in sea water with free methane gas²⁴.

upon dissociation that is proportional to its density (0.91 g cm⁻³) and molecular weight (124 g mol⁻¹). Assuming that methane in oversaturated pore water exists as methane hydrate above 450 m.b.s.f., pore space from 190 to 450 m.b.s.f. contains between 0 and 9% methane hydrate by volume. This range is quantitatively consistent with shipboard estimates made from porewater Cl⁻ profiles given certain assumptions regarding *in situ* porewater composition²⁰. Methane hydrate volumes from 190 to 450 m.b.s.f. on the Blake ridge also have been estimated from vertical seismic profiling¹⁸. This latter approach gives a similar average value for methane hydrate volumes but a smaller range in values (5–7% pore space) probably because vertical seismic profiling cannot detect the centimetre to metre-scale heterogeneity of methane hydrate distribution that is evident in sediment on the Blake ridge²⁰.

There should be a unique depth along the geotherm in a sediment sequence at which both solid methane hydrate and free methane gas are in equilibrium^{2,12,14,15}. Above this depth, only methane hydrate and methane-saturated pore water should be present; below, only free methane bubbles and methane-saturated pore water. Seismic, well-log and porewater information at sites 995 and 997 indicate that this phase boundary occurs at ~450 m.b.s.f. (Fig. 2)^{18,20}. Moreover, pore waters collected from PCS cores from ≥462 m.b.s.f. do not contain local freshwater anomalies that are produced when gas hydrate dissociates^{2,17,20}. Thus, oversaturated methane in PCS cores from ≥462 m.b.s.f. was present as free gas bubbles.

Free methane volumes at depth can be calculated from methane quantities measured at 1 atm and 15°C via the ideal gas law and *in*

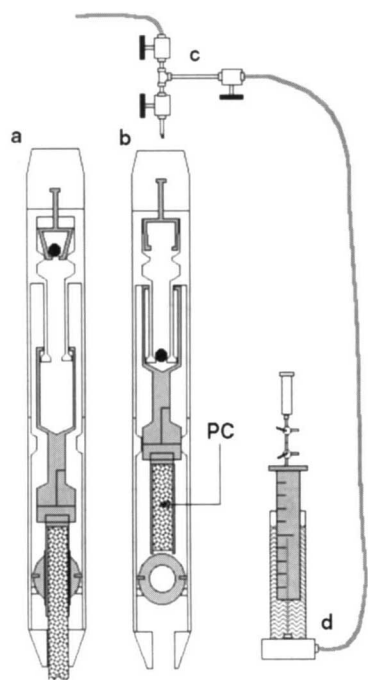


Figure 3 Diagram showing the Pressure Core Sampler (PCS) tool during downward drilling (a) and after core recovery (b) with attached gas manifold system (c) and bubbling chamber (d)^{20,21}. Recovery of a pressurized core of up to 1,320 cm³ (1 m long and 4.1 cm diameter) occurs when an actuation ball is released to redirect fluid flow, to raise a piston with core barrel, and to rotate a lower ball valve. To measure *in situ* gas volumes, the PCS was placed in an ice-bath on ship after each successful core recovery. Gas was released incrementally from the PCS into a He purged manifold (c) that was at ~15 °C and 1 atm and then bubbled into an inverted graduated cylinder (d) that was immersed in water saturated with NaCl at ~15 °C. Aliquots of gas were then removed from the inverted cylinder for analysis. This procedure was continued until atmospheric pressure was achieved in the PCS. The PCS was warmed to ~15 °C and an additional small volume of gas was measured. The volume of sediment inside the PCS then was measured after opening the tool. Repeated tests conducted during ODP Leg 164 have shown that all gas released from the PCS comes from the sediment core inside it, and not from any bore-hole water it might contain²⁰. Detailed descriptions of the PCS and historical efforts at recovering deep-sea sediment cores under pressure are reported elsewhere^{21,27}.

situ pressure and temperature. Sediment at 462 m.b.s.f. contains an oversaturated *in situ* methane quantity of 1.8 mol CH₄ per dm³ pore space (Fig. 2) and has *in situ* pressure and temperature conditions of ~323 atm and 20 °C (ref. 20). Therefore, pore space at this depth contains ~12% methane gas bubbles by volume. This direct evidence indicates that volumes of free gas beneath the gas-hydrate zone on the Blake ridge are significantly higher than have been previously estimated (1–2%) on the basis of seismic reflection profiles and a series of assumptions concerning acoustic properties in gas-rich sediment⁷. Even the data from vertical seismic profiling conducted during Leg 164 have been interpreted as indicating only small amounts of free gas (~1% pore space) beneath the gas-hydrate zone¹⁸, underscoring the need for direct measurements of the type we report here.

The average quantity of gas in PCS cores recovered between 190 and 600 m.b.s.f. at sites 995 and 997 is 0.55 mol CH₄ per dm³ pore space. Seismic reflection profiles indicate that gas-hydrate and free-gas zones extend over 26,000 km² of the Blake ridge (Fig. 1)¹⁹. If results presented here are representative of this entire area, gas-hydrate and free-gas zones on the Blake ridge contain approximately 4.7 × 10¹⁶ g CH₄, or 35 GT of carbon. Our estimate differs from that

recently made from vertical seismic profiling (40 GT of carbon over 100,000 km²)¹⁸ in that the amount of free gas directly measured beneath the gas-hydrate zone is significantly larger than that estimated from the indirect geophysical approach. As a consequence, the amount of gas that was estimated to occur in these holes by geophysical measurements is lower by a factor of three. Indeed, the volume of methane present as free gas on the Blake ridge may be greater than that stored in overlying gas hydrate (Fig. 2).

Although we agree with Holbrook *et al.*¹⁸ that some previous estimates of gas hydrate amounts on the Blake ridge are too high, reassessment of the size of the global reservoir of methane in gas hydrate and free gas must await future studies in other regions using direct measurement techniques such as those presented here. There is no indication from our results, however, to suggest that global estimates of 10³–10⁴ GT of methane carbon are in error or that methane hydrate and free-methane zones in marine sediment constitute relatively minor carbon reservoirs. The 35 GT of methane carbon on the Blake ridge is a quantity of methane that could meet the 1996 United States natural gas consumption rate for the next 105 years²⁵, and a quantity of carbon that is ~7% of total terrestrial biota²⁶.

Abundant geological evidence indicates that rapid drops in sea level and deep ocean warming have occurred in the past. Because several of these time intervals are characterized by a major input of carbon (from some source) to the ocean and atmosphere, and because the stability of gas hydrate decreases with reduced pressure and elevated temperature, it has been speculated that release of methane from oceanic hydrates has played a role in past climate change^{10–12}. A major assumption behind such hypotheses has been that a large mass of methane indeed exists in oceanic gas-hydrate zones. Results presented here validate this assumption (at least for the present-day Blake ridge). Release of large quantities of methane from free-gas zones also should be considered in any scenario that invokes dissociation of overlying methane hydrate during oceanographic change. □

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