three categories. Finally, the types of behavior found for these elements are strongly affected by both chemical and biological processes, and thus it is appropriate to say that they are 'biogeochemically' cycled.

See also

Aeolian Inputs. Anthropogenic Trace Elements in the Ocean. Atmospheric Input of Pollutants. Carbon Cycle. Conservative Elements. Hydrothermal Vent Fluids, Chemistry of. Marine Silica Cycle. Metal Pollution. Nitrogen Cycle. Platinum Group Elements and their Isotopes in the Ocean. Pollution: Effects on Marine Communities. Refractory Metals. River Inputs. Transition Metals and Heavy Metal Speciation.

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METHANE HYDRATES

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What is Gas Hydrate?

A solid, icelike substance composed of gas and water molecules is called gas hydrate. Water molecules form cage structures in which various kind of gases such as methane, ethane, propane, hydrogen sulfide, and carbon dioxide, are incorporated to form a clathrate structure (**Figures 1** and **2**). Naturally occurring gas hydrate is largely composed of methane and water, and is then properly called methane hydrate but is often referred to as gas hydrate, particularly in the field of earth and ocean sciences. Chemists and petroleum engineers have known about gas hydrates since the nineteenth century. However, most earth and ocean scientists were not aware of the existence of natural gas hydrate (methane hydrate) until it was recovered from a gas field in permafrost in the late 1960s and gas hydrate-related seismic reflectors and gas zonation were identified in deep-sea sediments in the early 1970s. Recent development of marine geological and geophysical surveys have revealed that gas hydrate is widely distributed in deep-sea sediments, and huge amounts of methane are probably trapped as a 'solid gas.' These findings raised three important issues related to human life: gas hydrate could become a potential energy resources, might play an important role in global climatic change, and might cause geological hazards such as slope failures and gigantic gas plumes.

Fundamental Properties

There are three structural types of gas hydrate for which a large number of natural gas molecules have been identified. These are cubic structures known as structures I and II, and the more recently discovered hexagonal structure H. Each structure type is char-

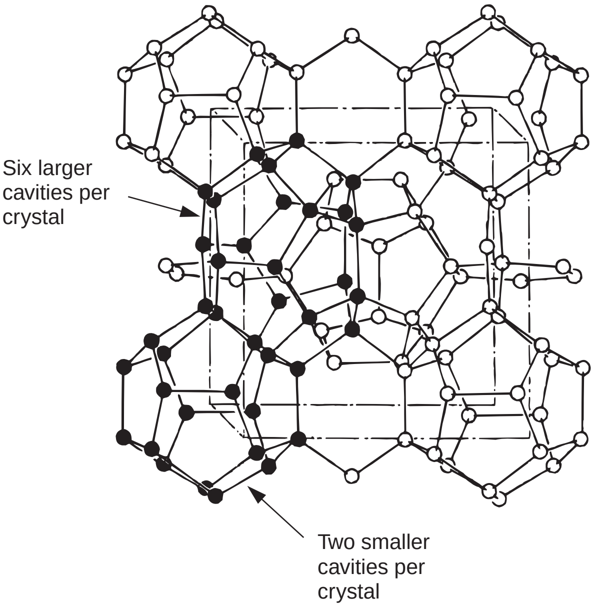

Figure 1 Structure I hydrate lattice composed of six larger cages and two smaller cages. (Hand *et al.*, 1974.)

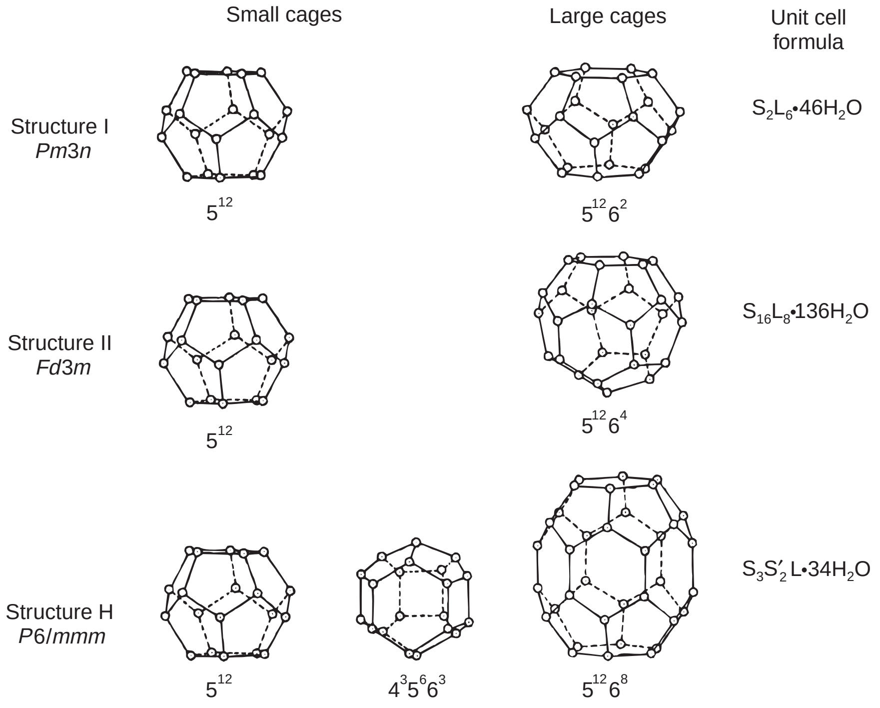

Figure 2 Five polyhedra of gas hydrates. The 12-hedron occurs in all three structures, whereas the 14-hedron, the 16-hedron, and 20-hedron are the cages of structure I, II, and H, respectively. (Ripmeester *et al.*, 1994.)

acterized by the number and type of each cage, which determines the ideal stoichiometry of the hydrate structure. The pentagonal dodecahedron (12-hedron) occurs in all three structures, whereas the 14-hedron, 16-hedron, and 20-hedron form cages of structures I, II, and H, respectively. In addition to these, structure H hydrate contains another 12-hedron cage (**Figure 2**). Hydrate structures are principally determined by the type of guest gas molecule; methane, ethane, hydrogen sulfide, and carbon dioxide form structure I hydrates, whereas propane forms a structure II hydrate. Structure H hydrate has been reported to contain significant amount of isopentane. Among the three types of hydrate, structure I (methane hydrate) is predominant in marine gas hydrate deposits.

The unit cell of structure I hydrate is composed of two small cages (12-hedra) and six large cages (14-hedra). Assuming that all the eight cages are occupied by methane, the molar ratio of methane to water is 8 : 46, and the ideal formula of methane hydrate is given as $CH_4 \cdot 5.75H_2O$. The volumetric ratio of methane to water in fully occupied gas hydrate at standard conditions is ~1:164.

Stability Conditions

Methane hydrate is stable at lower-temperature and high-pressure conditions with excess amount of free gas and water. These conditions are met within organic-rich sediments of deep-sea regions. **Figure 3** depicts the stability field of gas hydrates in deep-sea sediments. The solid curve indicates three-phase equilibrium conditions for the system of methane, water, and methane hydrate. The broken line represents the temperature profile of sea water. The ocean floor at a water depth of 2500 m ($T \sim 3°\text{C}$ and $P \sim 250$ bar) is well within the stability for methane hydrate, and methane hydrate can be formed if the bottom sea water is oversaturated with respect to methane. Such conditions are met at methane seep sites, e.g., on the continental slope of the Gulf of Mexico and atop mud-volcanoes of Caspian Sea. The sediments of shallow burial are also the zone of hydrate stability. The temperature of sediments increases with depth and exceeds the stability conditions at ~600 m below seafloor (mbsf), below which gas hydrate will be destabilized. The lower limit of the stability of gas hydrate is termed BGHS (base of gas hydrate stability). BGHS varies with water depth and thermal gradient, e.g., 300–400 mbsf at water depth of 1000–2000 m and 400–600 mbsf at 3000–4000 m.

Low-temperature and high-pressure conditions with adequate amounts of free hydrocarbon gases are also encountered in on-land sediments below the permafrost of polar regions, such as in Siberia, Alaska, and Arctic Canada.

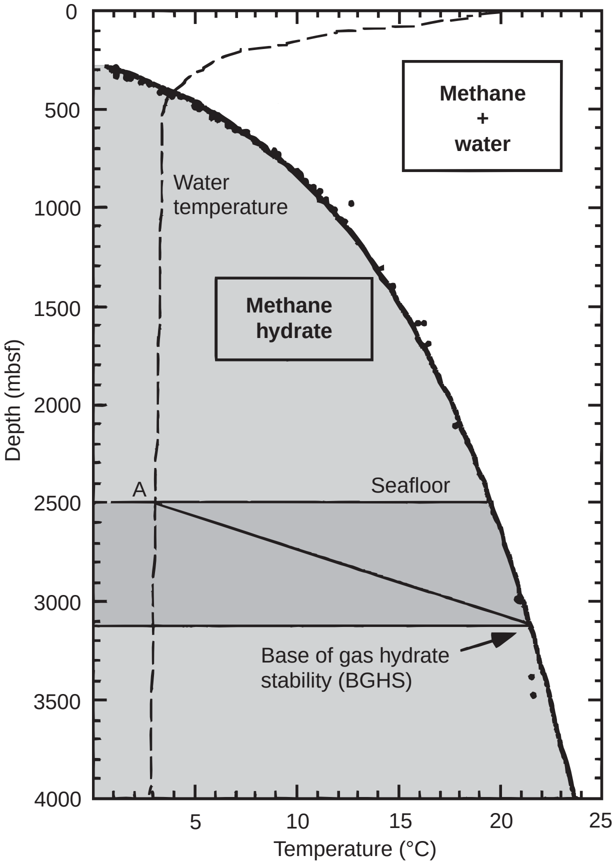

Figure 3 The conditions for the stability of methane hydrate in marine sediments. (Matsumoto, 1995.)

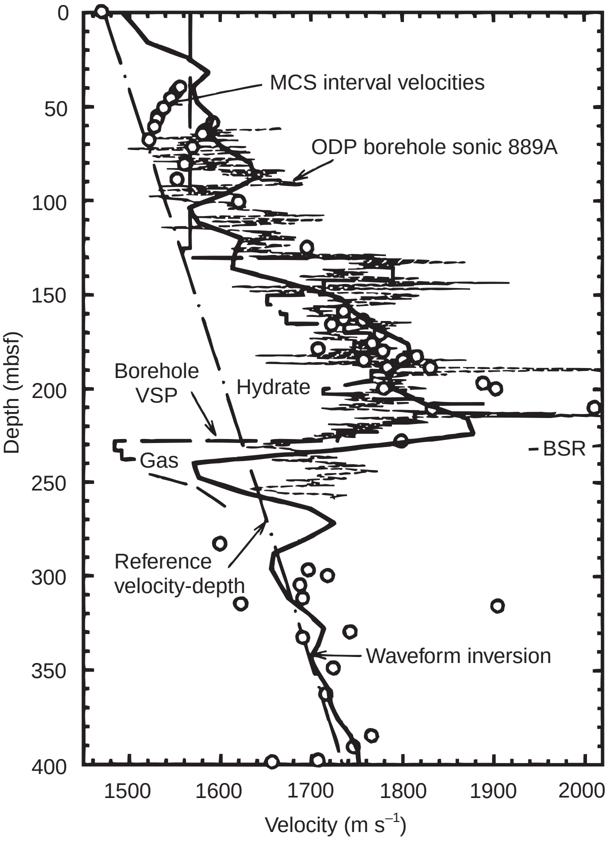

Figure 4 Velocity–depth estimates on the Cascadia continental slope where the BSR is located at 225 m below sea floor. (Spence *et al.*, 2000.)

Exploration of Marine Gas Hydrate

Exploration of methane hydrate was initiated by the Deep Sea Drilling Project (DSDP) commencing in 1968, and related marine geological and geophysical surveys. Gas hydrate drilling is one of the major initiatives of the Ocean Drilling Program (ODP, 1985–2003) and the planned Integrated Ocean Drilling Program (IODP, 2004–). R&D projects for exploration of gas hydrate resources have been conducted in the Nankai Trough off Japan Islands, on the continental margins of North America, and in the South China Sea, in close collaboration with scientific projects.

Seismic Survey

Marine seismic survey is the most efficient technique for exploring subsurface gas hydrate in deep-sea sediments. Sediments above BGHS are expected to contain gas hydrate, which occurs predominantly as interstitial pore cement with occasional fracture-filling veins. The acoustic velocity of hydrated sediments is significantly increased to 1.8–1.9 km s^{-1} (**Figure 4**), whereas the sediments below BGHS often contain gas bubbles and the acoustic velocity decreases to 1.4–1.6 km s^{-1}. Such a sharp velocity drop, or acoustic impedance contrast at BGHS causes high-amplitude reflection with reverse polarity. This reflector is termed a 'bottom-simulating reflector' (BSR) as it appears parallel to the seafloor reflector on seismograms. **Figure 5** shows one of the most beautiful BSR observed in Blake Ridge sediments off south-east North America. In **Figure 5**, the BSR cross-cuts gently dipping reflectors of bedding and fault planes. Blanking of the strata above the BSR (= gas hydrate zone) is likely due to the presence of gas hydrate, whereas enhanced reflections below the BSR are probably due to the presence of gas bubbles.

Drilling, Coring, and Well-logging

The presence of gas hydrate in deep-sea sediments is definitively confirmed by the recovery of gas hydrate samples through deep-sea drilling. As gas hydrate is sensitive to temperature and pressure changes and is easily dissociated during coring and recovery,

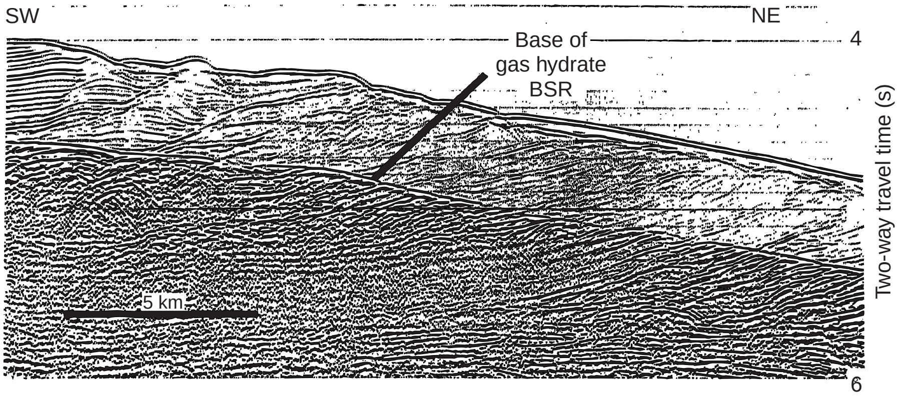

Figure 5 Multichannel reflection profile from the crest and eastern flank of the Blake Ridge. (Shipley *et al.*, 1979.)

special coring apparatus (pressure and temperature core sampler; PTCS; or pressure core sampler, PCS) has been designed to obtain gas hydrate samples. PTCS and PCS retain subsurface pressure (and temperature) during coring and recovery.

Figure 6 shows a solid gas hydrate recovered from the Blake Ridge sediments during ODP Leg164 and gas-hydrated coarse sands/granules taken from below the permafrost of Mackenzie Delta, Canada. The gas hydrate from Mackenzie is observed to cement interstitial pores, while the solid hydrate of the Blake Ridge is thought to fill fault-fractures.

Finely crystallized, pore-filling hydrate may be dissociated and totally disappear from hydrate-bearing sediments before the cores are inspected on board. Consequently, several proxy methods are employed to identify the presence of 'lost hydrate.' Pore waters extracted from sediment cores sometimes exhibit anomalously low chloride concentration. Low-chloride anomaly is explained as the result of mixing of pristine pore waters and 'fresh water' derived from gas hydrate (chloride anomaly method). The amount of gas hydrate is readily calculated from the anomaly values, assuming the base level of chloride concentration (**Figure** 7). Core temperature anomaly is another useful technique for identifying the existence of 'lost hydrate.' Core temperatures measured on board soon after core recovery exhibit anomalously low values, often below zero (**Figure** 8). This is because gas hydrate dissociation is an endothermic reaction.

Acoustic and resistivity well logging of boreholes provide critical information on distribution and amounts of subsurface gas hydrate. As shown in **Figure** 7, which illustrates the correlation of logging data with chloride concentration, low-chloride zones coincide with high resistivity and high velocity. Formation Micro-Image (FMI) is an advanced technique of high-resolution resistivity logging. FMI

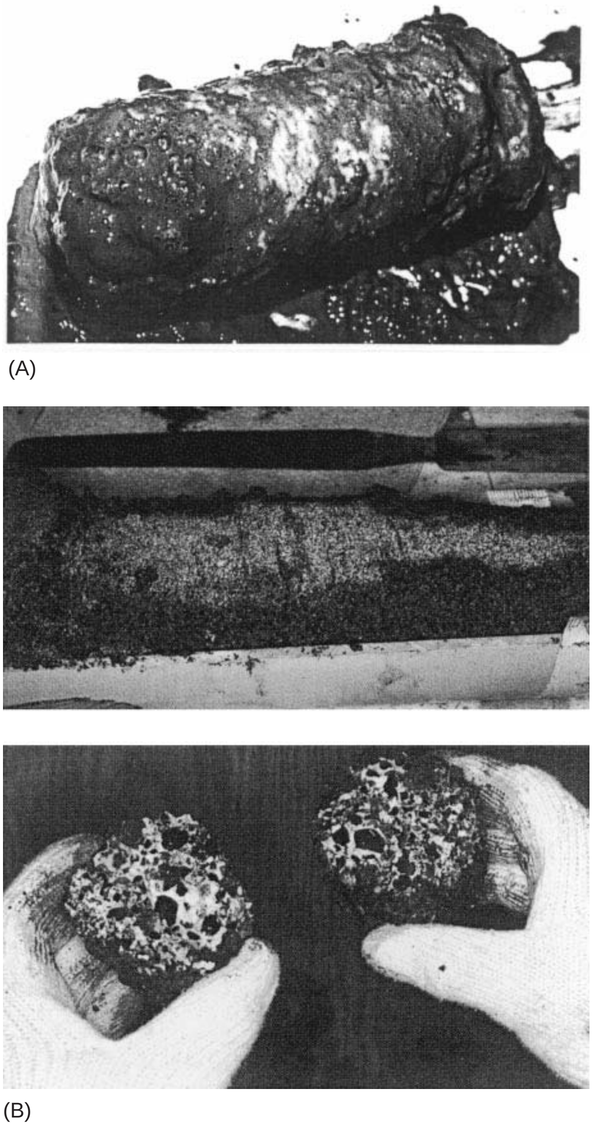

Figure 6 (A) Gas hydrate recovered at ODP Site 997 on the Blake Ridge (Matsumoto *et al.*, 2000), and (B) from Mallik 2L-38 research well in Mackenzie delta. (Uchida *et al.*, 1999.)

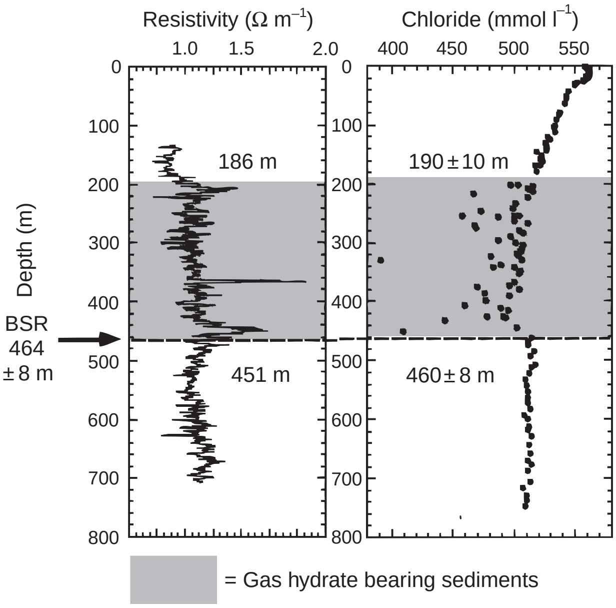

Figure 7 Chloride concentration and resistivity profiles at ODP Site 997, Blake Ridge. (Paull *et al.*, 1996.)

deployment in the Nankai Trough successfully demonstrated that a number of thinly bedded sand layers ($\sim 1\,\mathrm{cm}$) are selectively and intensively hydrated, probably reflecting higher permeability and existence of pore space for hydrate crystallization.

Submersible Dives

Neither seismic surveys nor drilling is useful to investigate ocean floor hydrate, but direct observation, sampling, and monitoring by submersible dives provide critical information for the study of gas hydrate exposed on the seafloor. Recent submersible dives to Hydrate Ridge of Cascadia and the continental slope of the Gulf of Mexico identified dense occurrence of gas hydrate on and within bottom sediments. Repeated dives in the Nankai Trough off central Japan by 'Shinkai 2000' and 'Shinkai 6500' ('Shinkai' means deep-sea) observed active, methane-bearing seeps and associated chemosynthetic communities, and carbonate crusts and chimneys, perhaps linked with dissociation of subsurface gas hydrate and migration of fluids.

Occurrence of Marine Gas Hydrate

Blake Ridge

Blake Ridge (or Blake Outer Ridge) is a classic region for the study of naturally occurring marine gas hydrate (**Figure 9**). DSDP Leg 11 first shed light on the issue of marine gas hydrate in Blake Ridge, south-eastern margin of North America, from the existence of an unusual, high-amplitude seismic reflector (later named BSR) and the occurrence of gassy sediments. The existence of gas hydrate was strongly suspected for the first time, but the drillings

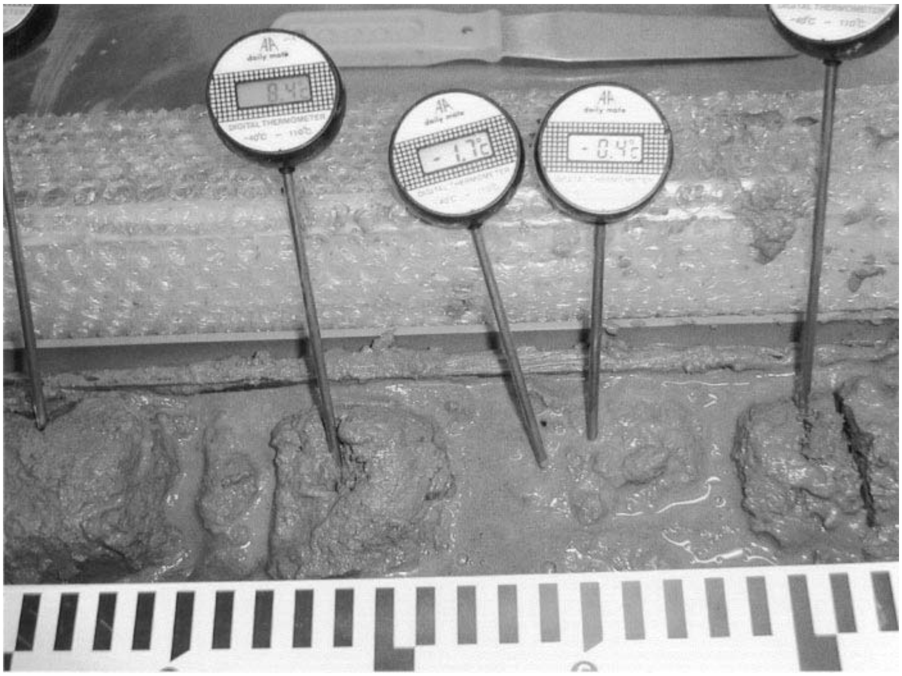

Figure 8 Photograph showing the anomalously low temperature of hydrate-bearing sediments recovered from Nankai Trough.

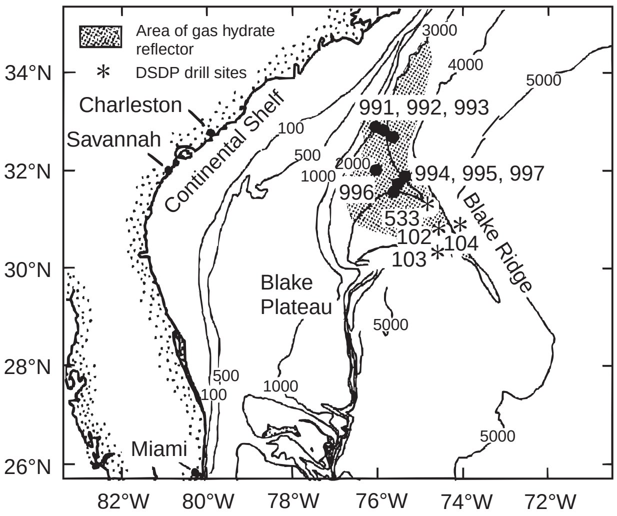

Figure 9 Map showing the location of Blake Ridge and DSDP Sites 102, 103, 104, 533, and ODP 991–997.

could not identify its existence at that time. On the other hand, the development of marine geophysical surveys revealed widespread distribution of high-amplitude reflectors (BSRs), in Blake Ridge and other continental margin sequences, stimulating interest in marine gas hydrates. In 1983, DSDP Leg 76 went to the Blake Ridge to recover gas hydrate. Site 533 located at water depth of 3194 m did not reach down to BSR, because of the safety policy of DSDP, but fortunately recovered layers a few centimeters thick of gas hydrate at 237.5 mbsf and 247.0 mbsf. Strong degassing and the soupy appearance observed in core samples, and chloride anomaly of pore waters, also suggested that gas hydrates were originally contained in the interval 392–399 mbsf. Gases released from gas hydrate were dominated by methane with high methane (C_1) to ethane (C_2) ratio ($C_1/C_2 = 2900$) and depleted in ^{13}C ($\delta^{13}C_{C1} = -70$ ‰ PDB), indicating biogenic origin (Kvenvolden and Barnard, 1983).

ODP Leg 164 visited the Blake Ridge for the third time in 1995. This was the first dedicated academic drilling to investigate naturally occurring marine gas hydrate, and was allowed to drill through BSR down to the free gas zone. The major objectives were to determine the distribution and amounts of subsurface gas hydrate, to refine the relation between BSR and gas hydrate, and to investigate fundamental properties of natural gas hydrate. Long holes (750–800 m) were drilled at Sites 994, 995, and 997 at water depth 2798 m, 2779 m, and 2770 m, respectively, on the Blake Ridge. These three sites form a 10 km long transect that extend from the ridge flank, where there is no BSR, to the ridge crest, where there is a very strong BSR. Gas hydrate samples were recovered from Sites 994 and 997. They occurred as massive nodules, veins, or flakes. The largest sample was a ~30 cm long piece of massive hydrate encountered at 331 mbsf at Site 997 (**Figure 6A**). Decomposing gas hydrates yielded gas of ~99.9 vol% CH_4, and < 0.02 vol% C2 + with $C_1/(C_2 + C_3) = 5000–15\,000$ and $\delta^{13}C_{C1} = -65.9–69.7‰$ PDB. Measurement of interstitial water chloride concentrations from high-resolution sampling revealed that sediments for the interval of ~200 mbsf and 450 mbsf (gas hydrate zone) at all three sites were characterized by low-chloride anomaly (**Figure 7**). This implies that the sediments of the gas hydrate zone had 1–2% hydrate filling the total sediment volume and some ranged up to 14%. This also indicates that gas hydrate could occur in sediments without BSR. Well log data showed distinct zones of high velocity and high electric resistivity that are coincident with zones where chloride anomalies indicate the presence of gas hydrates.

According to the experimental data on the stability of methane hydrate, observed bottom water temperature (~3.6°C) and thermal gradient (~3.4°C/100 m), the base of gas hydrate stability (BGHS) should occur at around 550 mbsf. However, both the BGHS and BSR were observed at ~450 mbsf. This discrepancy is not fully understood; it is perhaps related to such factors as a porous media effect, composition of sediments and gases, and heterogeneous thermal conductivity within hydrate-bearing sediments.

Nankai Trough

Gas hydrate BSRs are widely distributed in accretionary complex of the Nankai Trough off central Japan, approximating 35 000 km^2 (**Figure 10**). In 1990, ODP Leg 131 cored gas hydrate from Site 808 at a water depth of 4684.3 m on the lower slope of the complex. The location of Site 808 was selected at the place where there was no BSR, because drilling through BSR was prohibited for safety reasons at that time. The depth of the base of gas hydrate stability was inferred at ~220 m from bottom water temperature (~1.6°C) and thermal gradient (~11.1°C/100 m). Small chunks of hydrate and plant debris were observed in turbidite sandstone of wash core, which was taken from the depth range of 90–140 mbsf. Gas composition of gas hydrate was not directly determined but gas released from the sediments suggests that hydrate gas should be pure methane.

Exploratory wells were drilled in the eastern Nankai Trough in 1999–2000 for exploration of gas hydrate deposits. This was the first industry effort to evaluate the resource potential of marine gas

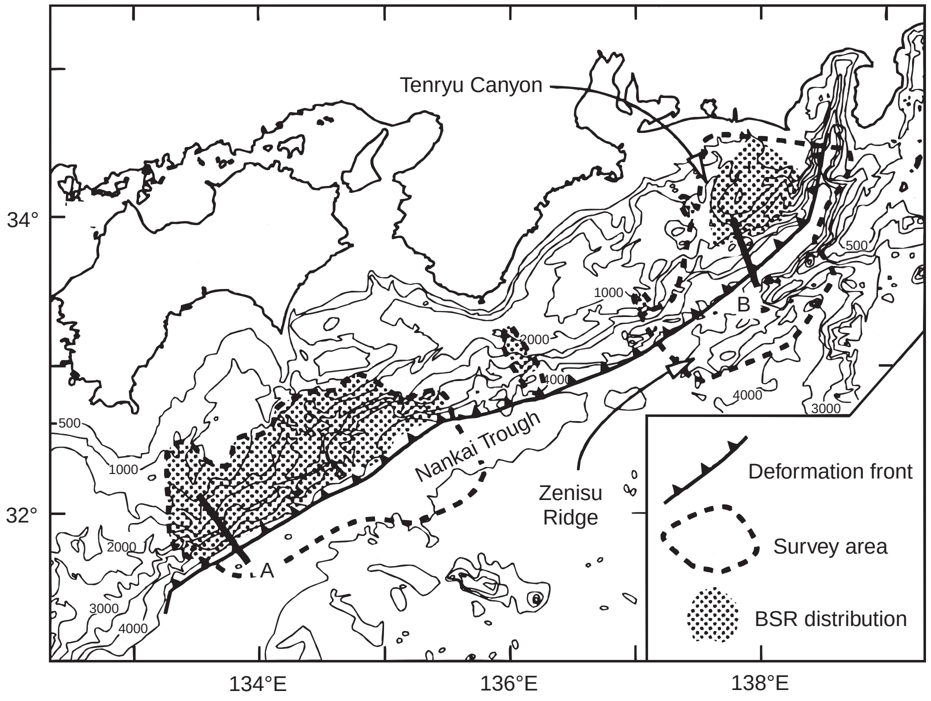

Figure 10 Map showing the distribution of BSR in Nankai Trough. (Modified from Ashi, 1994.)

hydrate deposits. The well site was located at a water depth of 945 m on a deep-sea terrace in a fore-arc basin. Well logs showed several high-resistivity zones for the interval 150 mbsf to 263 mbsf (gas hydrate zone) (**Figure 11**). Core recovery temperatures measured on deck were also anomalously low for this interval. Measurements of chloride concentration of 'pore waters,' that were extracted from sediment cores revealed that the sediments of high-resistivity zones contained ~ 10–80% hydrate filling pore spaces. A 25 m thick zone of high resistivity and low chloride at ~ 250 mbsf occurred in sandy unit, while the mud unit just overlying the sandy unit was not hydrated, with normal chloride concentration, implying that hydrate saturation is strongly controlled by the lithology of host sediments. Recovered gas hydrate occurred as fine to medium (<1 mm to a few millimeters long) crystallized aggregates filling the pore space of fine to medium, clean sand. Gases released from gas hydrate are composed of ~ 99.5% C_1 and ~ 0.5% C_{2+}. $\delta^{13}C_{C1}$ of -60 to $-72‰$ PDB, indicating biogenic origin. The base of gas hydrate stability (BGHS) is likely to occur within the hydrate-saturated sandstone, consistent with the depth of BSR at the drilling site. High- and low-velocity anomalies were identified below BGHS on acoustic logs, perhaps suggesting the presence of mixed free gas and gas hydrate below the dense hydrated saturated zone. The mixed zone may represent a 'transition' from one phase to the other, responding to temperature and/or pressure perturbation.

Deep-tow seismic survey conducted by French–Japanese team demonstrated BSRs at two horizons. The shallow one corresponds to the present P–T conditions, representing present BGHS. The other occurred at 10–30 m below the active BSR, termed the phantom BSR. Unusual 'double BSR' phenomena have also been reported from Cascadia margin and Norwegian Sea. Double BSR may be an acoustic expression of the mixed free gas and gas hydrate zone below the present BGHS.

Cascadia Convergent Margin

ODP Leg 146 first identified gas hydrates at Site 892 off Oregon in 1992 (**Figure 12**). BSR appears at 68 mbsf in the area, but gas hydrates were visually observed only at 4 and 17 mbsf. They occur as flat crystals 1–5 cm long, as crystalline aggregates, or as vein and interlayer beds a few centimeters thick. According to the results of pore water chlorinity measurements, invisible, finely crystallized hydrates are estimated to fill ~ 16% of the pore space.

Ocean floor gas hydrate at Cascadia was extensively surveyed by the R/V *Sonne* cruise in 1996 and by R/V *Ron Brown* in 1998. These employed video-guided and remotely operated instruments and exploration systems to observe discrete vent

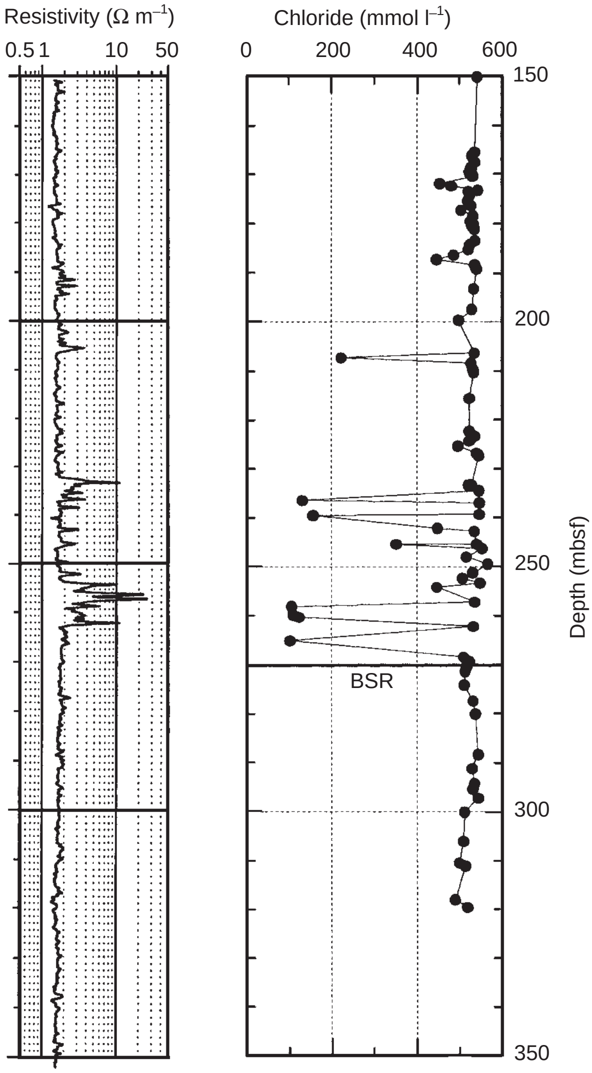

Figure 11 Comparison of electrical resistivity log and chloride concentration profile in Nankai Trough sediments. (Matsumoto, 2000.)

sites, to sample fluids, and to recover ocean floor gas hydrates and associated carbonates. Pure gas hydrate occurs in layers or joints several millimeters to decimeters thick. It also fills large secondary pore space, pushing apart the sediment framework along bedding planes. Carbonate sediments a few millimeters in thickness are intergrown with massive hydrates (**Figure 13**). The association of carbonate–hydrate is common throughout the area, causing acoustically hard and high reflections in sidescan sonar images. Such a surface feature was termed hydrate-pavement or mixed carbonate–hydrate pavement. Because of the wide distribution of the pavement, the small ridge at 44°40′ N and 125°06′ N was officially named Hydrate Ridge in 1998. Gases released from gas hydrate are dominated by methane and hydrogen sulfide, with small amounts of ethane and propane, $C_1/C_{2+} > 60\,000$, and $\delta^{13}C_{C1}$ is between -71.5 and $-62.4‰$ PDB, indicating that biogenic methane is the major component of the hydrate. Hydrogen sulfide content (1.5–3.1 vol%) is remarkably high when compared with subsurface gas hydrates at Blake Ridge and Nankai Trough.

The Cascadia margin is situated in a convergent zone of the Juan de Fuca and North American Plates, and bottom-reaching active thrust faults develop in the east of Hydrate Ridge. The formation of the hydrate pavement is thought to be related with tectonically induced, focused discharge and/or diffusive discharge of fluid. Suess and colleagues (1999) concluded that tectonically induced dewatering at convergent margin caused (1) destabilization of subsurface gas hydrate; (2) upward migration of low-salinity, methane-charged fluids; and (3) sulfate reduction at or near the sediment–water interface; and as a consequence of active discharge of CH_4–H_2S-containing fluids and alkalinity increase by sulfate reduction, (4) H_2S–CH_4-hydrate and carbonates were precipitated on and within the bottom sediments.

Gulf of Mexico

Gas hydrate in the Gulf of Mexico was first suspected from an extensive distribution of BSRs in the western part at a water depth of 1200–2000 m and 400–500 mbsf. In 1985, the Deep Sea Drilling Project drilled holes in Orca Basin at water depth of 2412 m where BSR was not clearly identified. The drilling recovered several hydrate samples from 20–50 mbsf. Based on gas composition, $C_1/(C_2 + C_3) = 159$ and $\delta^{13}C_{C1} = -71.3‰$, it was concluded that subsurface hydrate gases are of biogenic origin.

Ocean floor gas hydrate was found accidentally during the investigation of oil seepage. A number of shallow cores (< 4 m) were taken from Garden Banks, Green Canyon, and Mississippi Canyon on the continental shelf (**Figure 14**). The hydrates were discriminated, primarily from the origin of gas, into biogenic and thermogenic. Biogenic hydrates occur as purely white, flaky, and platy aggregates a few millimeters wide and 1–2 cm long. They are dominated by methane ($C_1/(C_2 + C_3) > 800$) and depleted in ^{13}C ($\delta^{13}C_{C1} = -66.5$ to $-70.4‰$). Thermogenic hydrates show variable occurrence from yellowish-brown, massive bulbous nodules to finer crystals dispersed in sediments. They contain significant amounts of C_2 and C_3 ($C_1/(C_2 + C_3) < 37$) and heavier $\delta^{13}C_{C1}$ (-43.2 to $-56.3‰$). Biogenic hydrates are classified as structure I methane

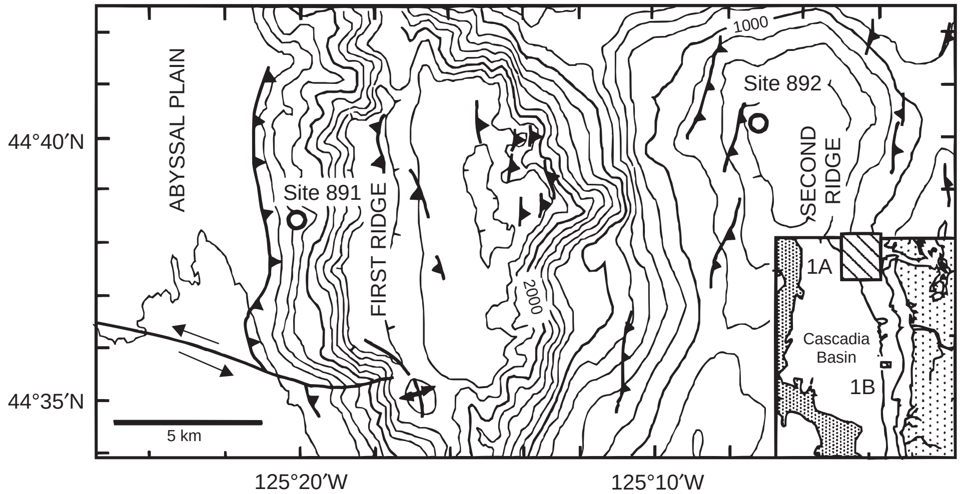

Figure 12 Map showing the location of ODP Sites 891 and 892 in the southern Cascadia margin. (Westbrook *et al.*, 1994.)

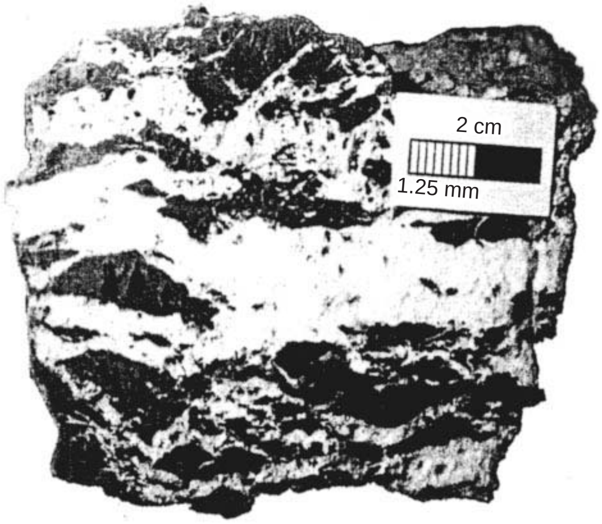

Figure 13 Photograph of interbedded hydrate-sediment specimen of Cascadia margin. (Suess *et al.*, 1999.)

hydrate, while thermogenic hydrates include structure II and even structure H. Ocean floor hydrates of the Gulf of Mexico are often associated with chemosynthetic communities such as tube worms and clams, oil droplets, and hydrocarbon gas seeps. Geologically, hydrate sites are located on or near diapiric arches, deep faults on diapir flanks, and collapse structures. Considering the occurrence and compositions, the accumulation of ocean floor hydrates of Gulf of Mexico is strongly related with upward migration and active discharge of fluid and deep-seated gases. Bottom water temperature at depths of 500–600 m is 6–8°C, which allows stabilization of methane and higher hydrocarbon gases.

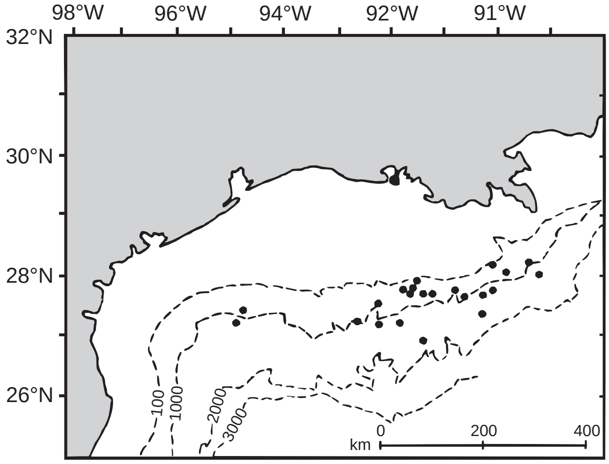

Figure 14 Map showing the locations of gas hydrate occurrence in the Gulf of Mexico. (Ginsburg and Soloviev, 1998.)

Caspian Sea

Seafloor gas hydrate in the Caspian Sea was first accidentally dredged in 1979 from the Vezirov Anticlinal High in the southern part of the Capsian at water depth of 480 m. Following this discovery, a number of gas hydrates were recovered from atop mud volcanoes Buzdag and Elm at water depth of 475 m and 660 m, respectively (**Figure 15**). The temperature of the bottom water is 5–6°C and the seafloor is well within the gas hydrate stability zone. Gas hydrate occurs as platy, flaky, or spicular crystals exposed on or embedded in clayey sediments. The amount of gas hydrate is visually estimated to be 2–35% of bottom sediments. Gases released from hydrate are dominated by methane ($\sim$ 74.7–95.3%) with significant amounts of C_2 (0.6–19.4%) and

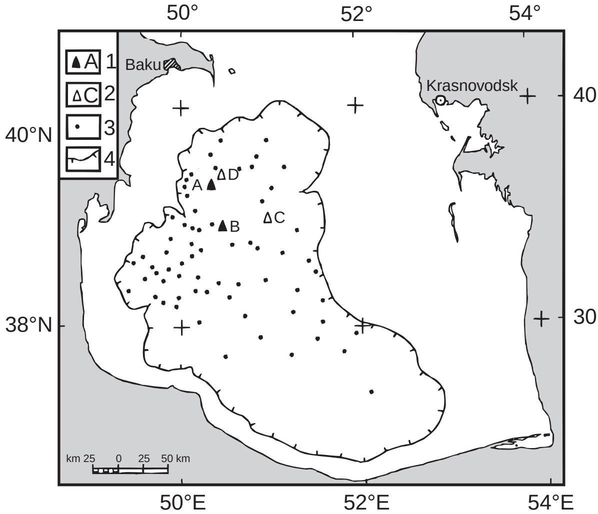

Figure 15 Map showing the locations of mud volcanoes with gas hydrate accumulation (1) and without hydrate (2 and 3). Line (4) indicates gas hydrate-bearing area. (Ginsburg and Soloviev, 1998.)

C_3 (1.5–6.0%). Corresponding to higher concentration of $C_2 + C_3$, $\delta^{13}C$ of methane is relatively enriched in ^{13}C, ranging between -44.8 and $-57.3‰$ PDB, suggesting greater contribution from thermogenic gases. Hydrate waters and waters squeezed from hydrate-bearing sediments are, unexpectedly, enriched in chloride ($\sim$ 13–50 g l^{-1}) compared with the bottom water (5.4 g l^{-1}). This implies that hydrate-forming fluids of mud volcanoes were hypersaline, perhaps $\sim$71 g l^{-1}, with excess hydrocarbon gases of thermogenic origin. More than 60 mud volcanoes have been identified in the deep part of the southern Caspian Sea. Some of them are thought to be undoubtedly hydrate-bearing.

Global Distribution and Amounts of Gas Hydrate

As shown in the stability diagrams (**Figure 3**), gas hydrate (or methane hydrate) is expected to occur in (1) marine and lake sediments of shelf, slopes, and rises, and (2) sediments in polar regions. In marine and lake sediments, gas hydrate can exist where the depth of water exceeds 300–500 m, depending on bottom water temperature. **Figure 16** illustrates worldwide location of known and inferred gas hydrate deposits in polar regions (squares) and in marine and lake sediments (circles).

Estimates of the amount of methane in gas hydrate are highly speculative and highly variable. **Table 1** shows variable estimates summarized by the Potential Gas Committee in 1981. Kvenvolden (1988) gave an estimate of 10^4 Gt as carbon ($\sim 1.9 \times 10^{16}$ m^3 as methane) for hydrate in the shallow geosphere, which is similar to the estimate of 2.0–2.1×10^{16} m^3, by MacDonald (1990).

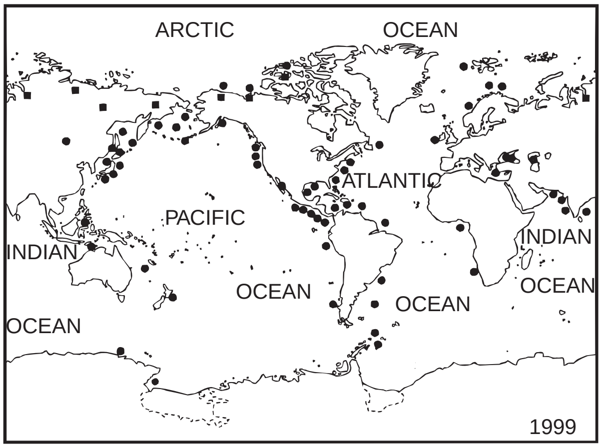

Figure 16 Map showing worldwide locations of known and inferred gas hydrate deposits in oceanic sediments (dots) and permafrost regions (squares). (Kvenvolden, 2000.)

Table 1 Worldwide estimates of the amount of methane in gas hydrate

Amount (m^3)	*Reference*
Continental	
1.4×10^{13}	Meyer (1981)
3.1×10^{13}	McIver (1981)
5.7×10^{13}	Trofimuk *et al.* (1977)
3.4×10^{16}	Dobrynin *et al.* (1981)
Marine	
3.1×10^{15}	McIver (1981)
5–25×10^{15}	Trofimuk *et al.* (1979)
7.6×10^{18}	Dobrynin *et al.* (1981)
Worldwide	
1.9×10^{16}	Kvenvolden (1988)
2.0–2.1×10^{16}	MacDonald (1990)

Potential Importance of Methane Hydrate

Since gas hydrate was found in marine sediments in the 1970s, interest in the relationship between natural gas hydrate and mankind has increased rapidly. This is because (1) enormous amounts of methane are trapped in gas hydrates of the shallow geosphere, and (2) gas hydrate is sensitive to changes in temperature and pressure and is easily dissociated to release methane to the ocean–atmosphere system. Natural gas hydrate is important as a potential energy resource, as a factor in global climate change, and as a trigger of geohazards such as submarine slides.

Energy Resources

The human race is facing serious issues concerning global environment and energy supplies. First, rapid build-up of atmospheric carbon dioxide during the last 100 years will cause global warming. Second, according to a scenario by US Department of Energy (1999), the world's annual production of conventional oil will fall in ~20 years. Under these circumstances, gas hydrate is expected to play an important role as a major natural gas resource in the twenty-first century, replacing the role of oil in the twentieth century. One of the merits of gas hydrate deposits is their relatively low environmental load. Natural gas is relatively clean compared with oil and coal, the amount of CO_2 emission being ~70% of that of oil and ~50% of that of coal consumption.

Expectation of gas hydrate as a future energy resource has grown rapidly, but the strategy for exploiting gas hydrate deposits and technologies for producing methane from the deposits have not been well established and developed. Three conceptual models for recovery of methane from marine gas hydrate deposits have been proposed: (1) depressurization, (2) thermal stimulation, and (3) inhibitor injection. Depressurization was considered for recovery of methane from the free gas zone below BGHS. Production of gas would decrease reservoir pressure, causing dissociation of gas hydrate above, which in turn increases the reservoir pressure. In thermal simulation and inhibitor injection methods, injection of warm sea water or steam, or a chemical inhibitor such as methanol would dissociate gas hydrates to produce methane within the gas hydrate zone.

Messoyakha, west Siberia, is a classic gas hydrate-related gas field, which produced gas by depressurization and methanol injection methods. Gas production from gas hydrate deposits started in 1969, and the production rate dropped in 1975. However, the reservoir pressure recovered in a few years, during which gas hydrate dissociation was enhanced in response to depressurization of the reservoir.

Japan launched a 5-year methane hydrate project in 1995, and will probably extend the project for another 10–20 years. Exploratory wells were drilled in the Nankai Trough for resource evaluation, and identified ~30 m thick, highly saturated, gas hydrate-bearing sand layers. The United States also commenced a >10-year gas hydrate project in 1998, including environmental issues as well as resource evaluation. The US project is aiming to produce gas from continental gas hydrate deposits in an Arctic region within 15 years.

Recently, gas hydrate has been considered as an efficient gas reservoir for transport of natural gas from production areas to consuming countries and as a 'fuel tank' for natural-gas vehicles.

Global Climatic Change

Methane is a 'greenhouse' gas with a global warming potential 20 times larger than that of carbon dioxide. The total amount of methane trapped in gas hydrate in the shallow geosphere has been estimated to be $\sim 2 \times 10^{16}\,m^3$ (**Table 1**), which is ~3000 times the amount in the atmosphere. Therefore, massive dissociation of gas hydrate could have a strong environmental impact, perhaps enhancing global warming. During global warming, melting of glaciers and ice caps cause a rise of sea level. The sea level rise affects marine sediments and permafrost differently. In an oceanic environment, sea level rise would increase hydrostatic pressure within sediments, thereby stabilizing subsurface gas hydrate. On the other hand, sea level rise causes a transgression of the polar ocean onto the permafrost regions. Gas hydrate of the polar region is destabilized and releases methane. During glacial climates, marine gas hydrate becomes unstable, responding to sea level fall, while polar continental shelves are exposed and become colder, and permafrost gas hydrate is stabilized. Thus, the net effect of global warming and cooling is still uncertain. However, a rapid rise in temperature caused by a rapid increase of atmospheric methane and carbon dioxide at the end of the last glacial maximum ~13 500 years ago has been attributed to dissociation of polar gas hydrate caused by melting of polar ice and temperature increase.

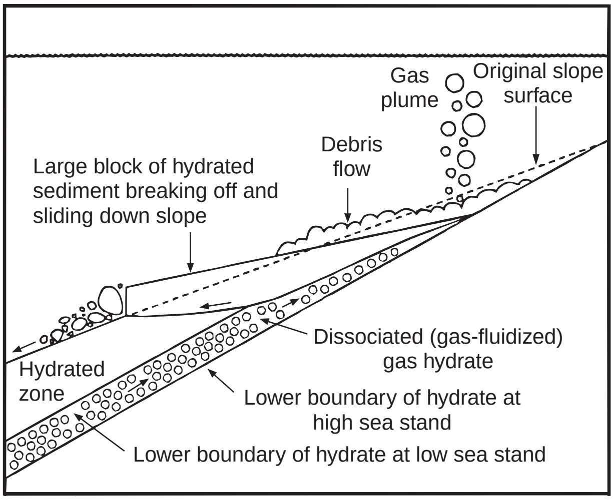

Figure 17 Diagram showing the effects of changes in pressure and temperature on submarine gas hydrate and the resulting seafloor failures and gas release. (Kvenvolden, 1993.)

The influence of global warming on gas hydrate and the environmental impact of dissociation of gas hydrate are much clearer during an ice-free age. Mass extinction of benthic foraminifers of intermediate water occurred at the late Paleocene thermal maximum. The event is characterized by large and rapid negative excursion in the oxygen and carbon isotopic composition of carbonate. $\delta^{18}O$ and $\delta^{13}C$ dropped by 3–4‰ and 2–3‰, respectively, and the excursions are thought to have occurred in $< 10\,000$ years. Oxygen isotopic excursion was explained as a result of temperature increase of sea water by approximately 6–7°C. Carbon isotopic excursion has been attributed to ^{13}C-depleted carbon derived from methane of marine gas hydrate, which is largely depleted in ^{13}C, ranging in $\delta^{13}C$ from $-60‰$ to $-90‰$ PDB. Simple mass-balance calculations indicate that 3‰-excursion in $\delta^{13}C$ of marine carbonates could be ascribed to dissociation of only $\sim 10\%$ of total gas hydrate. Temperature increase without significant sea level rise caused dissociation of subsurface and ocean floor gas hydrates, releasing large amount of methane into the ocean–atmosphere system. Released methane is ultimately oxidized in the ocean, resulting in dysaerobic–anoxic conditions and mass extinction of benthic forams.

Geological Hazard

Subsurface gas hydrate tends to concentrate near BGHS, forming a high-saturation zone, as hydrate-forming gases are largely supplied from below and accumulated just below BGHS. Lowering of sea level, either by eustasy or by tectonic uplift of the seafloor, or temperature increase raises subdepth of BGHS and thereby causes massive dissociation of gas hydrate in the basal part of hydrate zone. The solid hydrate layer becomes a zone of gas–water mixture. A fluidized layer develops between the old and the new BGHS, causing or at least facilitating a gigantic 'landslide' of a thick sequence of gas hydrate zone (**Figure 17**). A Storeaga Slide off Norway reaching down as far as Iceland is thought to be the largest example of gas hydrate-induced slide. Giant slides observed off Cape Hatteras, south-east North America, provide another example, which may be related with the sea level fall during the last glacial.

See also

Methane Hydrates and Climatic Effects. Seismology Sensors.

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METHANE HYDRATES AND CLIMATIC EFFECTS

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Introduction

Natural gas hydrates are crystalline solids that occur widely in marine sediment of the world's continental margins. They are composed largely of methane