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Gas Hydrates in Oceanic Sediment

by

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SUMMARY

The presence of natural gas hydrates in continental margin sediment worldwide has been inferred from the frequent occurrence of an anomalous seismic reflector which coincides with the predicted transition boundary at the base of the gas hydrate zone. Direct evidence for oceanic gas hydrates has been provided by visual observations of sediments from the Blake Outer Ridge, the landward wall of the Middle America and Peru Trenches, and from the Gulf of Mexico. The main objective of our work has been to determine the primary geochemical and geological factors controlling gas hydrate formation and occurrence and particularly in the factors responsible for the generation and accumulation of methane in oceanic gas hydrates. In order to understand the interrelation of geochemical/geological factors controlling gas hydrate occurrence, we have undertaken a multicomponent program which has included (1) comparison of available information at sites where gas hydrates have been observed through drilling by the Deep Sea Drilling Project (DSDP) on the Blake Outer Ridge and Middle America Trench; (2) regional synthesis of information related to gas hydrate occurrences of the Middle America Trench; (3) development of a model for the occurrence of a massive gas hydrate at DSDP Site 570; (4) a global synthesis of gas hydrate occurrences; and (5) development of a predictive model for gas hydrate occurrence in oceanic sediment. The first three components of this program were treated as part of a 1985 Department of Energy Peer Review. The present report considers the last two components and presents information on the worldwide occurrence of gas hydrates with particular emphasis on the Circum-Pacific and Arctic basins. A model is developed to account for the occurrence of oceanic gas hydrates in which the source of the methane is from microbial processes.

Natural gas hydrates are probably present within the uppermost 1,100 m (3,600 ft.) of oceanic sediment in the following regions of outer continental margins rimming the Pacific Basin: (1) the landward slope of the Middle America Trench off Central America, (2) the continental slope off western conterminous United States, (3) the landward slope of the western and eastern Aleutian Trench, (4) the continental slope of the Beringian margin, (5) the landward slope of the Nankai Trough off Japan, (6) the Timor Trough northwest of Australia, (7) the continental slope east of the North Island of New Zealand, (8) the basinal sediment of the Ross Sea and the continental margin off Wilkes Land, Antarctica, and (9) the landward slope of the Peru-Chile Trench. In some places these gas hydrates may contain and cap significant quantities of methane. Gas hydrates also occur in onshore and offshore sediment of the North American Arctic. Onshore, gas hydrates have been identified through drilling and logging in the Canadian MacKenzie Delta, the Sverdrup Basin and Arctic Platform, the Arctic Islands, and the North Slope of Alaska. Offshore, gas hydrates have been identified on marine seismic records from the Alaskan and Canadian Beaufort Sea. Also, evidence for gas hydrates has been encountered in offshore wells on the Canadian Beaufort Shelf and the Sverdrup Basin.

A model for the occurrence of oceanic gas hydrates assumes that for deep-sea sediment, methane is formed by decomposition of organic matter within the zone of gas hydrate stability, and that there is no significant contribution from upward migrating methane. Under these circumstances, the possible

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methane concentration is limited by the original concentration of methane precursors. The immediate methane precursor is dissolved carbon dioxide, which is reduced to methane through anaerobic respiration by microbial methanogenesis. The primary precursor is organic matter which ultimately limits the amount of gas hydrate that can form. The conversion of organic matter to carbon dioxide to methane (and methane hydrate) is proportional to the initial organic matter content. The total amount of carbon sequestered in the shallow geosphere as methane hydrates is estimated to be about 10,000 Gt (gigaton = 10^{15} g), a value which is considered to be a lower limit.

INTRODUCTION

Outer continental margins that rim the Pacific Basin may contain vast quantities of natural gas trapped in or beneath crystalline substances known as gas hydrates. These substances, which occupy the open spaces of sediment, are made up of rigid frameworks of water molecules in which natural gas is trapped and effectively condensed. Gas hydrates form under specific pressure-temperature conditions that are met in oceanic sediment at depths up to about 1,100 m below the sea floor and in water depths greater than about 300 m (Kvenvolden and Barnard, 1983a). The exact location of gas hydrates in oceanic sediment is further influenced by gas and water chemistries. The upper limit of the gas hydrate zone in oceanic sediment is ordinarily the sea floor; gas hydrates have been recovered within 6.5 m of the sea floor in sediment of the Black Sea (Yefremova and Zhizhchenko, 1975) and the Gulf of Mexico (Brooks and others, 1986).

The appropriate pressure-temperature conditions under which gas hydrates can theoretically form in a pure-methane and pure-water system are shown in figure 1; however, gas in continental-margin sediment is not pure methane, and pore water usually contains some salt. Impurities in the methane include small concentrations of ethane and hydrocarbon gases of higher molecular weight, as well as CO_2 (McIver, 1974; Claypool and others, 1973). The additional components in the gas mixture shift the phase boundary to the right in figure 1, whereas impurities in the water such as salts shift the boundary to the left. Thus, the resulting shifts in the equilibrium phase boundary tend to cancel each other, and unless the gas composition and salinity are known, a pure-methane and pure-water system provides the best first approximation for establishing the pressure-temperature relation of naturally occurring gas hydrates (Claypool and Kaplan, 1974). According to the phase diagram (fig. 1) gas hydrates are possible where pressures are greater than about 30 atmospheres with corresponding temperatures greater than 0°C. In sediments, subsurface temperatures, which are dependent on geothermal gradients, and lithostatic and hydrostatic pressures control the depth range in which the gas hydrates can exist. The base of the gas hydrate zone coincides with a pressure-temperature boundary that represents the maximum depth at which the gas hydrate is stable.

An additional requirement for natural gas hydrate formation is that large volumes of methane be present to stabilize the gas-hydrate structure. Up to about 164 volumes of methane can be present for each equivalent volume of water (Davidson and others, 1978). Only under special geological

10
50
100
METHANE
GAS+ICE
METHANE
HYDRATE+
ICE+GAS
METHANE
GAS+WATER
500
+ NaCl, N₂   + CO₂, C₂H₆,
              H₂S, C₃H₈
1000
METHANE
HYDRATE+
WATER+GAS
5000

Ice-water phase boundary
Hydrate-gas phase boundary

DEPTH (METERS)
PRESSURE (ATM)
TEMPERATURE (° C)

10000   -10   0   10   20   30   40

1
5
10
50
100
500
1000
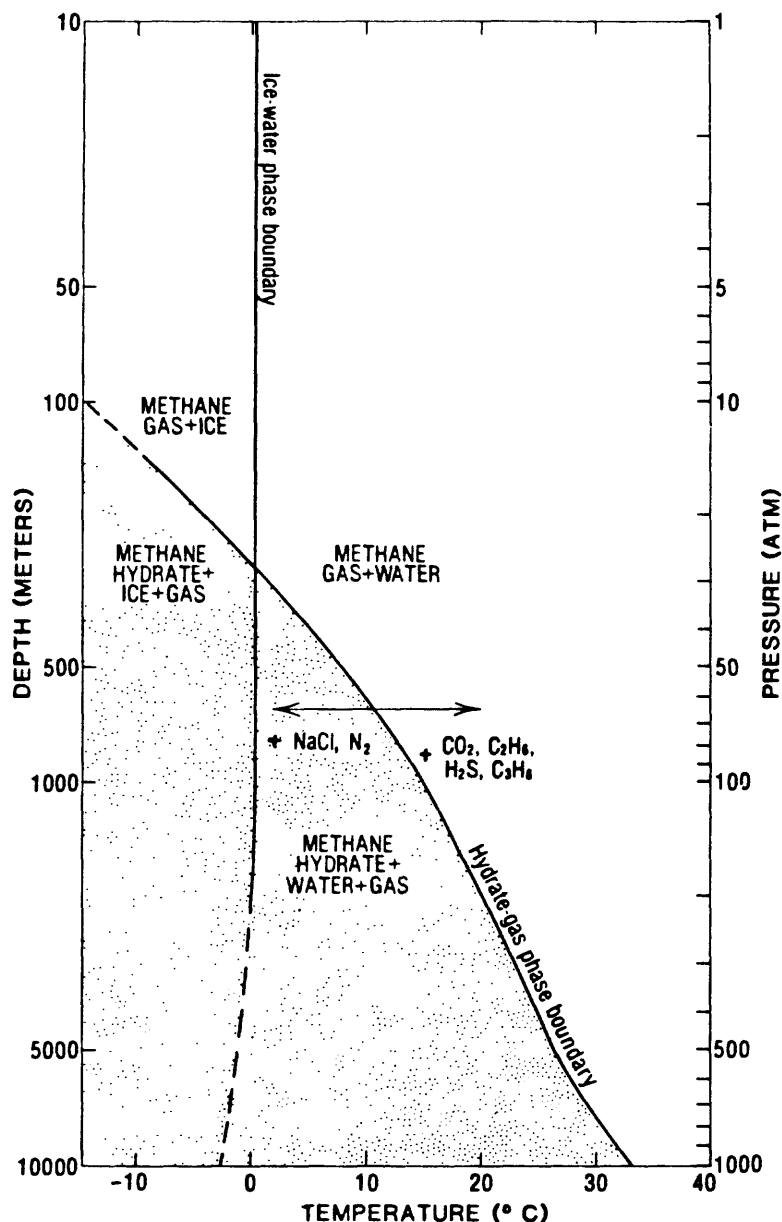
Figure 1. Phase diagram showing boundary between free methane gas (no
pattern) and methane hydrate (pattern) for a pure-water and pure-
methane system. Addition of NaCl to water shifts the hydrate-gas
phase boundary to the left. Adding CO_2, H_2S, ethane, and propane
to methane shifts that boundary to the right, increasing the region
of the gas-hydrate stability field. For natural gas in marine
sediment, the shifts are of similar magnitude but in opposite
directions. The effects approximately cancel each other. Other
possible factors affecting the position of the boundary, such as
the effects of clays, are not considered. Thus, the boundary for a
pure-water and pure-methane system provides a reasonable estimate
of the pressure-temperature conditions under which natural gas
hydrates, composed mainly of methane, will be stable on continental
margins (Claypool and Kaplan, 1974). Depth scale assumes
lithostatic and hydrostatic pressure gradients of 0.1 atm/m.
Redrawn after Katz and others, (1959) and modified from Kvenvolden
and McMenamin (1980).

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circumstances involving high rates of formation and entrapment can methane approaching this large amount be found. The source of methane for gas-hydrate formation may be either microbial or thermogenic. Microbial methane results from the breakdown of organic matter by methanogens, usually in shallow sediment; thermogenic methane comes from the thermal alteration of organic matter in sedimentary rock at a much greater depth. In either case organic matter must be present. Large amounts of organic matter can be expected to accumulate in continental-margin settings but usually not within distal sediment out in the ocean basins; therefore, gas hydrates are likely to be confined to sediment deposited on continental slopes and rises at the margins of ocean basins.

The identification of gas hydrates in oceanic sediment has been based mainly on the appearance of an anomalous acoustic reflector on marine seismic records (Shipley and others, 1979). This reflector correlates with the base of the gas hydrate zone and approximately parallels the sea floor. If the geothermal gradient is known, the depths at which this reflector appears can be predicted on the basis of the pressure-temperature stability field for gas hydrates (fig. 1). This bottom-simulating reflector (BSR) probably results from the velocity contrast between sediment containing gas hydrates (higher velocity) and the underlying sediment (lower velocity). The lower velocity is believed to result from the absence of gas hydrate and the possible presence of free gas. BSRs attributed to gas hydrates have been observed on marine seismic records from the Blake Outer Ridge offshore Florida (Stoll and others, 1971; Ewing and Hollister, 1972; Shipley and others, 1979; Dillon and others, 1980; Paull and Dillon, 1981, Markl and Bryan, 1983), offshore North Carolina (Popenoe and others, 1982), and offshore New Jersey (Tucholke and others, 1977). Shipley and others (1979) also described BSRs attributable to gas hydrates in sediments in the western Gulf of Mexico, off the northern coasts of Colombia and Panama, and along the Pacific Coast of Central America from Panama to Acapulco, Mexico. That gas hydrates are present in sediments at some of these areas has been confirmed by drilling and sampling in the Blake Outer Ridge (Kvenvolden and Barnard, 1983b), offshore Guatemala (Harrison and Curiale, 1982; Kvenvolden and McDonald, 1985), and offshore Mexico (Shipley and Didyk, 1982). BSRs have also been observed offshore Peru (Shepard, 1979; von Huene and others, 1985), and drilling has confirmed the presence of gas hydrates there.

Not all BSRs can be related to the presence of gas hydrates. In some areas, these acoustic features may also result from temperature-controlled diagenetic effects. During Deep Sea Drilling Project (DSDP) Leg 19, Scholl and Creager (1973) noted seismic reflectors that tend to parallel the sea floor in some Bering Sea sediments draped on the Umnak Plateau, and they first used the acronym BSR for the bottom-simulating reflector. At two drill sites, 184 and 185, the reflector was penetrated. Although some methane was detected in sediment at site 185, they saw no evidence for gas hydrates. Scholl and Creager (1973) attribute this reflector to a lithologic transition from hemipelagic diatom ooze to indurated claystone. Hein and others (1978) confirmed that opal-A is transformed to opal-CT at the depth of the BSR in the Bering Sea sediment. Thus, there are two types of BSRs, one indicating the base of the gas hydrate zone and the other signaling a diagenetic boundary (Marlow and others, 1981). For the remainder of this paper, BSR will refer,

unless otherwise indicated, to the anomalous acoustic reflector associated with gas hydrate occurrence. This reflector approximately parallels the sea floor at a depth that can be predicted from the physical-chemical properties of gas hydrates. The reflector is generally characterized by a polarity reversal and a large reflection coefficient (Shipley and others, 1979).

WORLDWIDE OCCURRENCES OF OCEANIC GAS HYDRATES

Kvenvolden and Barnard (1983a) described 23 offshore localities around the world where gas hydrates are known or inferred to occur in oceanic sediment. Additional offshore localities where gas hydrates are expected include the Canadian Beaufort Sea (Neave and others, 1978), Beaufort Sea shelf (Judge, 1984), Sverdrup Basin (Judge, 1982), off North Island, New Zealand (Katz, 1981, 1982), off Norway (Bugge, 1987; Kvenvolden and others, in press), and off Peru (Kvenvolden and Kastner, in preparation). Locations of these gas hydrate occurrences are shown in figure 2 and identified on table 1. This report focuses on the gas hydrates in outer continental margins of the Pacific and Arctic Oceans.

Circum-Pacific Occurrences

Central America (Middle America Trench)

Shipley and others (1979) noted that marine seismic-reflection records across the continental slopes of Panama, Costa Rica, Nicaragua, Guatemala, and Mexico commonly, but not always, have BSRs, which they attributed to gas hydrates. Figure 3 illustrates one well-developed BSR on a marine seismic-reflection profile recorded over the landward slope of the Middle America Trench offshore from Mexico. This BSR behaves as predicted for a reflector from the base of gas hydrates in that it approximately parallels the sea floor, and the subbottom depth of the reflector increases with increasing water depth. Information on the seismically inferred gas hydrates of the Circum-Pacific margin including occurrences offshore from Central America is summarized in table 2 and figure 4. Where gas-hydrate-related BSRs have been observed, estimates of geothermal gradients have been made (Shipley et al., 1979; Yamano et al., 1982). Along the Middle America Trench, the average geothermal gradients range from 22°C/km off Mexico to 66°C/km off Panama (table 2).

In 1979, coring on three DSDP legs recovered gas hydrates off Central America. Leg 66 drilled the landward slope of the Middle America Trench in an area near Mexico (fig. 5) where BSRs are common (Watkins and others, 1982). Solid gas hydrates were recovered from three holes (Shipley and Didyk, 1982); these occurred as icelike inclusions or, more commonly, as icelike substances occupying pore space and cementing volcanic ash and fine sand (table 3). A large amount of methane was released during decomposition of the icelike material, demonstrating that these substances were indeed gas hydrates.

On Leg 67, further drilling was done into the landward slope of the Middle America Trench near Guatemala (fig. 5) along a transect where no BSRs were originally observed (Aubouin, von Huene, and others, 1982); later
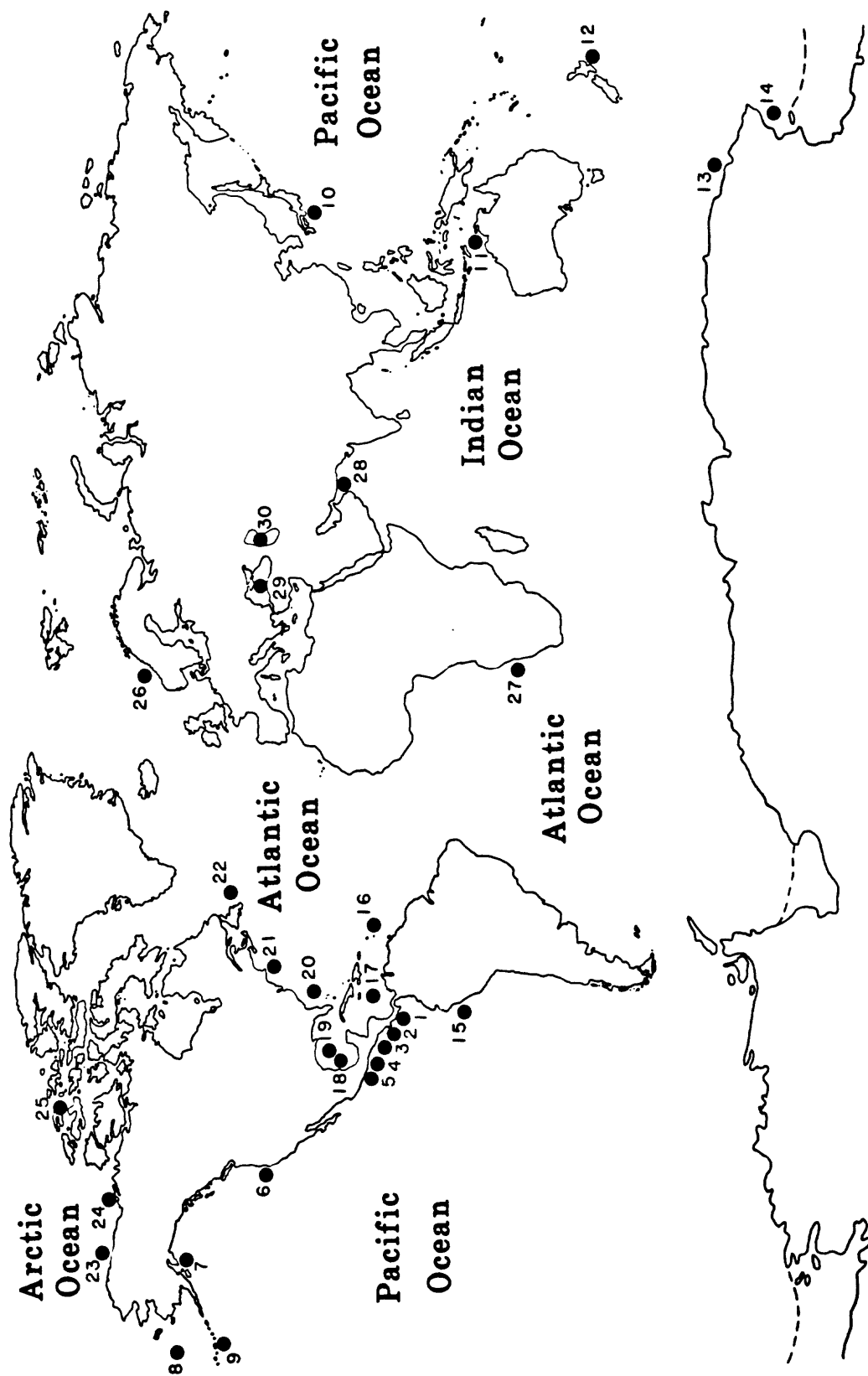
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Figure 2. The Earth showing locations of known and inferred gas hydrates in sediment of continental margins (●).

Table 1. Gas hydrates in oceanic sediment

| Designation on Figure 2	Location	Evidence	Reference
1.	Pacific Ocean off Panama	BSR	Shipley and others (1979)
2.	Middle America Trench off Costa Rica	BSR	Shipley and others (1979)
		Samples	Kvenvolden and McDonald (1985)
3.	Middle America Trench off Nicaragua	BSR	Shipley and others (1979)
4.	Middle America Trench off Guatemala	BSR	Shipley and others (1979)
		Samples	Harrison and Curiale (1982)
		Samples	Kvenvolden and McDonald (1985)
5.	Middle America Trench off Mexico	BSR	Shipley and others (1979)
6.	Eel River Basin off California	BSR	Field and Kvenvolden (1985)
7.	Eastern Aleutian Trench off Alaska	BSR	Kvenvolden and von Huene (1985)
8.	Beringian Margin off Alaska	BSR	Marlow and others (1981)
9.	Middle Aleutian Trench off Alaska	BSR	McCarthy and others (1984)
10.	Nankai Trough off Japan	BSR	Aoki and others (1983)
11.	Timor Trough off Australia	Gas	McKirdy and Cook (1980)
12.	Hikurangi Trough off New Zealand	BSR	Katz (1981)
13.	Wilkes Land Margin off Antarctica	BSR	Kvenvolden and others (1987)
14.	Western Ross Sea off Antarctica	Gas	McIver (1975)
15.	Peru-Chile Trench off Peru	BSR	Shepard (1979)
		Samples	Kvenvolden and Kastner (in prep.)
16.	Barbados Ridge Complex off Barbados	BSR	Ladd and others (1982)
17.	Colombia Basin off Panama and Colombia	BSR	Shipley and others (1979)
18.	Western Gulf of Mexico off Mexico	BSR	Shipley and others (1979); Hedberg (1980)
19.	Gulf of Mexico off southern USA	Samples	Brooks and others (1984)
20.	Blake Outer Ridge off southeastern USA	BSR	Markl and others (1970); Shipley and others (1979)
		Samples	Kvenvolden and Barnard (1983b)
21.	Continental Rise off eastern USA	BSR	Tucholke and others (1977)
22.	Labrador Shelf off Newfoundland	BSR	Taylor and others (1979)
23.	Beaufort Sea off Alaska	BSR	Grantz and others (1976)
24.	Beaufort Sea off Canada	Logs	Weaver and Stewart (1982)
25.	Sverdrup Basin off Canada	Logs	Judge (1982)
26.	Continental Slope off western Norway	BSR	Bugge and others (1987)
27.	Continental Slope off southwest Africa	Slides, Slumps	Summerhays and others (1979)
28.	Makran Margin, Gulf of Oman	BSR	White (1979)
29.	Black Sea, USSR	Samples	Yefremova and Zhizhchenko (1975)
30.	Caspian Sea, USSR	Samples	Yefremova and Gritchina (1981)
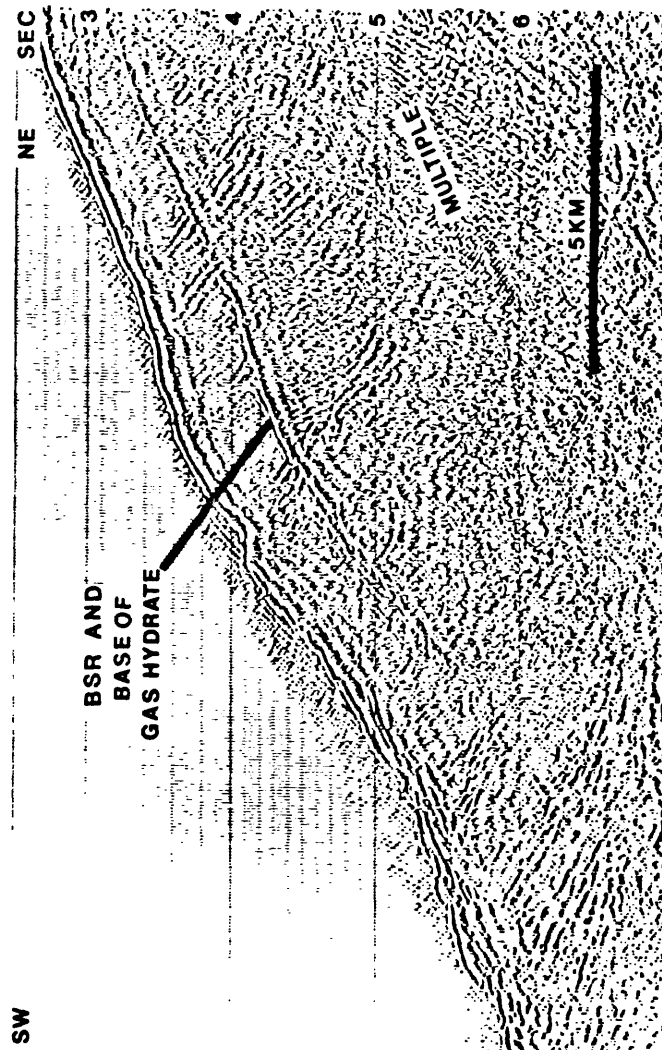
Figure 3. A 24-fold multichannel seismic-reflection profile of the landward slope of the Middle America Trench offshore from Mexico. The bottom-simulating-reflector (BSR) at the base of the inferred gas hydrate approximately follows the topography of the seafloor and deepens with increasing water depth (from Shipley and others, 1979).

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Table 2. Seismically inferred gas hydrates of the Circum-Pacific Margin

| Location[1] | Water Depth(m) | Subbottom Depth of BSR(m) | Geothermal Gradient($^\circ$C/km)[2] | | | References |
			min	max	ave	
Central America						
Panama	1,875-2,100[3]	380-475[4]	66	82	77	Shipley and others (1979)
						Yamano and others (1982)
Costa Rica	750-1,350[3]	290-430[4]	30	44	35	Shipley and others (1979)
						Yamano and others (1982)
Nicaragua	800-2,400	190-570[4]	30	35	33	Shipley and others (1979)
						Yamano and others (1982)
Guatemala	1,875-2,250[3]	570[4]	27	32	30	von Huene and others (1982)
Mexico	1,950-3,900[3]	570-950[4]	22	31	28	Shipley and others (1979)
						Yamano and others (1982)
Western U.S.	725-2,800	135-315	55	66	55	Field and Kvenvolden (1985)
South Alaska	500-2,300	300-800	31	24	30	MacLeod (1982)
						Kvenvolden and von Huene (1985)
Aleutian Islands	4,500	1,000	23	21	22	McCarthy and others (1984)
Bering Sea Margin	500-3,000	200-500	Not determined			Cooper and others (in press)
Japan	2,535-3,850	465-380	42	66	54	Yamano and others (1982)
New Zealand	1,000-2,500	380-760[4]	20 (by inference)			Katz (1982)
Antarctica	1,000-2,300	650-400[5]	32	47	39	Kvenvolden and others (1987)
Peru	800-3,200	350-570[4]	Not determined			Shepard (1979)

1 Locations refer to offshore areas adjacent to the named places.

2 Geothermal gradients were calculated by the referenced authors using water depths and subbottom depths of BSKs.

3 Estimated using a water veolocity of 1,500 m/s.

4 Estimated using a sediment velocity of 1,900 m/s.

5 Estimated using a sediment velocity of 1,730 m/s.
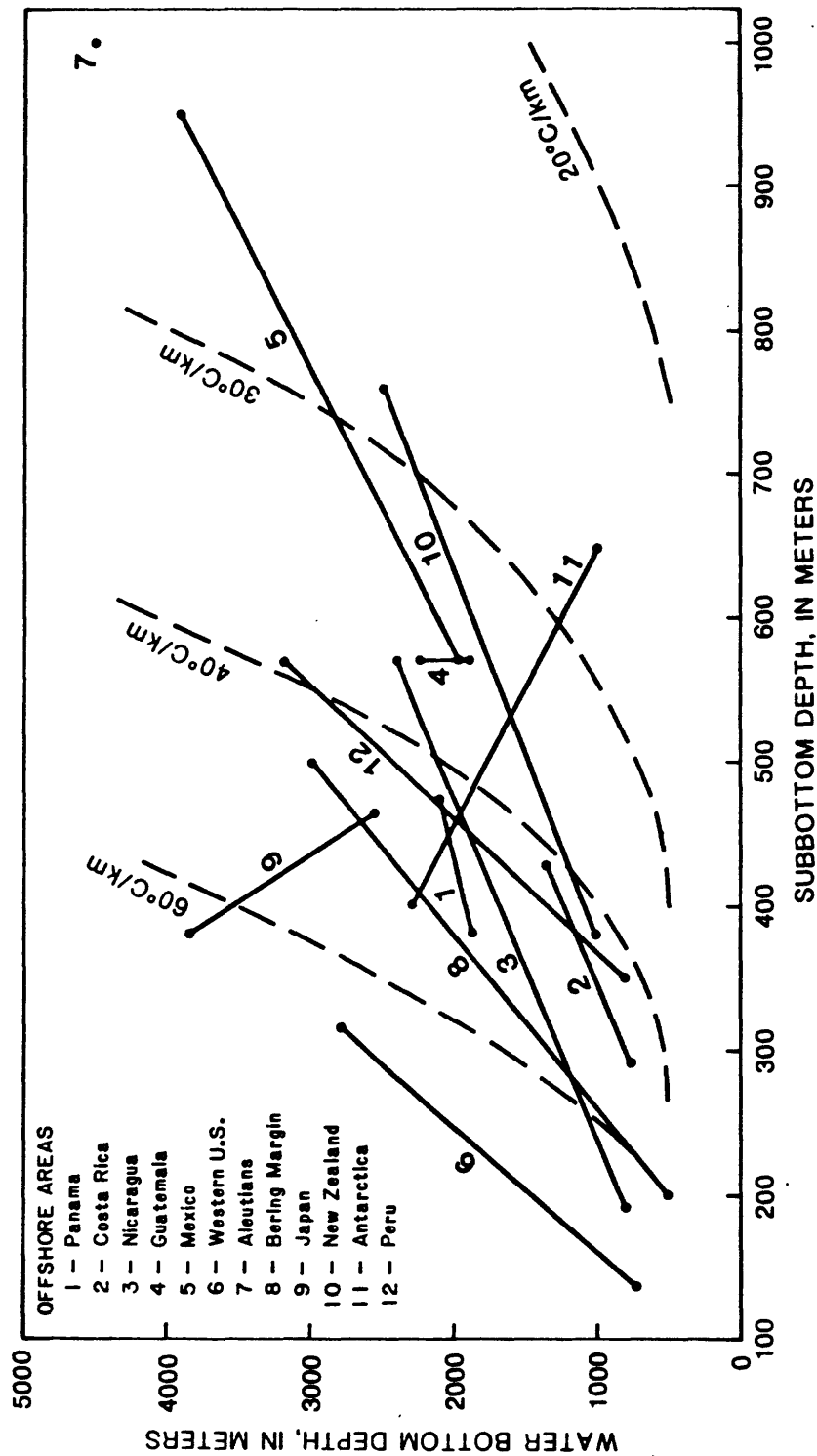
Figure 4. Graph showing water-bottom depths and subbottom depths to BSRs for regions of the Circum-Pacific margin. Data are from table 2. Lines connect maximum and minimum values from each area. Note that subbottom depths of BSRs normally increase with increasing water depths except for areas off Japan and Antarctica where geothermal gradients are believed to change laterally and increase in the direction of deepening water. Dashed curves represent geothermal gradients calculated from figure 1 and based on assumed bottom-water temperature of 2 °C. (Kvenvolden and Cooper, in press).
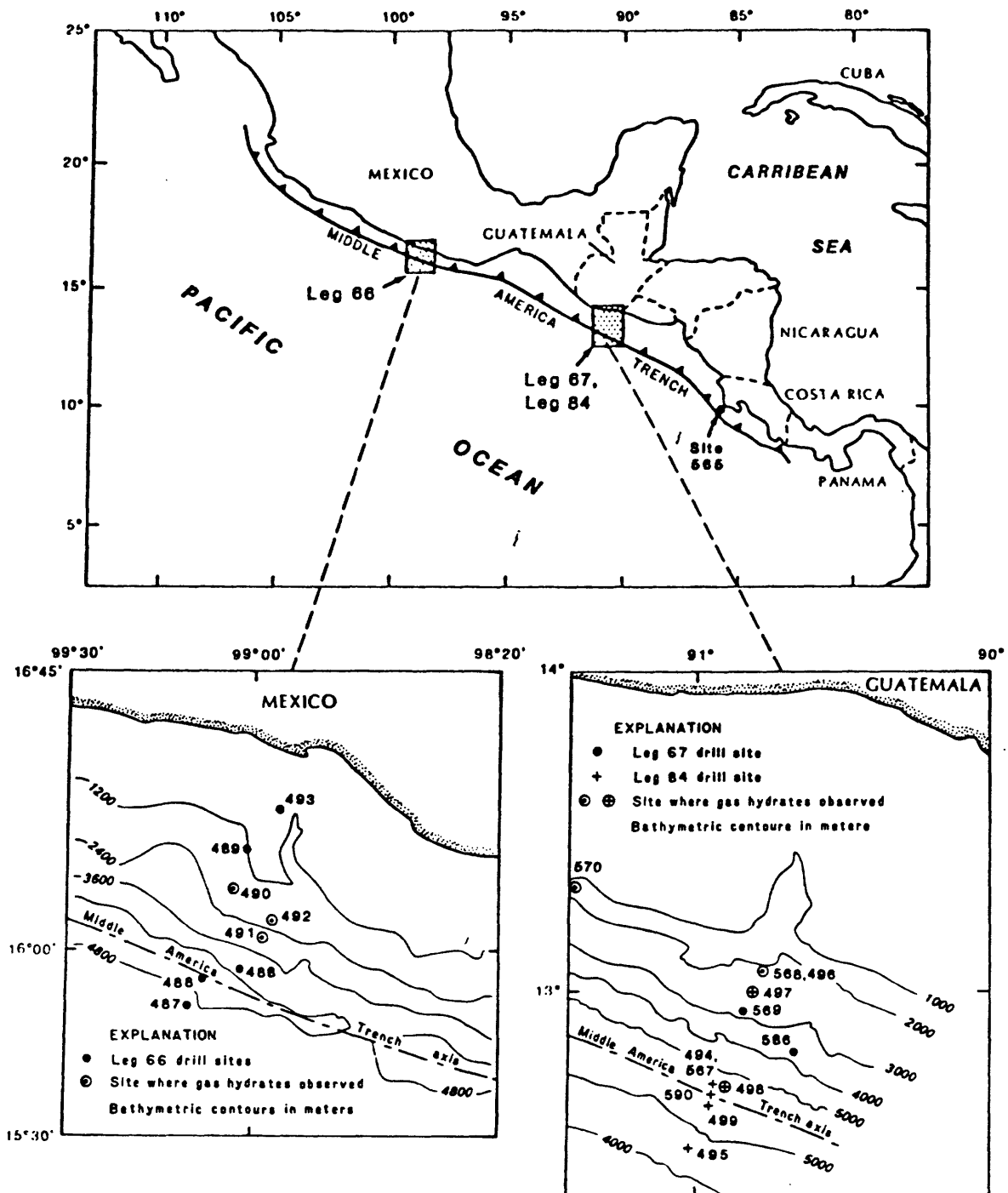
Figure 5. Map showing locations of DSDP sites of Legs 66, 67, and 84 on the landward slope of the Middle America Tranch where gas hydrates were recovered during drilling. Legs 67 and 84 were drilled in the same region except for Site 565 which was drilled on Leg 84 offshore from Costa Rica (Kvenvolden and Cooper, in press).

Table 3. Description of gas hydrates recovered by DSDP off Central America

| Leg[1]	Site	Water Depth(m)	Subbottom Depth(m)	Description
66	490	1761	140	Inclusion in mud
66	490	1761	146	Cementing ash
66	490	1761	167	Cementing ash
66	490	1761	365	Cementing ash
66	491	2883	89	Inclusion in mud
66	491	2883	163	Cementing sand
66	491	2883	168	Inclusion in mud
66	492	1935	141	Cementing ash
66	492	1935	170	Cementing ash
67	497	2350	368	Inclusion found in core catcher
67	498	5480	310	Cementing vitric sand
84	565	3396	285	Inclusions in mud
84	565	3430	310	Inclusion and associated with sand
84	568	2434	404	Inclusion is fractured mudstone
84	570	1910	192	Cementing laminated ash
84	570	1965	246	Inclusion in fractured mudstone
84	570	1968	249	Massive gas hydrate 1.05 cm long
84	570	1982	264	Inclusion in fractured mudstone
84	570	1991	273	Inclusion in fractured mudstone
84	570	2021	303	Cementing ash
84	570	2055	338	Cementing sand

[1]Leg 66, Shipley and Didyk (1982); Leg 67, Harrison and Curiale (1982); Leg 84, Kvenvolden and McDonald (1985).

reprocessing of the seismic records did, however, reveal a weak BSR there (von Huene and others, 1982). On the other hand, a seismic line about 10 nautical miles (18 km) west of the drill sites showed a well-defined BSR (Ladd and others, 1982). At Site 497 a piece of solid gas hydrate was recovered from a core catcher near the bottom of the hole. Gas hydrates cementing vitric sands were recovered near the bottom of a hole at Site 498 (table 2).

In 1982, DSDP Leg 84 again drilled into the landward slope of the Middle America Trench (fig. 5) at five sites (566 through 570) near Guatemala and at one site (565) off Costa Rica (von Huene, Aubouin, and others, 1985). A weak BSR occurs on seismic records at Site 568 (von Huene and others, 1982). Gas hydrates recovered at three sites (565, 568, and 570) appeared as solid pieces of white, icelike material occupying fractures in mudstone, as rapidly outgassing, coarse-grained sediment, and, at site 570, as a core of massive gas hydrate (table 3).

Organic geochemical studies, particularly on samples recovered on Leg 84, have concluded that the methane in the gas hydrates is microbial based on the carbon isotopic relationships and molecular compositions of the natural gas mixtures (Kvenvolden and others, 1984; Kvenvolden and McDonald, 1985; Claypool and others, 1985). Inorganic geochemical studies of pore waters in sediment associated with gas hydrates on Leg 67 showed that the salinity and chloride contents of these pore waters decrease with increasing depths (Hesse and Harrison, 1981; Harrison and others, 1982); these observations were further documented on Leg 84 (Kvenvolden and McDonald, 1985; Hesse and others, 1985). Gas hydrates decompose during drilling, thereby releasing freshwater (and methane) into the surrounding sediment and thus decreasing the salinity of the sediment pore water.

Western Conterminous United States

A well-defined BSR, inferred on the basis of its depth and pervasiveness to be associated with gas hydrates, has been identified on marine seismic-reflection profiles recorded from the continental margin of northern California (fig. 6) by Field and others (1980), Biddle and Seely (1983), and Field and Kvenvolden (1985). The BSR (fig. 7) lies at subsurface depths of 135 to 315 m beneath the Klamath Plateau off northernmost California and probably southernmost Oregon in water depths of about 725 to at least 2,800 m (table 2). The BSR deepens with increasing water depth (fig. 4), and the gas hydrate apparently covers an area of at least 3,000 km^2. The geothermal gradient in the area, as calculated from BSRs, averages about 55°C/km (table 2). This acoustically inferred gas hydrate is the only reported occurrence in the continental margin of the western conterminous United States. Recent piston coring in this region has recovered gas hydrates from the near-surface sediment (J.M. Brooks, oral communication, 1987).

South Alaska and the Aleutian Islands (Aleutian Trench)

In the Gulf of Alaska (fig. 8), BSRs have been observed on seismic-reflection profiles across the upper continental slope bordering the Aleutian Trench southeast of Kodiak Island (Kvenvolden and von Huene, 1985). In this area, BSRs were observed at subbottom depths of 570 to 670 m in water depths

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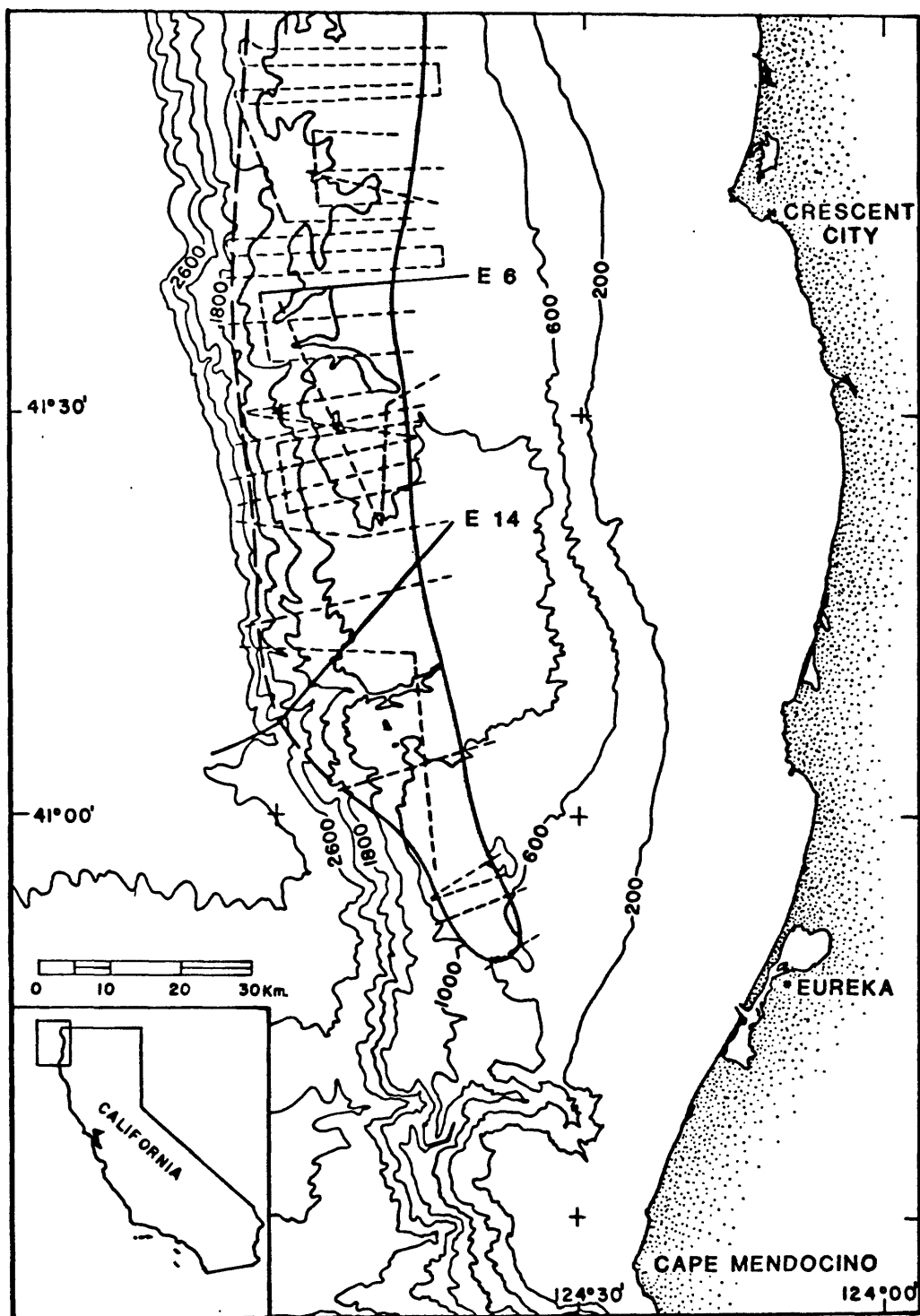
Figure 6. Map of the northern California continental margin showing
tracklines of seismic reflection profiles used to delineate the
area of gas hydrates based on the occurrence of BSRs. The area
boundary is dashed on the seaward side to indicate poor control.
The area probably extends north offshore from Oregon. The
contour interval is 400 m starting with the 200 m (shelf edge)
isobath. Redrawn from Field and Kvenvolden (1985).

17
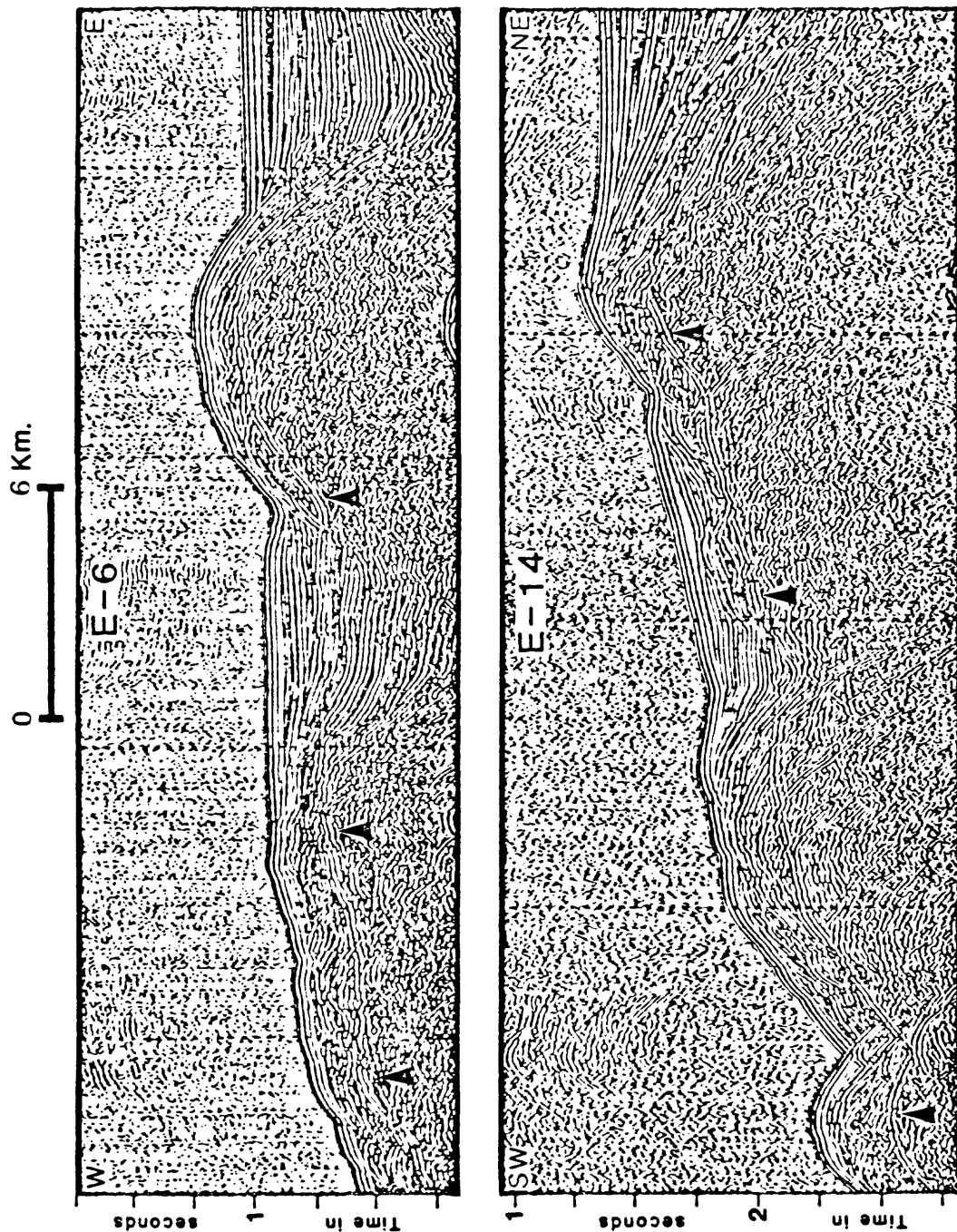
Figure 7. Single channel, high resolution, seismic reflection profiles illustrating the BSR (arrows) beneath the Klamath Plateau offshore from northern California. Profile locations are shown in figure 6 (Field and Kvenvolden, 1985).

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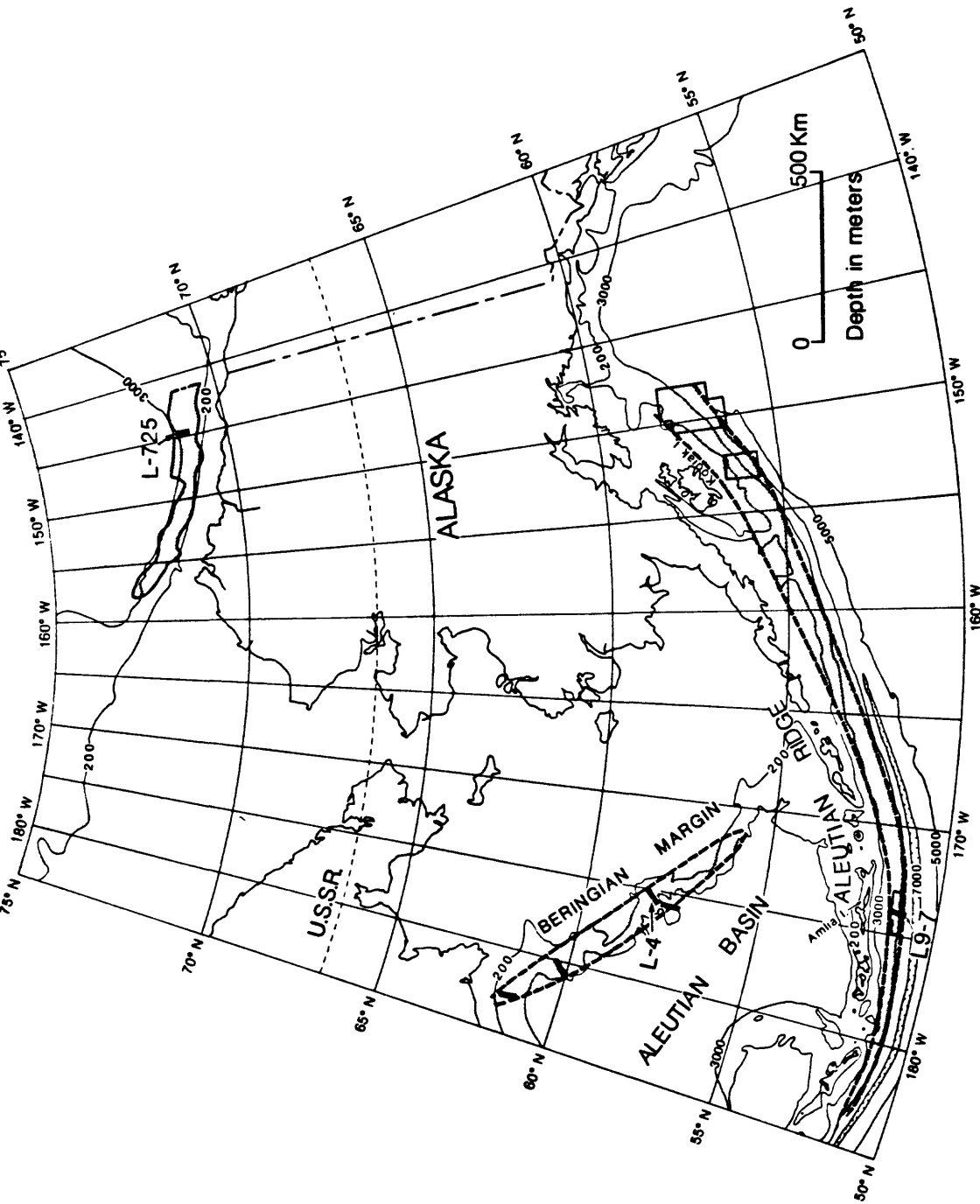
Figure 8. Map showing the locations of gas hydrates (areas enclosed by dashed and solid lines) offshore from Alaska as inferred from marine seismic reflection profiles and the occurrences of BSRs. The extent of gas hydrate occurrence along the Beringian Margin has been assumed from observations of BSRs on four seismic profiles and the general physiography of this margin. Likewise, the occurrence of gas hydrates south of the Aleutian Ridge has been interpolated from seismic information obtained near Kodiak Island on the east and near Amila Island on the west.

of 1,600 to 2,300 m (table 2). MacLeod (1982) also identified BSRs in sediments of the Gulf of Alaska, but he did not give specific locations; he showed that subbottom depths of the BSRs ranged from about 300 to 800 m for water depths of about 500 to 2,300 m. In this area the average geothermal gradient is calculated to be about 30°C/km (table 1).

Evidence for gas hydrates has been noted in sediments of the Aleutian terrace, which borders the Pacific side of the Aleutian Ridge (Scholl and others, 1983; McCarthy and others, 1984). Seismic-reflection profiles crossing the southern flank of the Atka basin, south of Amlia Island, commonly show BSRs at subbottom depths of about 1,000 m in water about 4,500 m deep (fig. 9); the geothermal gradient here is estimated to be about 22°C/km (table 2). DSDP drilling at Site 186 near the Atka basin encountered very high concentrations of methane, but not gas hydrates (Creager, Scholl, and others, 1973). The high methane concentrations may result from the decomposition of gas hydrates during drilling, and the BSRs may mark the base of the zone of gas hydrate occurrence. On figure 8, we have extrapolated the area of possible occurrence of gas hydrates along the south flank of the Aleutian Ridge based on the similarity of geologic and tectonic framework between the areas where the BSRs have been identified.

Beringian Margin

BSRs have been observed on marine seismic-reflection profiles recorded in the Bering Sea on the continental slope and rise of the Beringian margin (Marlow and others, 1981). In this area, BSRs have been related to two sources--gas hydrates and diagenetic alteration of siliceous sediments. Cooper and others (in press) have identified two BSRs which often occur simultaneously; for example, in figure 10 the more shallow of the two BSRs (BSR-GH) generally lies at 0.3 to 0.6 s subsurface and marks the base of the zone of gas hydrates. The deeper BSR (BSR-DB) is usually found at 0.9 to 1.2 s subbottom and is thought to follow the silica-diagenetic boundary between overlying and partially unconsolidated opal-A-rich sediment and underlying more indurated mudstone rich in opal-CT. The characteristics of these BSRs as documented by Cooper and others (in press) differ significantly (table 4).

The shallow BSR (BSR-GH) is of most importance to our discussion of gas hydrates, but knowledge of both types of BSRs is necessary to prevent misinterpretation of seismic records. The BSRs associated with gas hydrates of the Beringian margin are usually weak reflectors that are most easily observed beneath eroded knolls and areas of deformed strata underlying the continental slope and rise at water depths of 500 to 3,000 m. On figure 8, we have extrapolated the area of possible occurrence of seismically inferred gas hydrates along part of the Beringian margin based on these marine seismic data.

Japan (Nankai Trough)

On the western side of the Pacific Basin (fig. 2, location 10), gas hydrates are believed to occur in sediments of the landward slope of the Nankai Trough near the Japanese islands of Kyushu and Shikoku (Aoki and others, 1983). Marine seismic-reflection records show a strong BSR, averaging

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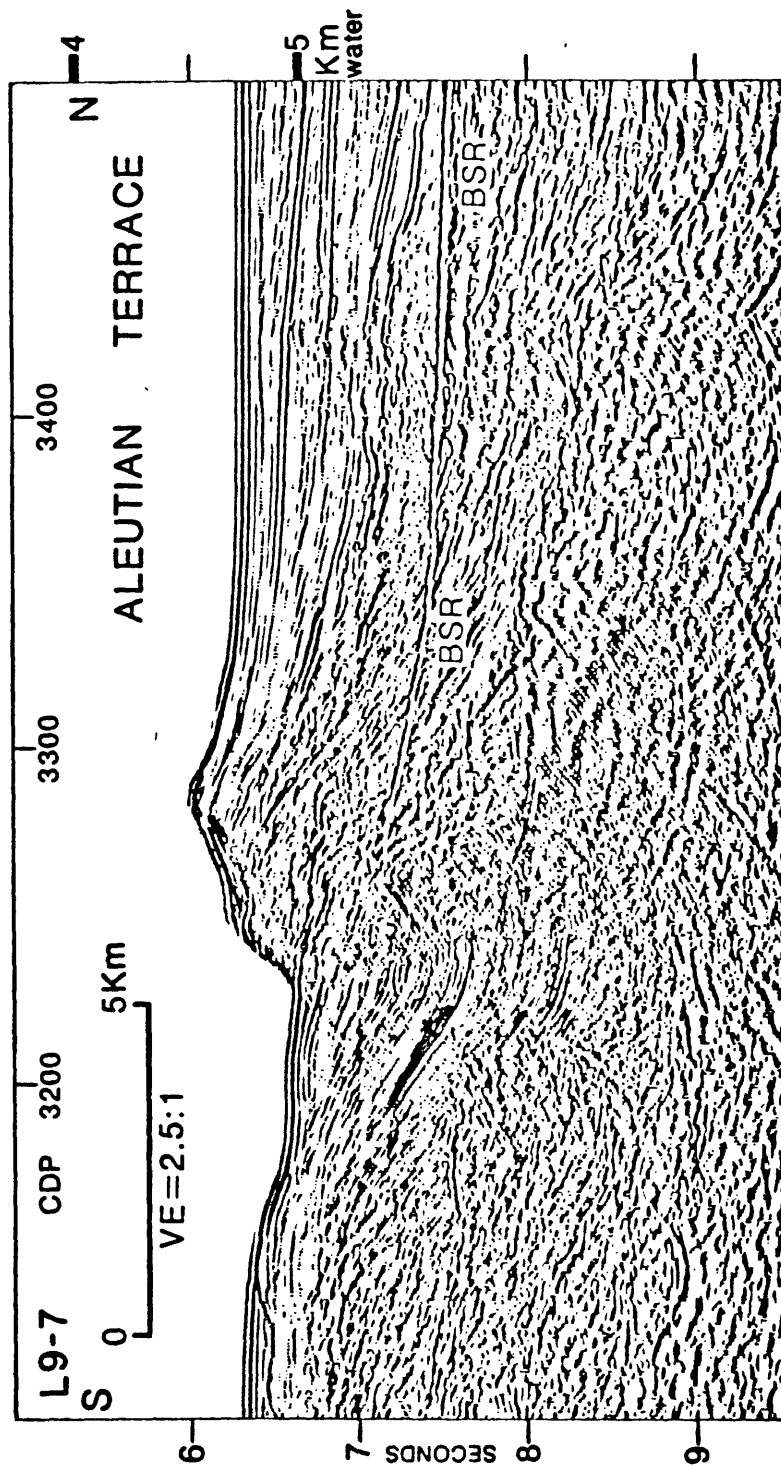
Figure 9. Segment of multichannel reflection profile (L9-7) on the slope of the Aleutian Terrace south of the Aleutian Ridge (fig. 8). The reflector (BSR), inferred to be the base of the gas hydrate zone, is noted. Modified from McCarthy and others (1984).

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Figure 10. Seismic-reflection profile L4 across the Beringian Margin continental slope (fig. 8). The profile shows two BSRs, one at the base of an inferred gas hydrate (BSR-GH) and one at a diagenetic boundary (BSR-DB) (Cooper and others, in press).

Table 4. Characteristics of bottom simulating reflectors (BSRs) found for
sediments of the Bering Sea (Kvenvolden and Cooper, in press)

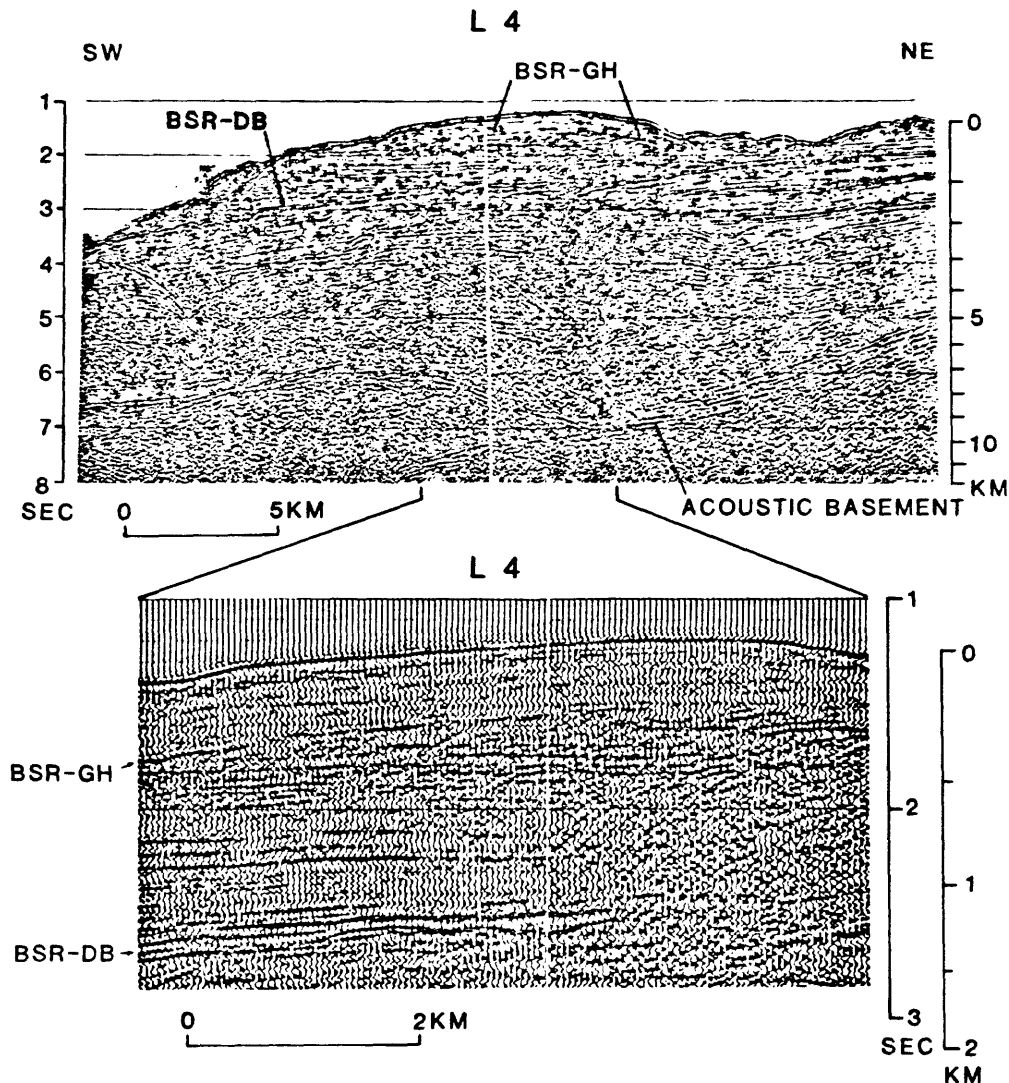| BSR-GH (Gas Hydrate)	BSR-DB (Diagenetic Boundary)
I. General	
A. Description: Reflection that marks the base of a gas hydrate zone - the transition from gas hydrate to free gas.	Reflector that marks a silica diagenetic boundary between overlying opal-rich (opal-A) sediment to underlying, indurated, cristobalite-bearing (opal-CT) mudstone.
B. Areal Distribution: Presumed regional in extent, in water depths greater than 500 m. Identifiable most easily in areas with bathymetric relief and undeformed sediment.	Regional extent in deep-water (>200 m) areas where siliceous diatomaceous sediments are found or are presumed to be present.
C. Controlling factors: Sufficient gas concentrations and suitable pressure-temperature conditions.	Appropriate conditions (pressure, temperature, geochemistry) for diagenesis of biogenic to crystalline silica.
II. Geophysical Signature	
A. Geometry: Reflector that mimics seafloor bathymetry and commonly cuts across other layered sub-seafloor reflectors.	Same description as BSR-GH but found at greater sub-seafloor depths.
B. Sub-seafloor depth: Depth to BSR-GH INCREASES with increasing water depth - usually found at 200-500 m (0.3-0.6 s) sub-seafloor.	Depth to BSR-DB DECREASES or is the same with increasing water depth - usually found 700-1000 m (0.9-1.2 s) sub-seafloor.
C. Sub-seafloor velocity: Higher than typical sediment velocity ABOVE the BSR-GH.	Higher than typical sediment velocity BELOW the BSR-DB.
D. Phase of BSR reflector: INVERTED (negative) phase.	NORMAL (positive) phase.
E. Amplitude of BSR reflector: Highly variable, commonly faint in multi-channel seismic data. Hydrate zone above BSR-GH often associated with diffuse and faint reflectors.	Usually large amplitude and easily identifiable except where BSR-DB is conformable with other reflectors.
III. Significance for Hydrocarbon Distribution	
A. General: Gas hydrate zone may (1) contain significant included gas and (2) act as a seal that prevents upward migration of hydrocarbons.	Diagenetic boundary (1) has a major decrease in porosity and permeability beneath the boundary and (2) may influence migration path and hydrocarbon trapping.
B. Traps: Hydrocarbons (liquid? and gas) may be trapped and accumulate beneath impermeable gas hydrate zone.	In areas of bathymetric relief, laterally migrating hydrocarbons may be trapped against diagenetic boundary in porous interbedded strata.
C. Migration of hydrocarbons: Possible lateral migration of hydrocarbons along base of gas hydrate zone.	Possible migration beneath BSR-DB via fractures in highly indurated rocks or in unaltered strata originally poor in biogenic silica.
D. Operational hazards: Pockets of overpressured gas trapped beneath gas hydrate zone.	BSR-DB may form a slip surface above which sediment bodies may slide.

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about 0.5 s below the sea bottom, which is thought to correspond with the base of the zone of gas hydrates (table 2). The BSRs show negative reflection polarities, as would be expected for gas hydrates; however, the BSRs do not increase in subbottom depth with increasing water depth as theoretically required by pressure-temperature constraints on gas hydrate occurrence (fig. 4). Instead, the reflectors become more shallow in the deeper water, possibly as a result of increasing heat flow and, consequently, increasing geothermal gradients down slope toward the Nankai Trough (Yamano and others, 1982).

Australia (Timor Trough)

McKirdy and Cook (1980) suggested that gas hydrates may account for the higher-than-average concentrations of methane in sediment at DSDP Site 262, located on the axis of the Timor Trough northeast of Australia in water 2,315 m deep (fig. 2, location 11). They based their conclusions on consideration of unusual relationships between alkalinity and salinity profiles and the high amounts of methane they observed. Pore-water salinity at Site 262 increases significantly with increasing depth, an effect attributed to an influx of highly saline water from underlying or nearby evaporite deposits. This influx of saline water would mask any pore water freshening due to the presence of gas hydrates. Thus, the evidence for gas hydrate at this site is equivocal.

New Zealand (East Coast Fold Belt)

Southeast of North Island, New Zealand (fig. 2, location 12), BSRs occur on a number of marine seismic-reflection profiles across the lower continental slope where water depths range from 1,000 to 2,500 m (Katz, 1981; 1982). The BSRs at subbottom depths between about 380 and 760 m cut across the bedding planes of the offshore portion of the East Coast Fold Belt (table 2); seismic reflections are stronger in the core of anticlines and weaker or nonexistent in synclines. The BSRs suggest that gas hydrates occur within a belt 500 km long and several tens of kilometers wide, covering an area of 10,000 to 20,000 km^2. In contrast to the BSRs off Japan, the BSRs off New Zealand tend to increase in subbottom depth with increasing water depth (fig. 4). This is the expected behavior for a gas hydrate-related BSR in an area with a uniform geothermal gradient, which is inferred by Katz (1982) to be about 20°C/km (table 2).

Antarctica (Wilkes Land Margin and Ross Sea)

Gas hydrates have been inferred by Kvenvolden and others, (1987) to be present in sediments offshore from Wilkes Land (fig. 2, location 13). A multichannel seismic-reflection survey (Eittreim and others, 1984) revealed a BSR (fig. 11) that had characteristics suggesting the base of a zone of gas hydrate: (1) the reflector is at a depth consistent with the pressure-temperature stability field of gas hydrate, and (2) the reflector shows a reversal of polarity. A third criterion that the subbottom depth of the reflector increases with increasing depth of water is not met (fig. 4), possibly because of oceanward increasing geothermal gradients as in the case of the inferred gas hydrate off Japan (Yamano and others, 1982).

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(A)   SEGMENT OF MULTICHANNEL SEISMIC LINE 3

(B)   LINE 3 SHOTPOINTS
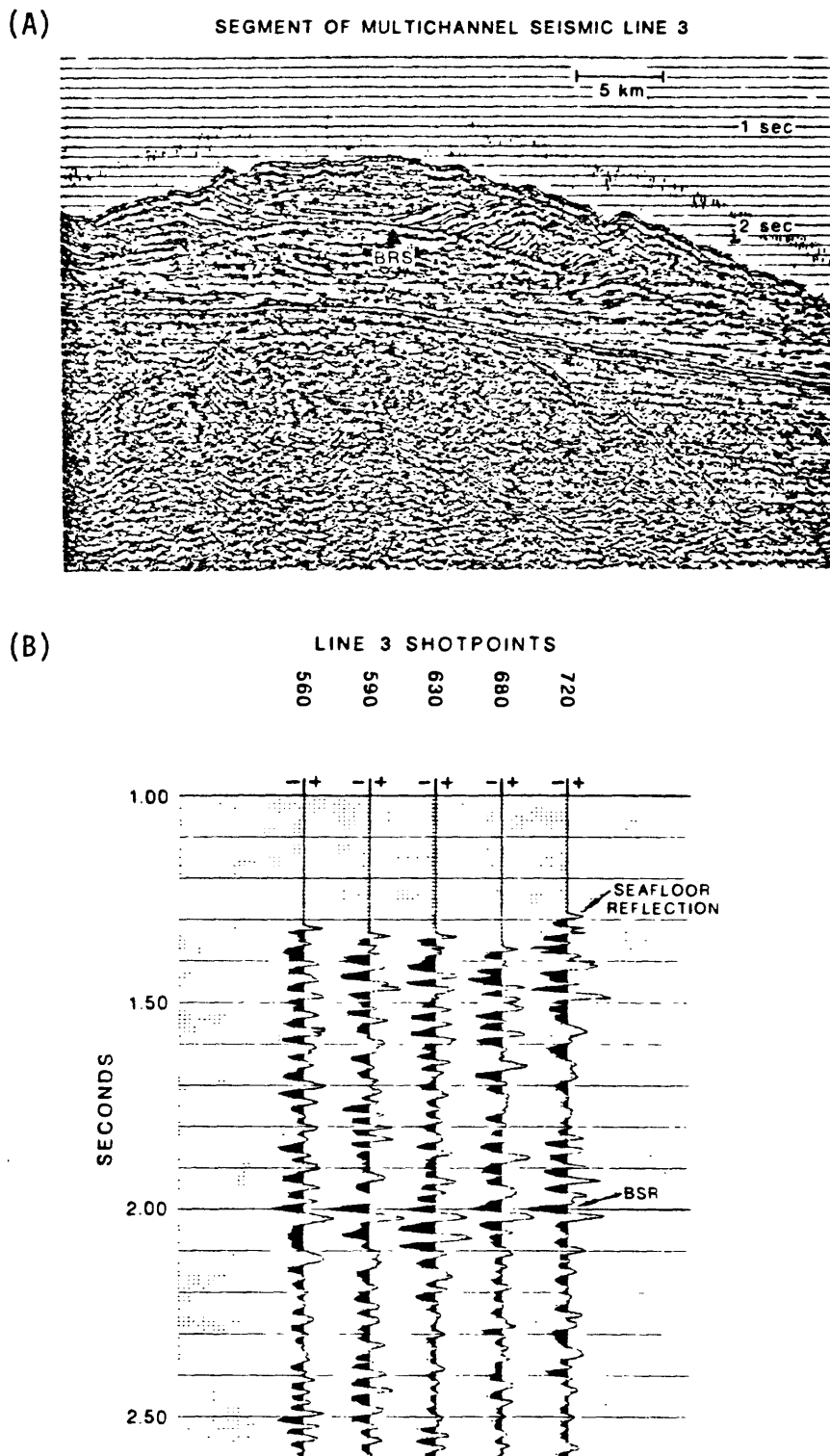
Figure 11. (A) Segment of multichannel seismic Line 3 from the Wilkes Land
            margin of Antarctica showing an anomalous acoustic reflector (BSR)
            which may mark the base of a zone of gas hydrate, and (B) five
            single-trace seismic-reflection records from Line 3 showing
            reversal of reflection polarity at the BSR. Dark peaks are
            negative polarity. The seafloor reflection and the BSR are of
            opposite polarity (from Kvenvolden and others, 1987).

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Gas hydrates may exist beneath the Ross Sea continental shelf (fig. 2, location 14). In 1973, DSDP drilled four holes there, and hydrocarbon gases were detected at Sites 271, 272, and 273 (Hayes and Frakes, 1975). Shipboard observations of hydrocarbon gases were later augmented by the shore-based studies of McIver (1975), who suggested that the high concentrations of methane recovered at these sites may have been mobilized from gas hydrates. Studies of interstitial water for the DSDP Ross Sea sites showed that salinity values decrease with increasing depth (Mann and Gieskes, 1975). Initially this decrease was thought to indicate freshwater intrusion, but we now know that decreasing salinity of the sediment pore water can also be indicative of gas hydrates (Hesse and Harrison, 1981). We believe that the combination of decreased salinity and high concentrations of methane support McIver's original suggestion that gas hydrates exist in Ross Sea sediments. However, BSRs have not been reported in the extensive seismic-reflection data coverage of the Ross Sea continental shelf and margin (Hinz and Block, 1983; Cooper and others, 1987).

Peru (Peru-Chile Trench)

Near Peru (fig. 2, location 15), BSRs inferred to indicate gas hydrates have been observed on most seismic-reflection profiles obtained over the landward slope of the Peru-Chile Trench (Shepard, 1979). Between about 5° and 7°S latitude, these reflectors occur at subbottom depths between about 350 and 570 m where water depths range from 800 to 3,200 m (table 2). The BSRs here become deeper with increasing water depth (fig. 4). Also at 9°S latitude, von Huene and others (1985) pointed out a discontinuous BSR on another multichannel seismic-reflection record across the outer continental margin of central Peru. On Leg 112 of the Ocean Drilling Program in this region, gas hydrate samples were recovered in cores at two drill sites (Kvenvolden and Kastner, in preparation).

Arctic Occurrences of Gas Hydrates

Gas hydrates have been identified both onshore and offshore in the North American Arctic. Table 5 summarizes the depth intervals of expected gas-hydrate occurrences in the Arctic Ocean region, and figure 12 shows the locations of areas where gas hydrates are believed to be present. Only offshore occurrences of gas hydrates are considered in this report.

Beaufort Sea (Alaska and Canada)

The most extensive offshore occurrence of gas hydrates in the North American Arctic lies north of Alaska (figs. 12 and 13) beneath the Beaufort Sea (Grantz and others, 1976; Grantz and Dinter, 1980; Grantz and others, 1982a). Seismic surveys show that the area of continental slope across which the seismically inferred gas hydrates occur exceeds 7,500 km^2 and may encompass a significant part of the Arctic Ocean basin where water is deeper than 400 m to 600 m. The BSRs from sediment of the Beaufort Sea are most strongly developed beneath bathymetric highs (fig. 14). These strong reflectors may result from the presence of free gas beneath an impermeable cap of gas hydrate (Grantz and others, 1976). The geothermal gradient has been predicted to be 50 ± 9°C/km on the basis of the depth of gas hydrates in this

Table 5. Predicted intervals of gas hydrate occurrence in the Arctic Basin

	Minimum depth to top of gas hydrate (m)	Maximum depth to bottom of gas hydrate (m)	Interval thickness (m)	Reference
Offshore				
Alaska Beaufort Sea Shelf	?	300 to 700	300 to 700	Grantz and Dinter, 1980
Canadian Beaufort Sea Shelf	200[a]	1560[a]	1360	Weaver and Stewart, 1982
Sverdrup Basin	140	1270	1130	Judge, 1982
Onshore				
Mackenzie Delta				
East	190	1860	1670	Judge, 1982
West	340	730	390	Judge, 1982
Sverdrup Basin	140	1270	1130	Judge, 1982
Arctic Islands				
Western	140	1100	960	Judge, 1982
Eastern	140	960	820	Judge, 1982
Arctic Platform	140	1400	1260	Judge, 1982
Alaskan North Slope	177	1119	942	Collett, 1983

[a] Depth below mean sea level. All other depths are measured from the sea bottom on ground level.
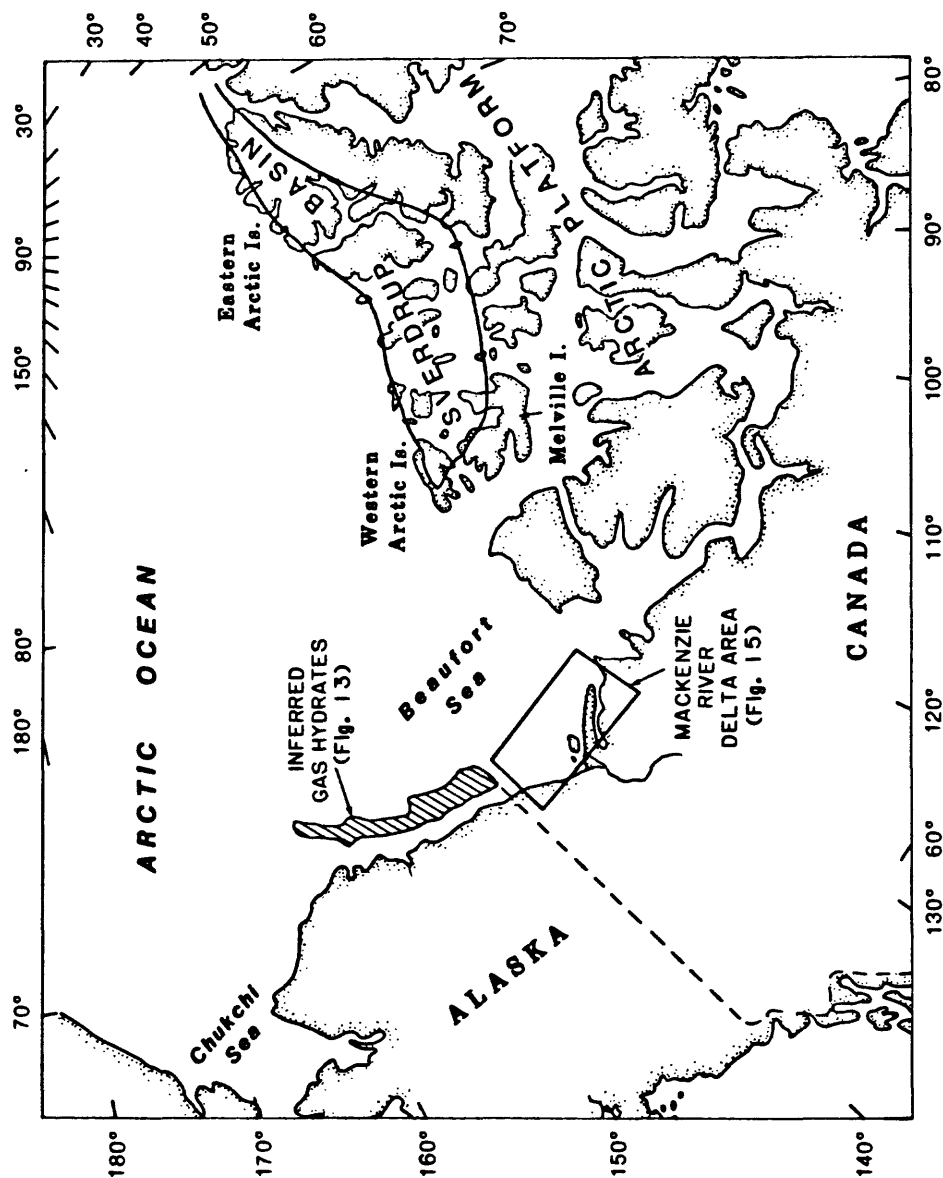
Figure 12. Map of a portion of the Arctic Ocean showing offshore regions of probable gas hydrate occurrence north of Alaska, in the Mackenzie River delta area, and in the Sverdrup Basin. Modified from Kvenvolden and Grantz, in press).
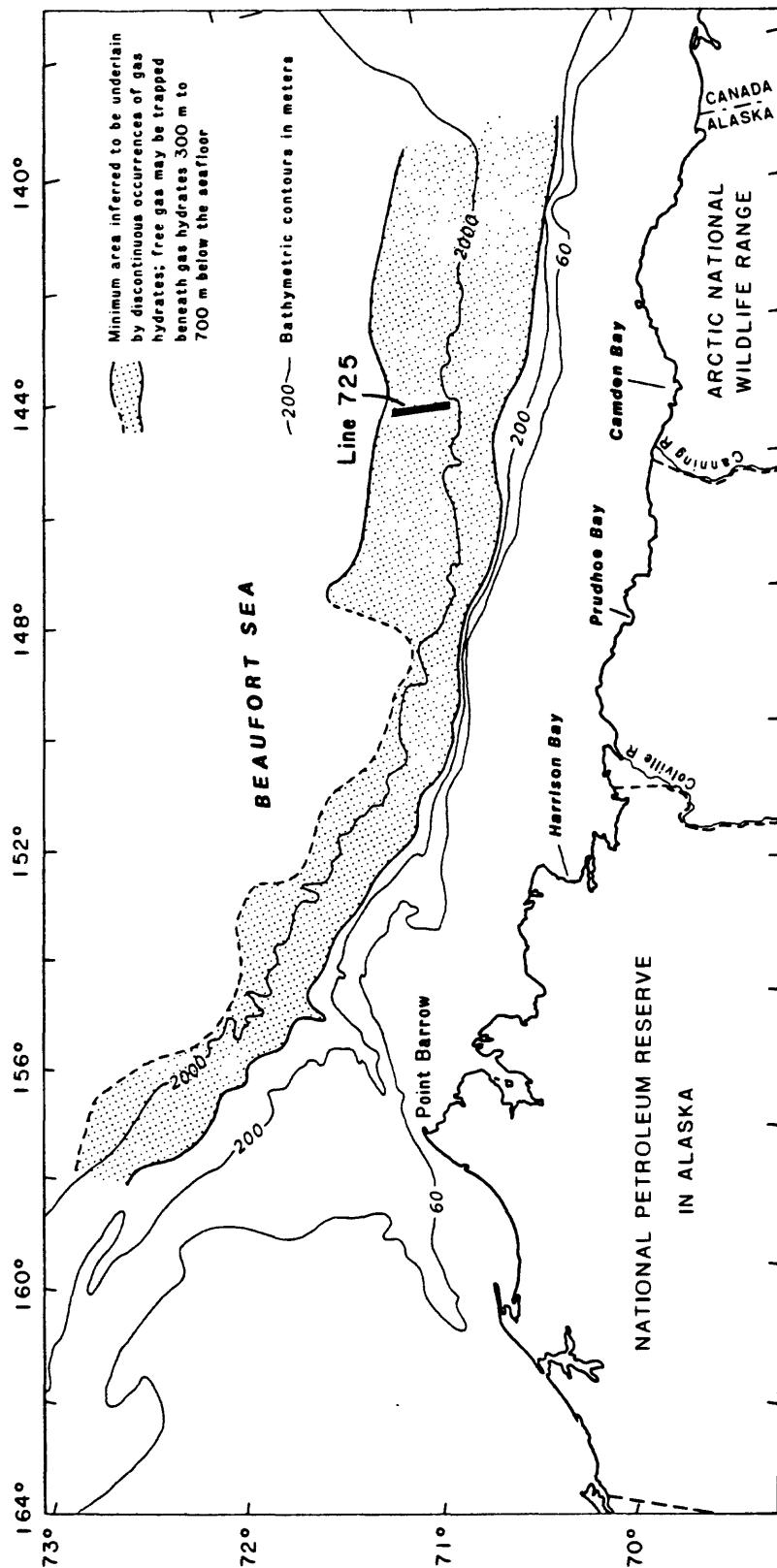
Figure 13. Map showing the minimal areal extent of gas hydrate offshore northern Alaska in the Beaufort Sea. Redrawn after Grantz and others (1982a).
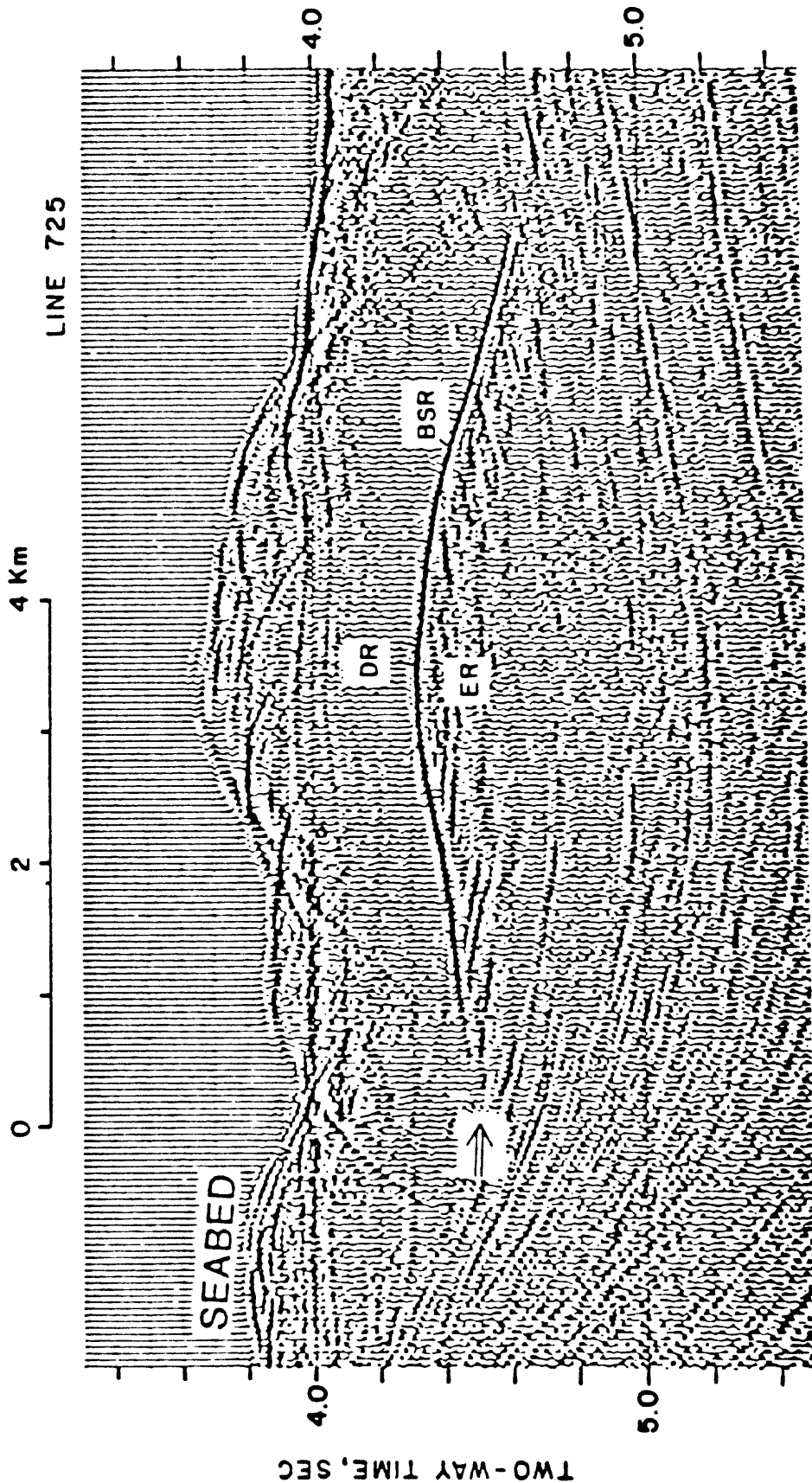
Figure 14. Multichannel seismic reflection profile (L-725) from offshore northern Alaska showing the anomalous acoustic reflector (BSR) which may mark the base of the zone of gas hydrate; approximate location of profile is shown on figure 13. DR = diminished reflection thought to be caused by gas hydrates; ER = enhanced reflection interpreted to represent gas-charged sediment (from Grantz and others, 1982a).

area (MacLeod, 1982). Drilling has not yet directly tested for gas hydrates in this region, so the presence of gas hydrates remains inferential.

Surveys of Neave and others, (1978) suggest that gas hydrates are present in sediment under the Canadian Beaufort Sea. Northwest of the Mackenzie Delta in the Netserk well area (fig. 15), low temperatures and gas were encountered in drill holes, and low sonic velocities were measured and interpreted to be caused by gas. Neave and others, (1978) infer from this combination of evidence that gas hydrates are present and responsible for the observed gas.

Beaufort Sea Shelf

The presence of gas hydrates in the Mackenzie Delta-Beaufort Sea areas had been indicated by a detailed examination of good-quality down-hole logs from 161 wells. Gas hydrates have been identified in about 27 of the wells to depths in excess of 1,200 m both onshore and offshore (Judge, 1984). Weaver and Stewart (1982) discuss 10 wells (fig. 15) where, on the basis of well-log interpretations, both permafrost and gas hydrates are believed to exist. Although these wells are technically offshore, the gas-hydrate occurrences are much like the onshore occurrences in that they are associated with permafrost. The predicted intervals of gas-hydrate occurrences in four wells having the most convincing well-log evidence for gas hydrates are:

Well name	Predicted interval (m below mean sea level)
Nerlerk	200 to 1,450
Koakoak	230 to 1,500
Ukalerk	250 to 1,480
Kopanoar	230 to 800

These intervals are predicted on the basis of a gas composition of greater than 99 percent methane, which is the usual composition for gas in the upper 200 m of sediment in the Beaufort Sea. No carbon isotopic compositions have been determined for the methane, but the gas mixture, being almost pure methane, suggests that its source is microbial and not thermogenic. For six additional wells on the Beaufort Sea Shelf, Weaver and Stewart (1982) predicted the base of the gas-hydrate zone as follows:

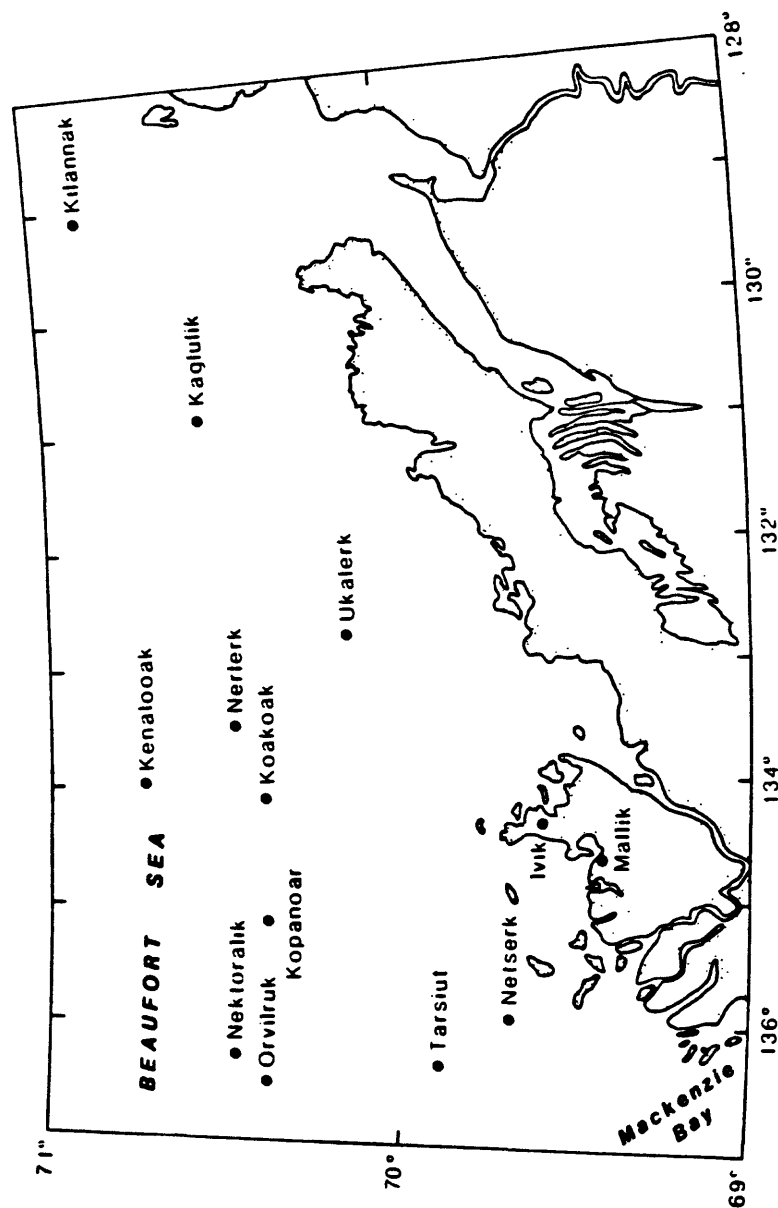| Well name	Predicted base of gas hydrates (m below mean sea level)
Tarsiut	800
Orvilruk	800
Nektoralik	900 to 1,300
Kenalooak	1,200 to 1,560
Kaglulik	800+
Kilannak	700

Figure 15. Map of the Mackenzie River Delta region showing locations of wells where the occurrence of gas hydrates have been identified through drilling, formation testing, and logging. Modified from Bily and Dick (1974) and Weaver and Stewart (1982).

Thus, the predicted depth below sea level of the base of gas hydrates varies from 800 m in the western part to at least 1,500 m in the eastern part of this area of the Beaufort Shelf. The geothermal gradient below the permafrost is typically 30°C/km. Although gas hydrates are apparently common on the Beaufort Shelf, insufficient amounts of gas hydrates have been discovered to justify producing gas from these zones (Weaver and Stewart, 1982).

Sverdrup Basin

Gas hydrates have been identified by analyses of well logs and drilling histories in offshore wells in the Sverdrup Basin (fig. 12), although specific information regarding these offshore wells is currently not available. In this basin the depth interval of possible gas-hydrate occurrence in 11 wells is between 140 m to 1,270 m (table 5, Judge; 1982). In one offshore well, the mud-gas log showed gas kicks and gas-cut mud at depths between 523 m and 600 m, indicating a possible gas-hydrate occurrence (Arctic Petroleum Operators Association Drilling Subcommittee, 1980).

Estimate of Extent of Gas Hydrates in the Arctic Basin

Rough estimates of the extent of inferred gas hydrates and of the magnitude of the volume of gas that may be trapped in the inferred gas-hydrate zone and underlying zone of free gas in the Arctic basin may be made by extrapolating from knowledge of gas-hydrate occurrences north of Alaska (Kvenvolden and Grantz, in press). Approximately 75 percent of the multichannel and 60 percent of the single-channel seismic-reflection profiles of Grantz and others, (1972, 1974, and 1982b) that cross areas of the Alaskan Beaufort and northeastern Chukchi Seas having water depths from about 400 m to 2,800 m show a BSR, DR (diminished reflector), ER (enhanced reflector), or other features suggestive of gas hydrates (fig. 14). The seaward extent of the gas hydrates is not clear because the gas-hydrate BSR, if present where water depths are great, would be essentially parallel to sedimentary layering and difficult to recognize. The thickness of the zone with gas hydrates, as inferred from the observed subseabed depth of the BSR, is 300 m to 700 m or more. In general, only the lower half, or less, of this interval is believed to be occupied by the DR zone, which is inferred to actually contain the gas hydrates. To estimate the magnitude of the hydrate-related gas deposits of the Arctic basin, it is assumed that (1) the methane in gas hydrates in the Arctic basin is mainly or entirely microbial in origin; unfortunately, no carbon isotopic ratios are available to verify this assumption; (2) sediments sufficiently rich in organic matter to produce significant accumulations of gas hydrates are only deposited near the continental margins or in the deltas of major rivers, and (3) the inferred distribution of gas hydrates off Alaska is a reasonable guide to their distribution around the Arctic basin.

The zone of gas-hydrate occurrences north of Alaska, as inferred from seismic-reflection data, is about 80 km wide (fig. 13). For this estimate it is assumed that gas hydrates in the Arctic lie only within a belt 80 km seaward of the 400-m isobath, except off the mouths of the Mackenzie River of Canada and the Lena River of Siberia. Off these major rivers, which deliver abundant nutrients and organic matter to the Arctic basin, the zone is extened to the 2,800-m isobath. This area is roughly 700,000 km^2. From the inferred

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distribution of gas hydrates off Alaska, it is assumed that only 75 percent of this area, or about 525,000 km^2, is underlain by gas hydrates. The interval above the BSR is 300 m to 700 m thick, but the DR zone, which is inferred to contain the gas hydrates, occupies half or less of this interval. The average thickness of the sediments above the BSR is about 400 m, and it is estimated that the DR zone occupies 10 percent of this interval, which yields an estimated average thickness of 40 m for the actual gas-hydrate zone. A minimum value of 30 percent is arbitrarily taken as the average porosity of the sediment in the hydrate zone. One m^3 of gas hydrate would yield, on decomposition, a maximum of 164 m^3 of methane gas at standard temperature and pressure (STP). Because it is unlikely that the gas hydrate is fully saturated, a decomposition yield of 140 m^3 of methane is assumed. The product of these measurements, estimates, and assumptions gives a rough estimate of the volume of methane that might be tied up as gas hydrates in sediments beneath the Arctic Ocean.

(1) Area underlain by gas hydrates: $0.75 \times (7 \times 10^{11})$ m^2 = 5.25×10^{11} m^2.

(2) Estimated average thickness of zone containing gas hydrates: 0.1×400 m = 40 m.

(3) Estimated average porosity of gas hydrate zone: 30%.

(4) Yield: m^3 methane per m^3 methane gas hydrate = 140.

(5) Total: 5.25×10^{11} m^2 x 40 m x 0.3 x 140 = 8.8×10^{15} m^3 or 3.1×10^4 trillion cubic feet (Tcf) of methane (STP).

No attempt was made to estimate the volume of free gas occupying the ER zone beneath the BSR (for example, see fig. 14), but that amount also appears to be large. Gas is presumably being added to the ER zone by some biogenic generation of new gas below the BSR, by breakdown of the gas hydrates within the DR zone where the geotherms are rising as a result of sea-floor aggradation, and possibly by leakage of deeper thermogenic gas. The free-gas buildup is presumably balanced by loss of gas to upslope migration and possibly by local leakage into or through the interval above the BSR. It is conceivable that the volume of free gas beneath the BSR is comparable to that estimated to be trapped in the overlying gas hydrates.

MODEL FOR FORMATION OF OCEANIC GAS HYDRATES

Because the appropriate pressure and temperature conditions for gas hydrate stability are so widespread in oceanic sediments, dissolved gas concentration is the limiting factor for gas-hydrate occurrence. Gas hydrates will form in marine sediments where dissolved methane occurs in sufficient concentration to (a) stabilize methane hydrate (with respect to dissolution in the surrounding pore water), and (b) provide excess methane to solidify a significant fraction of the pore water. There are two general situations in which large amounts of methane can be present at shallow depths of burial in marine sediments: (1) methane can originate at greater depths and migrate up to a temperature regime at shallower depths where methane hydrate is stable; and (2) methane can accumulate in abundance in organic matter-rich sediments

undergoing active microbial methanogenesis. The first situation depends on geological circumstances that are uncommon in very deep-water marine environments (e.g., thick sedimentary sequences, fault conduits, diapirs, etc.) and that cannot be adequately predicted or explained by geochemical factors. Such a situation is illustrated by the thermogenic gas hydrates found in the Gulf of Mexico (Brooks and others, 1984). The second situation (active microbial methanogenesis) is the more general case, and is amenable to study by marine geochemistry.

Methane in Deep-Water Oceanic Sediment

Microbial methanogenesis is a well-studied process that takes place in swamps, land-fills, sewage digestors, and other environments (Mah and others, 1977). Methane generation in anoxic shallow-water marine sediments also is well-documented (Martens and Berner, 1974). Methane at shallow depths of burial in sediment of continental slopes and rises has been observed in the course of scientific coring operations conducted by the Deep Sea Drilling Project and the Ocean Drilling Program. With few exceptions, the gas encountered in deep-water sediment on continental margins is relatively pure methane that is enriched in 12_C, the light stable isotope of carbon (Claypool and others, 1973). At a given locality, the isotopically lightest methane is present at the shallowest depth of gas occurrence, almost always just beneath the depth at which dissolved sulfate in the pore water is completely removed by the earlier process of bacterial sulfate reduction. Thus the evidence for microbial origin of the methane at shallow depths of burial in continental margin sediment is the combination of the chemical and isotopic composition of the gas, and the consistent relationship between the depth of initial methane occurrence and changes in the pore water chemistry that are consistent with the operation of sequential early diagenetic processes (Claypool and Kaplan, 1974). Alternative interpretations of the origin of shallow methane in marine sediments invokes chemical and isotopic fractionation during upward migration of gas of higher temperature origin (Colombo and others, 1969; Morris, 1976). Although this alternative interpretation is still preferred by some geochemists, it does not account for the relationship between methane occurrence and pore water chemistry.

Through Leg 115 of the Ocean Drilling Program, coring operations have been carried out at about 720 drill sites, and at 90 of these drill sites methane gas shows were encountered and confirmed by gas chromatographic analysis. A review of the geological and geochemical characteristics of deep ocean coring sites in which gas shows were present indicates the following common factors: (a) location on or near continental margins; (b) rapid rates of sedimentation (>40 m/my); (c) high organic carbon contents (>0.5 weight percent). Moreover, when the pore water chemistry at these sites was investigated, it always showed evidence of the sequence of early diagenetic processes: aerobic respiration, sulfate reduction, and methanogenesis.

The manner in which cores are collected does not permit quantitative measurement of the amount of methane present, although subjective observation suggests that the amounts are variable. The size and frequency of gas expansion pockets in the core liners, the occasional forcible ejection of cores from the core liners, and the rare visible occurrence of methane hydrates are examples of subjective indications of increasing levels of

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methane concentration in cores of marine sediment. A critical question with regard to methane occurrence in deep sea sediment is the physical state of the methane under in situ conditions. The pressure and temperature conditions of the uppermost thickness of deep sea sediment are such that a gas phase is not stable in the presence of excess water. The methane present in deep sea sediment at burial depths of less than a few hundred meters must be present either as (1) gas dissolved in water, or (2) gas dissolved in water plus gas hydrate. (The exact thickness of the gas hydrate stability zone depends on water depth, bottom water temperature, and geothermal gradient, and to some extent on lithology.) The amount of methane that can be retained in solution in the pore water of the sediment also depends on temperature and pressure, and is on the order of a few standard volumes of methane per volume of water. In contrast, the amount of methane that can be combined with water as gas hydrate is just over 200 standard volumes of gas per volume of water. (Naturally occurring gas hydrates are usually not fully saturated, so the actual methane:water standard volume proportions are more like 160:1.)

Global Extent of Oceanic Gas Hydrates

In order to evaluate how widespread is the occurrence of methane hydrate, one approach is to evaluate possible sources of methane, and the concentrations in which it is likely to occur in deep sea sediments. Methane is formed by the decomposition of sedimentary organic matter, and this decomposition can take place either within or beneath the zone of gas hydrate stability. The common situation for deep sea sediments appears to be that the methane is formed by decomposition of organic matter within the zone of gas hydrate stability, and that there is no significant contribution from upward migrating methane. Under these circumstances, the possible methane concentration is limited by the original concentration of methane precursors. The immediate methane precursor is dissolved carbon dioxide, which is reduced to methane through anaerobic respiration by microbial methanogenesis. At the normal pH of marine sediments, carbon dioxide is present as dissolved bicarbonate ion, and the typical maximum bicarbonate concentration in pore waters of gassy sediments is about 50 millimoles per kilogram. The equivalent dissolved carbon dioxide concentration is about one standard volume of gas per volume of water. In rare instances, dissolved bicarbonate concentrations as high as 150 or 200 millimoles per kilogram have been observed, which would be equivalent to dissolved carbon dioxide concentration of 3 or 4 standard volumes of gas per volume of water. Thus, if the concentration levels in marine sediments of the immediate methane precursor (total dissolved carbon dioxide) is used as an indicator of possible levels of methane concentration, the suggestion is that methane would be mainly present as dissolved gas with little excess available for the formation of gas hydrate.

The ultimate source of carbon for the formation of methane is fermentable organic matter deposited with the sediment. Organic matter content is usually measured and expressed as weight percent organic carbon by dry weight of sediment. Deep sea sediment that contains methane commonly has organic carbon contents in the range of 0.5 to 1 percent. If a comparable amount of carbon had been completely converted to methane in sediment with 50 percent porosity and grain density of 2.2 g/cc^3 the corresponding gas concentrations would be about 20 to 40 standard volumes of gas per volume of water. Stated in other

terms, at 50 percent porosity, an amount of organic carbon equivalent to about 0.1 percent must be converted to methane in order to saturate the pore water with respect to gas hydrate stability, and an amount of organic carbon equivalent to 2 percent must be converted to methane in order to combine with half of the available pore water as gas hydrate.

The fermentative decomposition of organic matter to produce methane is no more than 50 percent efficient, so a "significant" occurrence of gas hydrate in marine sediment (for example, 10 percent of the available porosity filled with gas hydrate) probably requires fermentative decomposition of about 1 percent organic carbon. Under conditions of steady-state diagenesis, such a situation would be represented by sediment with 2 percent organic carbon contents at the depth of the onset of methanogenesis, and decreasing to 1 percent organic carbon at the depth of the base of the gas hydrate stability zone. Thus, an indirect method can be used to estimate the possible abundance of gas hydrate in deep sea sediment: determine the area of the world ocean in which sediment with 2 percent or more organic carbon content are accumulating, and assume that conversion to methane (and methane hydrate) is proportional to the initial organic carbon content. The method, because of its simplicity, does not consider the total environment required for gas hydrate occurrence but rather focuses on one aspect, namely organic carbon, for which worldwide data are available.

Organic Carbon in Oceanic Sediment

Several compilations exist of the distribution of organic carbon in marine sediment. Most of these are published by Russian investigators and are reported at a scale that makes precise areal evaluations difficult. Figure 16 shows the general pattern of distribution of organic carbon in surficial sediments of the world oceans (Premuzic and others, 1982). In general, under conditions of normal open ocean circulation, sediment with the highest organic carbon contents (1 to 2 percent) is deposited in a relatively narrow band at the base of the continental slope. In the major upwelling regions, high organic productivity results in an oxygen minimum zone impinging on the slope and shelf. In these upwilling regions, the area of high organic carbon content is more extensive, and the level of organic carbon is much higher (2 to 6 percent). The area of the world ocean with seafloor sediment containing greater than 1 percent organic carbon is about 10×10^6 km^2. About 16 percent of this area represents sediment in upwelling regions.

Volumetric Estimate of Oceanic Gas Hydrates

Given the above estimate of the area of marine sediment in which methane could be generated in sufficient amount to form gas hydrates, a crude estimate can be made of the possible volume of methane hydrate in marine sediment. The average thickness of the gas hydrate stability zone is about 0.5 km, so the total volume of sediment in which gas hydrate could exist is about 5×10^6 km^3. The average porosity of sediment in the gas hydrate stability zone is 50 percent, so the volume available for possible gas hydrate accumulation is 2.5 $\times 10^6$ km^3. If 10 percent of the available porosity is filled with gas hydrate which yields 160 standard volumes of gas per volume of hydrate, then the volume of methane present in marine gas hydrates could be 4×10^{16} m^3 or

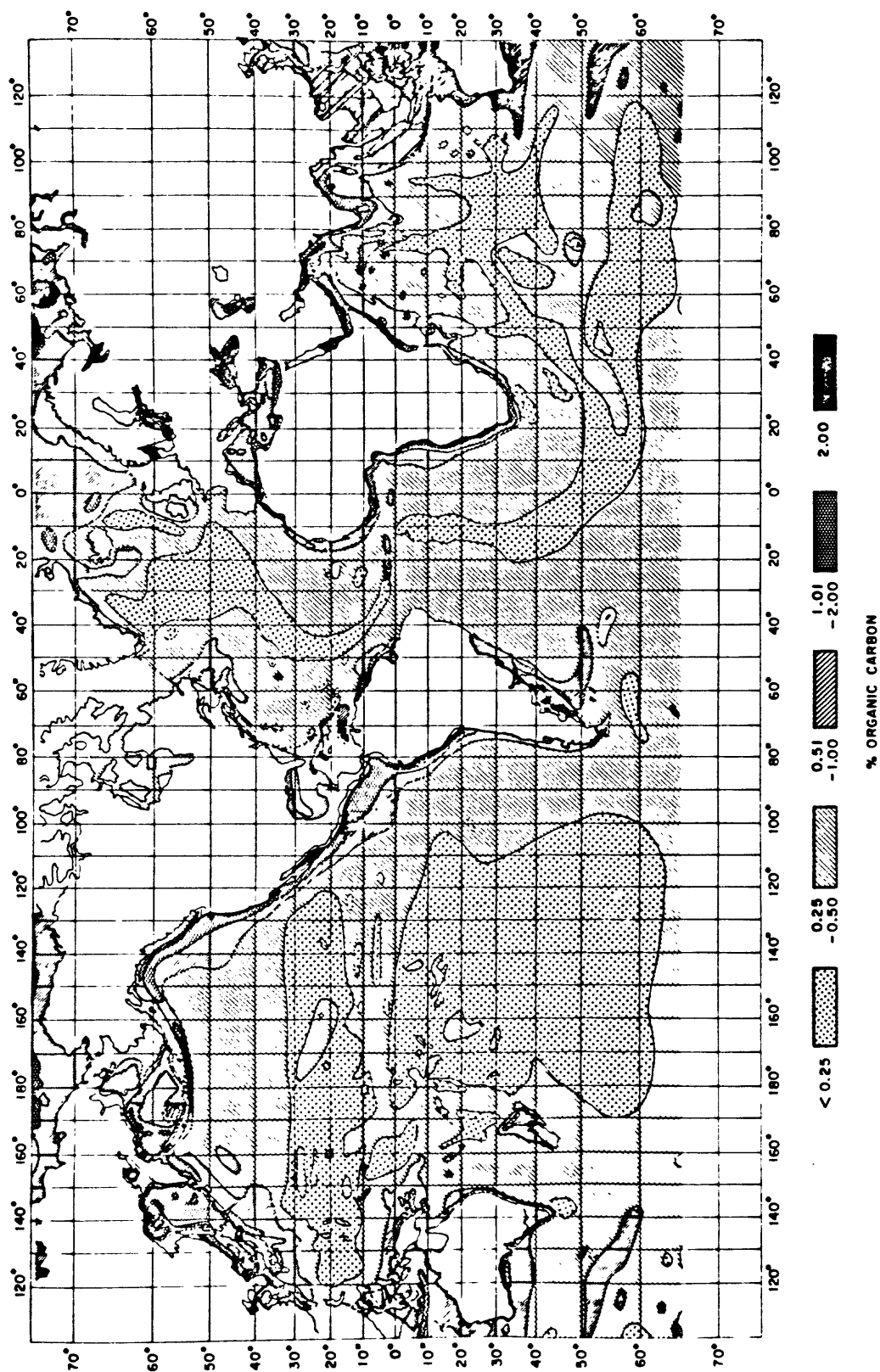Figure 16. Distribution of organic carbon in the seafloor sediment of world oceans and seas (Premuzic and others, 1982).

% ORGANIC CARBON

< 0.25   0.25 -0.50   0.51 -1.00   1.01 -2.00   2.00

1.4 x 10^6 Tcf. This estimate could be refined downward by taking into consideration the fact that most of the sediment in the area estimated above probably contained insufficient organic carbon to generate the volumes of methane required to occupy 10 percent of the available porosity with gas hydrate. The estimate could also be refined upward by taking into consideration that sediment accumulating under upwelling areas could have significantly more methane than is allowed for in the average figures. Such refinements are not justified based on the present state of our understanding.

ESTIMATES OF AMOUNT OF METHANE IN GAS HYDRATES

Resource estimates for methane in gas hydrates are highly speculative and highly variable. Although gas hydrates are believed to occur worldwide (fig. 2), knowledge of their occurrences is incomplete, and methods of estimating gas reserves in known occurrences are poor. An attempt was made by the Potential Gas Committee (1981) to summarize such estimates as shown in table 6 where the original values, given in m^3 and Tcf (trillions of cubic feet) of methane, have been converted to gigatons (10^{15} g) of methane carbon (Gt). Estimates of the amount of carbon in methane hydrates of outer continental margin (oceanic) sediment range from 1,700 to 4,100,000 Gt. In Arctic permafrost regions (continental), the values of these estimates range from 7.5 to 18,000 Gt. Clearly, most of the methane hydrates are thought to be sequestered in outer continental margins, and the range of values given by Trofimuk and others, (1977) of 2,700 to 14,000 Gt appears most reasonable. They attempted to incorporate many complex factors in their calculations, including regional and world coefficients of present and past temperatures, sediment thickness, percentage of organic material, and percentage of methane production and conservation.

As discussed previously, an attempt was made to estimate the extent of gas hydrates in the outer continental margin of the Arctic Basin by extrapolating information from the seismically-inferred gas hydrate offshore from northern Alaska (Kvenvolden and Grantz, in press). By taking into account areal extent, sediment thickness, sediment porosity, and the yield of methane from gas hydrate, a total volume of methane of about 10^{15} m^3 was calculated. This amount is equivalent to about 540 Gt of carbon as methane in sediment at the outer margin of the Arctic Basin.

The length of the Arctic Basin margin is about 5 percent of the total length of continental margins worldwide. If oceanic gas hydrates in general are distributed as they are inferred to be in the Arctic, then the total amount of methane carbon in gas hydrates of outer continental margins would be approximately 11,000 Gt, an estimate within the range of values given by Trofimuk and others (1977).

The assessment discussed earlier of the worldwide occurrence of methane hydrate was based on the determination of the volume of oceanic sediment (5×10^6 km^3) that has sufficient organic matter (> 1 percent organic carbon) to allow methane to be generated in a sufficient amount to form gas hydrates. From this volume a crude estimate was obtained of about 4×10^{16} m^3 of methane which is equal to about 16,000 Gt as the amount of methane carbon that may be

Table 6. Estimates of the amount of methane in gas hydrates of oceanic and
continental margin settings. Adapted from Potential Gas Committee
(1981).

	m^3	Tcf	Gt	Reference
Oceanic				
	3.1×10^{15}	1.1×10^5	1.7×10^3	McIver (1981)
	$5-25 \times 10^{15}$	$1.8-8.8 \times 10^5$	$2.7-13.7 \times 10^3$	Trofimuk and others (1977)
	7.6×10^{18}	2.7×10^8	4.1×10^6	Dobrynin and others (1981)
Continental				
	1.4×10^{13}	5.0×10^2	0.75×10^1	Meyer (1981)
	3.1×10^{13}	1.1×10^3	1.7×10^1	McIver (1981)
	5.7×10^{13}	2.0×10^3	3.1×10^1	Trofimuk and others (1979)
	3.4×10^{16}	1.2×10^6	1.8×10^4	Dobrynin and others (1981)

m^3 = cubic meters

Tcf = trillions of cubic feet (10^{12})

Gt = gigatons (10^{15} g) of methane carbon

present in gas hydrates from microbial processes alone. This estimate is just slightly larger than the largest value (14,000 GT) given by Trofimuk and others (1977).

Given all of the uncertainties as well as the similarities in magnitudes of these estimates, it seems reasonable to suggest that the amount of carbon in methane hydrates is about 10,000 Gt. The amount could be larger especially when all possible sources of methane are considered from both microbial and thermogenic processes. The actual value is probably not smaller than 10,000 Gt.

GAS HYDRATES IN THE GLOBAL CARBON CYCLE

The major features of the global carbon cycle have been considered in great detail by Bolin (Bolin and others, 1979; Bolin, 1983; Bolin, 1986; Moore and Bolin, 1986/87). From these considerations, figure 17 has been adapted to emphasize the organic carbon portion of the global carbon cycle and the possible magnitudinal importance of gas hydrates. The cycle has three main parts dealing with processes that take place in the air, on land, and in the sea.

The most important organic compound in the atmosphere is methane. The current concentration is about 1.7 ppm (Khalil and Rasmussen, 1983), which is equivalent to 4.8 Gt of methane (Revelle, 1983) or about 3.6 Gt of carbon. Atmospheric methane concentrations are increasing at a rate such that the amount is expected to double in the next 40-50 years (Rasmussen and Khalil, 1981). The atmospheric fate of methane is complex, however, depending mainly on the concentrations of hydroxyl radical (HO) which, in turn, depends on the concentrations of several trace constituents including CO, NO_x, O_3, etc. (Davidson and others, 1987).

On land, about 830 Gt of organic carbon resides in the biota composed of leaves, needles, grass, fine roots, wood and bark. At the surface and near-surface, there are three major compartments containing organic carbon: surface detritus (60 Gt), soil (1,400 Gt), and peat (500 Gt). At depth, fossil fuels (oil, coal and gas) contain about 5,000 Gt of carbon. All of these reservoirs of organic carbon are significantly smaller than the reservoir of organic carbon attributable to gas hydrates (10,000 Gt).

In the ocean, organic carbon occurs in three main regions -- surface, intermediate water, and deep water. Surface biota contains about 3 Gt of organic carbon whereas surface dissolved organic carbon amounts to about 30 Gt. Intermediate waters contain about 250 Gt of dissolved organic carbon, and deep waters, about 700 Gt. The largest pool of organic carbon resides as dispersed organic matter in oceanic and terrestrial sediment and sedimentary rocks. The total amount of both inorganic and organic carbon in this pool is 20,000,000 Gt. Except for this large pool, gas hydrates, the carbon of which apparently is currently included in this pool, constitute a major reservoir of carbon in the shallow geosphere in both terrestrial and marine sediment. Because of the potential size of this reservoir (10,000 Gt), it should be identified in considerations of the global carbon cycle.
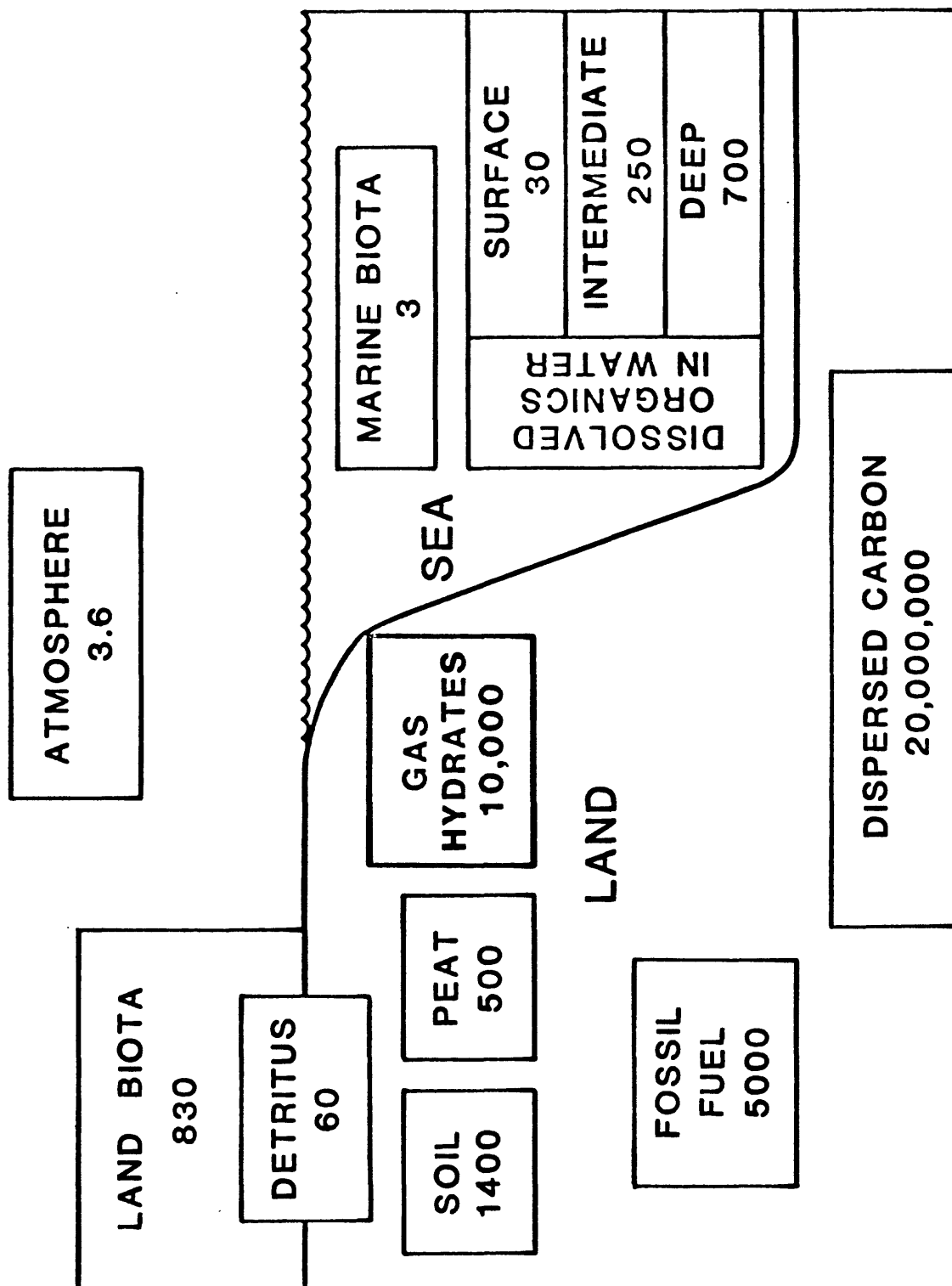
41

Figure 17. The global carbon cycle adapted from Bolin (1983) and Moore and Bolin (1986/87) showing the addition of a compartment for the gas hydrate reservoir. Numbers are given in gigatons (10^{15} g) of methane carbon.

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