



USGS Woods Hole Science Center

Coastal and Marine Geology Program

Open-File Report 96-272

Offshore Gas Hydrate Sample Database with an Overview and Preliminary Analysis

James S. Booth

U.S. Geological Survey
Northeast Section
Marine and Coastal Geology Program
Woods Hole
Massachusetts

Mary M. Rowe

Naval Research Laboratory
Stennis Space Center
Mississippi

Kathleen M. Fischer

Naval Research Laboratory
Stennis Space Center
Mississippi

June 1996

Booth, J.S., Rowe, M.M., and Fischer, K.M., 1996, Offshore gas hydrate sample database with an overview and preliminary analysis: U.S. Geological Survey Open-File Report 96-272, 1 plate, 31 p. URL: pubs.usgs.gov/of/1996/of96-272/

Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

This pdf file is text only for OF 96-272. Plate 1 (database) is a separate, downloadable file, either in excel or in adobe format, which prints a poster 44 inches wide by 24 inches tall.

U.S. Department of Interior / U.S. Geological Survey / Coastal and Marine Geology

Table of Contents

1. Synopsis
2. Introduction
3. Profile of Gas Hydrate Sample Data
 - 3.1 Geographic Locations
 - 3.2 Water Depth and Subseabed Depth
 - 3.3 Physiographic Provinces and Tectonic Settings
 - 3.4 Habit or Mode of Occurrence
 - 3.5 Associated Sediment Textures
 - 3.6 Thickness of Hydrate Zones and Dimensions of Pure Hydrates
 - 3.7 Origin: Biogenic vs. Thermogenic
4. Sample, BSR and Phase Boundary Relationships
5. Salient Tendencies of Gas Hydrate Samples
6. Acknowledgments
7. Bibliography
 - 7.1 Gas Hydrate Sample Database
 - 7.2 Methane Hydrate Phase Boundary Estimates
 - 7.3 Cited in Text
 - 7.4 Gas Hydrate Overviews
8. Appendix: Column Descriptions for Database

1. Synopsis

A database of offshore gas hydrate samples was constructed from published observations and measurements. More than 90 samples from 15 distinct regions are represented in 13 data categories. This database has permitted preliminary description of gas hydrate (chiefly methane hydrate) tendencies and associations with respect to their geological environment.

Gas hydrates have been recovered from offshore sediment worldwide and from total depths (water depth plus subseabed depth) ranging from 500 m to nearly 6,000 m. Samples have come from subbottom depths ranging from 0 to 400 m. Various physiographic provinces are represented in the data set including second order landforms such as continental margins and deep-sea trenches, and third order forms such as submarine canyons, continental slopes, continental margin ridges and intraslope basins. There is a clear association between fault zones and other manifestations of local, tectonic-related processes, and hydrate-bearing sediment.

Samples of gas hydrate frequently consist of individual grains or particles. These types of hydrates are often further described as inclusions or disseminated in the sediment. Moreover, hydrates occur as a cement, as nodules, or as layers (mostly laminae) or in veins. The preponderance of hydrates that could be characterized as 2- dimensional (planar) were associated with fine sediment, either as intercalated layers or in fractures. Hydrate cements were commonly associated with coarser sediment.

Hydrates have been found in association with grain sizes ranging from clay through gravel. More hydrates are associated with the more abundant finer-grained sediment than with coarser sediment, and many were discovered in the presence of both fine (silt and clay) and coarse sediment.

The thickness of hydrate zones (i. e., sections of hydrate-bearing sediment) varies from a few centimeters to as much as 30 m. In contrast, the thickness of layers of pure hydrate or the dimensions of individual hydrate grains were most often characterized in terms of millimeters or centimeters, although a pure hydrate layer discovered in the Middle America Trench off Guatemala was as much as 3-4-m-thick. The data suggest that grains, or thin veins or laminae of pure gas hydrate may be ubiquitous in many hydrate zones but that typically they may only comprise a minor component of the thicker zones.

In more than 80 percent of the hydrate samples the methane was of biogenic origin. The methane in the remainder was either classified as (or may be at least part) thermogenic. Each site where thermogenic gas was identified is characterized by faults or other manifestations of a dynamic geological environment (e.g., diapirs, mud volcanoes, gas seeps).

Every sample in the database came from within the zone of theoretical methane hydrate stability, as determined on the basis of assumed regional pressure and temperature gradients. Most show that they were situated --- expressed in terms of depth --- well above the phase boundary and about 70% of the samples were located more than 100 m above the assumed regional position of that boundary. The calculated subseabed positions of the phase boundaries and the BSRs (bottom simulating reflector) are essentially identical. This may be taken as general corroboration of the regional phase boundary calculations and the concept of the BSR.

Three provocative aspects of marine gas hydrates have been disclosed by the database:

1. gas hydrates are frequently situated at much shallower subseabed depths than the assumed contemporary position of the regional phase boundary
2. hydrates are often found in areas typified by faults or other indicators of a dynamic geological environment
3. zones of gas hydrate-bearing sediment tend to be tens of centimeters to tens of meters thick but the hydrate within the thicker zones tends to be only a minor constituent.

Whether existing as dispersed particles, cements, or pure layers or veins, gas hydrates tend to be characterized by dimensions of a few centimeters or less.

2. Introduction

Toward understanding the processes that lead to highly concentrated or massive deposits of marine gas hydrates, a database of offshore gas hydrate samples was constructed from published observations and measurements (Appendix). More than 90 samples from 15 distinct regions are represented in 13 data categories. This database has permitted identification of clathrate-hydrate tendencies and associations with respect to their geological environment. Herein we provide a profile of the database and focus on some of the more conspicuous aspects of gas hydrate occurrence in marine sediments.

- The data on gas hydrates are sparse, often clustered and inherently biased. This report is primarily, therefore, a straightforward presentation and description of the database (Appendix) the data characteristics, and the apparent gross associations and tendencies within the data.
- A considerable amount of research has been conducted on gas hydrates, including marine gas hydrates.^[1] Although a comprehensive review of this

^[1] An abridged list of gas hydrate overview publications is provided in the references section.

previous work is inappropriate for this data release, it may be useful to review certain gas hydrate fundamentals with respect to their formation and dissociation, and nature of these inclusion compounds in marine sediments.

Any gas hydrate is stable only within a specific combination of temperatures (T) and pressures (P). The natural bounds in terms of T and P that would control the distribution of gas hydrates is shown in Figure 1, where pressure in this context represents hydrostatic pressure (water depth plus subseabed depth, assuming no excess pore pressures) and temperature is largely controlled by the geothermal gradient. Accordingly, most of the world ocean below 500 m water depth (100 m seawater \approx 1 MPa) has low enough temperatures and high enough pressures to form and sustain methane hydrate.^[2] In high latitudes (colder water temperatures) less pressure is required and the depth of hydrate stability is even shallower.

Because water and methane must be present in the proper ratio range to form a hydrate (formula: $\text{CH}_4 n\text{H}_2\text{O}$, where $5.75 < n < \approx 19$ (Sloan, 1990),^[3] a condition of extreme concentration of methane must exist in the interstitial water of the sediments. However, this is only a local, not a global, requirement: this criterion can be met in a microenvironment such as an individual pore. At any scale seawater generally must be supersaturated with respect to methane by a factor of about 20 or more in order for hydrate nucleation to take place (i.e., for a hydrate with a minimal number of gas molecules occupying its cavities to form). An abundant source of methane at some depth greater than that at which the hydrate exists is typically implied (even if such a source itself was created by downward transport of biogenic methane or its antecedents). Moreover, gas hydrates may be ephemeral because pressure and temperature conditions are always changing. If such changes result in displacement of the hydrate outside its stability zone, as through temperature increases induced by subsidence, pressure reduction associated with eustasy, or many other geologic processes, it will decompose. Finally, a hydrate may be moved horizontally or vertically relatively great distances from its original position and/or its original methane source in response to tectonic forces or other geologic process.

3. Profile of Gas Hydrate Sample Data

3.1. Geographic Locations

Gas hydrates have been physically observed in samples of offshore sediment (including inland seas) worldwide, as shown in Figure 2. Figure 2 also shows

^[2] Methane hydrate is used for illustration because it is by far the most abundant hydrate found in marine sediments.

^[3] For a methane hydrate, which is a Structure I hydrate and therefore has 8 cavities (cages) encompassed by 46 water molecules, the ideal (100%) occupancy ratio is $\text{CH}_4:5.75 \text{ H}_2\text{O}$.

sites in which the presence of gas hydrates is inferred from geophysical, geochemical, or well- logging data. To some extent the distribution pattern shown In Figure 2 reflects bias in selection of research areas and in sampling. Nonetheless, the predilection of hydrate- bearing sediment to be associated with outer continental margins is consistent with both the pressure and temperature constraints of hydrate formation (especially that of methane hydrate), and the notion that these areas favor generation of methane and other related gases because of their relatively thick sediments and ample supply of source material (organic debris).

3.2. Water Depth and Subseabed Depth

Gas hydrate samples have been recovered from a range of water and subbottom depths. Figure 3 shows the considerable spread with respect to both categories, as well as total depth. Water depths from 500 m to nearly 6,000 m and subbottom depths to 400 m have yielded samples.

3.3. Physiographic Provinces and Tectonic Settings

The data set includes many types of physiographic provinces. Second order landforms such as continental margins and deep-sea trenches are represented, as are third order forms such as submarine canyons, continental slopes, continental margin ridges and intraslope basins. (See Appendix.) Three samples were recovered from the axes of trenches. Tectonically, both active (9 occurrences) and passive (6 occurrences) regions are well-represented among the 15 sites. There is a clear association between fault zones and other manifestations of tectonic-related processes, and gas hydrates. ^[4] About 75% of the hydrate samples were found within or proximal to such features. Fault zones are widespread on margins and may provide preferential pathways for migration of gas-rich fluids. Additionally, vents show that fluids have locally breached the sea floor and deformation by compressional forces may augment the process of gas concentration and thus promote hydrate formation (Hyndman and David, 1992).

3.4. Habit or Mode of Occurrence

Gas hydrate samples have been described most frequently as consisting of individual grains or particles. In this form they often were further described as existing as inclusions or as being disseminated. Hydrates have been frequently observed as cements and also as laminae or layers. The terms "massive" and "nodule" have also been applied to hydrate samples, as have a variety of other

^[4] The extent of the association between hydrate occurrence and tectonic activity that is manifest by the database maybe somewhat misleading in that Brooks and others (1991, 1994) intentionally selected core sites in fault zones in anticipation of finding hydrates in those locales and the data are included in this database.

terms. From these descriptions two types of occurrences based on geometry can hydrate crystallization along or parallel to bedding planes, or in joints or fractures; and 3-dimensional (granules, nodules, "massive"), which encompasses individual particles large enough to distort or crosscut bedding planes. A third category, cement, is also utilized. It represents an occurrence in which the hydrate has filled the sediment interstices apparently with little destruction or modification of the host sediment fabric. The drill hole data showed that no particular category (habit) was dominant. As indicated by Figure 4, almost all of the 2-dimensional samples were associated with fine sediment, either intrinsically or in fractures. 3-dimensional samples were numerous in fine sediments as well, but were also identified in sediment of more than one basic grain size. Hydrate cements clearly were associated with coarser material.

3.5. Associated Sediment Textures

It is possible that gas hydrate habit may be influenced by the texture of the host sediment, but the assertion that hydrate nucleation itself may be somewhat influenced by the texture of the sediment cannot be supported by the database. Hydrates have been found in association with the spectrum of grain sizes from gravel through clay. More are associated with finer-grained sediment than with coarser sediment. Given the preponderance of fines (silt and clay) over sand and gravel in sediments in general, this finding is not considered conclusive.

Gravel was a common grain size at many sites. Because the focus of this work concerns factors that may affect hydrate formation, any textures made as a product of gas hydrate formation or dissociation are not included in the analysis. Specifically, the breccias described in Appendix (Black Sea, Caspian Sea) may be a consequence of expansion of the pore fluid in veins or joints as it converts to gas hydrate; that is, volume increase in association with hydrate formation ^[5] may have fractured the sediment. Because carbonate concretions may be a product of the dissociation of hydrates, the observed associations with carbonate gravel (rubble) (Column N, Appendix) does not necessarily have connotations regarding preferences with respect to the genesis of hydrates.

Based on visual descriptions from Deep Sea Drilling Program (DSDP) or Ocean Drilling Project (ODP), three of the 28 hydrate samples (11%) are associated with sands; however, nearly 30% of the samples were recovered from zones having both sands and finer-grained sediment. Results of visual grain size classification of the sediment by the authors cited in the database are shown in Figure 5.

^[5] The specific volume of methane hydrate is approximately 27% greater than seawater (density of basic structure is about 0.78; at full occupancy ; i.e., all cavities filled, density is about 0.90).

3.6. Thickness of Hydrate Zones and Dimensions of Pure Hydrates

Gas hydrate may have an inconsistent presence over a considerable vertical distance in a sediment column at any particular site. For example, the section of hydrate-bearing sediment is more than 200 m thick at Site 4, Middle America Trench off Mexico. Within such sections individual zones that have a more uniform hydrate presence are often evident. The database table shows the number and thickness of relatively uninterrupted vertical extent of hydrate-bearing sediment at each site. ^[6] The data show the variation in drilled sediment to be from a few centimeters (Site 4, Middle America Trench off Guatemala) to as much as 30 m (Japan Sea). Within a hydrate-bearing zone pure hydrate layers have been estimated to be as much as 3-4-m-thick (Site 3, Middle America Trench off Guatemala). Some recovered pure hydrates were no more than 1-4 mm diameter beads (site 1, Gulf of Mexico). The thickness and mass of pure hydrate for drill hole gas hydrate data are shown in Figure 6.. The drill hole data were used exclusively in this histogram because gravity coring devices may not fully penetrate a substantial hydrate zone at the sea floor. Additionally, regardless of the recovery system, if hydrate-bearing marine sediment samples are not maintained at their in situ temperature and pressure, the hydrate particles will begin to dissociate -- and thus begin to diminish in size -- before they can be measured. Estimates of the size of the pure hydrate samples (Figure 6, inset) shows that of the 16 samples measured, 15 had their minimum dimension in the range of millimeters to a few centimeters. Only the layer in the sediment off Guatemala was measured in meters. In contrast, in 14 of 24 cases hydrate zones measured more than 10 cm thick and in 7 cases ($\approx 30\%$) the zones were more than a meter thick. Four were "10's of meters" thick (Figure 6, inset).

The data on zone thickness and dimensions of pure hydrates (Figure 6) suggest that although hydrates may be widespread in a given zone of sediment, they characteristically comprise only a minor volumetric component of the thicker zones.

3.7. Origin: Biogenic vs. Thermogenic

The origin of the encaged gas may be indicative of the distance of upward migration of the gas before it became a part of a clathrate hydrate. Biogenic hydrocarbon gases (which are overwhelmingly ($\geq 99\%$) methane) are those a few ten's of produced as a direct consequence of bacterial activity and are usually generated meters below the seabed, although Parkes and others (1990) discovered such bacterial activity exists in sediment several hundred meters beneath the seabed. Typically, generation of biogenic gas is associated with fine-grained sediment due to its characteristically higher initial organic content. In

^[6] Criteria of individual investigators for separating proximal zones was not stated in the cited literature.

contrast, the manufacture of thermogenic hydrocarbon gases usually occurs at subbottom depths exceeding 1,000 m (Floodgate and Judd, 1992). These hydrocarbon gases are produced under conditions of high temperature and great pressure from kerogens (which are derived from organic matter). With respect to methane as a thermogenic ^[7] gas, it is dominant only in the last stage (post mature or metagenesis stage) of hydrocarbon production. If identified in a hydrate, thermogenic methane may indicate considerable upward migration of the gas.

Of the 43 samples in the database for which there were determinations of gas origin, eight were either classified as or may be part thermogenic. Each of these eight was from a sea floor environment (of the total of 20 sea floor samples). Moreover, of the 15 regions listed in the database, 12 have gas that is predominantly of biogenic origin, two have, or likely have, both biogenic and thermogenic gases (Gulf of Mexico, Nigeria), and one has only thermogenic gas (Caspian Sea). The three thermogenic or mixed thermogenic gas sites are among the shallowest described in the database and, although they all plot above the methane hydrate phase boundary, it is noteworthy that some are a mixture of ethane, propane and other light hydrocarbons as well as methane. Ethane and propane are stable under less pressure at equivalent temperatures than is methane hydrate. Each site where thermogenic gas was identified is in an area characterized by two or more of the following features: faults, vents and seeps, diapirs, mud volcanoes.

4. Sample, BSR, and Phase Boundary Relationships

The phase boundary comprises the combinations of temperature and pressure at which a state of equilibrium exists between a free gas-seawater mixture and gas hydrate, assuming a proper molar ratio exists between methane and water. This is the subbottom depth at which the temperature has risen to a level, as controlled by the geothermal gradient, that precludes hydrate stability. It is ideally characterized by a zone of free gas and seawater overlain by a zone of gas hydrate. A representation of the phase boundary is shown in Figure 7.

Every sample in the database came from the methane hydrate stability zone Figure 8. Most show that in situ they were -- using pressure (depth) rather than temperature as a reference variable -- situated well above the phase boundary. This is one of the more striking revelations from this limited analysis of the database. If we assume that the methane supply originates from depths greater than that of the phase boundary, why are most of the samples found well above the phase boundary? Once the phase boundary is encountered by the rising gas-rich fluid, should not the gas hydrate form there?

^[7] Thermogenic is synonymous with petrogenic.

Clearly, gas hydrates are not restricted to the domain of the phase boundary. These hydrates; that is, those situated well above the present regional phase boundary, herein are termed internal gas hydrates.

Four possible explanations for an internal hydrate are:

1. it formed at a time when its phase boundary was shallower; it is relict
2. it formed as a consequence of locally-controlled or locally-induced pressures and/or temperatures rather than under regional phase boundary conditions
3. it formed by site-specific gas enrichment, either in the absolute or relative sense
4. it formed elsewhere and was transported to its present location; it is allochthonous.

Another perspective of this is provided in Figure 9. It shows that the average position of a gas hydrate sample is approximately 300 m above its calculated regional phase boundary and that 70% of the samples are more than 100 m above the assumed position of that boundary. Figure 9 also shows the position of the BSR (Bottom Simulating Reflector) in the sediment column with respect to the phase boundary. The BSR is an acoustic reflector that approximately marks the interface between the base of the gas hydrate zone and free gas below; i.e., the phase boundary. On seismic reflection records it represents the velocity difference between the overlying hydrate-bearing sediment, which has a higher acoustic velocity than saturated sediment, alone, and the underlying, probably gas-bearing sediment, which has a lower velocity than normal sediment. The BSR tends to be parallel to the sea floor because its position, in general, is controlled by the regional geothermal gradient and the hydrostatic pressure rather than geologic factors such as bedding planes. Figure 9 shows that the calculated positions of the phase boundaries and the BSR's are fundamentally in concert. ^[8] In Figure 10 the relationship is examined more closely. Due to the small number of data points (n=8) a level of significance was not determined for the apparently high correlation. However, it would appear that there is not only a close match on the scatter plot between the depth of a BSR and the depth of the site phase boundary, but that the ideal relationship between them in a regression equation (slope=1, y-intercept=0) is nearly achieved (dashed line). This may be taken as independent corroboration of the regional phase boundary calculations: verification of the geothermal gradients, the hydrostatic pressures, and the equations used in the calculations is implied. Alternatively, the agreement may be viewed as corroboration of the basic concept of the BSR.

^[8] The general absence of BSR's in association with DSDP holes (Column I, Appendix) is due to a JOIDES safety policy that forbade drilling in areas with BSRs until 1988.

5. Salient Tendencies of Gas Hydrate Samples

The database shows three prominent characteristics of the marine gas hydrate samples:

1. they tend to exist well above their regional phase boundary (Fig. 8 and Fig9)
2. they tend to be associated with faults, diapirs, deformation, vents or seeps (Column P, Appendix)
3. they tend to be a minor component of the thicker sediment zones in which they are found; i.e., the size of individual hydrate particles, thickness of individual layers or veins, or thickness of cemented layers is characteristically measured in millimeters or centimeters, and these particles or layers tend to be disseminated in sediment zones that can be meters to ten's of meters thick (Fig. 6).

The tendency of gas hydrates to be located well above the calculated position of their phase boundary infers that geological factors other than regional temperature and pressure may be involved in their placement. It also may imply that the supply of methane with respect to the criteria for hydrate formation was variable, episodic, interrupted, or exhausted. Thus, any of the several plausible hypotheses for hydrate formation must include an explanation of the geologic circumstances that established the conditions for hydrate formation, the relative vertical placement of the hydrate-bearing sediment, and explanations pertaining to methane supply.

The association of gas hydrates with features (especially faults) that indicate active geologic forces also suggests that conditions other than regional temperatures and pressures may exert control over the placement of gas hydrates. For example, processes such as uplift or upward migration of relatively warm, methane-rich pore fluids to stratigraphic levels where regional temperatures (i.e., controlled by geothermal gradient) are innately lower may be fundamental to hydrate formation.

The third of the more notable characteristics pertains to the nature of the typical hydrate-bearing sediment section. The quintessential site is a relatively thick yet discrete zone of sediment in which the pure hydrate is a minor constituent and occurs as small-sized grains or thin layers (pure hydrate or as a cement). This indicates that the quantity of methane delivered to the sediment may locally (e.g, within a pore, between sediment laminae or within a fracture) exceed that required to induce hydrate nucleation and minimal growth, but that large-scale layers are less likely to form even though there may be an ample and continuous supply of methane. The implication of this typical site is that properties of the host sediment, such as those relating to bulk diffusion or permeability, may exert control on the mode of occurrence and concentration of pure gas hydrates, but that the gross properties of the sediment section, geologic features, and geologic

processes control methane supply and dictate the thickness of the hydrate-bearing zone.

6. Acknowledgments

We are grateful for the input and insight on hydrate field data given by Ben Clennell (University of Leeds) and Martin Hovland (Statoil). William P. Dillon (USGS) provided valuable discussion on data interpretation. The efforts of Colleen Hurter (Woods Hole Oceanographic Institution), Dave Foster (USGS) and George Heimerdinger (NOAA), who provided support during the building of the database, are also acknowledged. The thorough reviews by Dave Twichell (USGS) and Joe Gettrust (NRL-Stennis Space Center) were greatly appreciated. We especially thank Bob Oldale (USGS), who provided invaluable comments and suggestions for the manuscript. This work was a part of the U.S. Geological Survey marine gas hydrates research program. Naval Research Laboratory contribution MR/7432--96-8016.

7. Bibliography

7.1. Gas Hydrate Sample Database

Brooks, J.M., Cox, H.B., Bryant, W.R., Kennicutt, M.C., II, Mann, R.G., and MacDonald, T.J., 1986, Association of gas hydrates and oil seepage in the Gulf of Mexico: *Organic Geochemistry*, v. 10, p. 221-234.

Brooks, J.M., Field, M.E., Kennicutt, M.C., II, 1991, Observations of gas hydrates in marine sediments, offshore northern California: *Marine Geology*, v. 96, p. 103-109.

Brooks, J.M., Anderson, A.L., Sassen, R., MacDonald, I.R., Kennicutt, M.C., II, and Guinasso, N.L., Jr., 1994, Hydrate occurrence in shallow subsurface cores from continental slope sediments, *in* Sloan, E.D., Jr., Happel, J., and Hnatow, M.A., eds.: *International Conference on Natural Gas Hydrates*, *Annals of the New York Academy of Sciences*, v. 715, p. 381-391.

Ginsburg, G.D., Soloviev, V.A., Cranston, R.E., Lorenson, T.D., and Kvenvolden, K.A., 1993, Gas hydrates from the continental slope, offshore Sakhalin Island, Okhotsk Sea: *Geo-Marine Letters*, v. 13, p. 41-48.

Harrison, W.E., and Curiale, J.A., 1982, Gas hydrates in sediments of holes 497 and 498A, *in* Aubouin, J., von Huene, R., and others, *Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C.*, v. 67, p. 591-594.

Kvenholden, K.A., and Barnard, L.A., 1983, Gas hydrates of the Blake Outer Ridge, Site 533, *in* Sheridan, R.E., Gradstein, F., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 76, p. 353-365.

Kvenvolden, K.A., and MacDonald, T.J., 1985, Gas hydrates of the Middle America Trench-Deep Sea Drilling Project Leg 84, *in* von Huene, R., Aubouin, J., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 84, p. 667-682.

Kvenvolden, K.A., and Kastner, M., 1990, Gas hydrates of the Peruvian outer continental margin, *in* Suess, E.R., von Huene, R., and others, Proceedings of the Ocean Drilling Program, Scientific Results: U.S. Government Printing Office, Washington, D.C., v. 112, p. 517-526.

Mathews, M.A., and von Huene, R., 1984, Site 570 methane hydrate zone, *in* von Huene, R., Aubouin, J., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 84, p. 773-790.

Pflaum, R.C., Brooks, J.M., Cox, H.B., Kennicutt, M.C., II, and Sheu, Der-Duen, 1986, Molecular and isotopic analysis of core gases and gas hydrates, Deep Sea Drilling Project Leg 86, *in* Bouma, A.H., Coleman, J.M., Meyer, A.W., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 96, p. 781-784.

Shipboard Scientific Party (Leg 66), 1982a, Site 490, *in* Watkins, J.S., Moore, J.C., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 66, p. 151-217.

Shipboard Scientific Party (Leg 66), 1982b, Site 491, *in* Watkins, J.S., Moore, J.C., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government, Washington, D.C., v. 66, p. 219-287.

Shipboard Scientific Party (Leg 66), 1982c, Site 492, *in* Watkins, J.S., Moore, J.C., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government, Washington, D.C., v. 66, p. 289-340.

Shipboard Scientific Party (Leg 67), 1982a, Site 497: Middle America Trench upper slope, *in* Aubouin, J., von Huene, R., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 67, p. 193-243.

Shipboard Scientific Party (Leg 67), 1982b, Site 498: Middle America Trench lower slope, *in* Aubouin, J., von Huene, R., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 67, p. 245-266.

Shipboard Scientific Party (Leg 84), 1985a, Site 565, *in* von Huene, R., Aubouin, J., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 68, p. 21-77.

Shipboard Scientific Party (Leg 84), 1985b, Site 568, *in* von Huene, R., Aubouin, J., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 67, p. 167-232.

Shipboard Scientific Party (Leg 84), 1985c, Site 570, *in* von Huene, R., Aubouin, J., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 67, p. 283-336.

Shipboard Scientific Party (Leg 146), 1994, Site 892, *in* Westbrook, G.K., Carson, B., Musgrave, R.J., and others, Proceedings of the Ocean Drilling Program: Initial Reports, 146 (Pt.1), College Station, Tex., (Ocean Drilling Program), p. 301-378.

Shipboard Scientific Party (hole 796), 1990, Site 796, *in* Tamake, K., Pisciotto, K., Allen, J., and others, Proceedings of the Ocean Drilling Program: Initial Reports, 127, College Station, Tex., (Ocean Drilling Program), p. 247-322.

Shipboard Scientific Party (Leg 131), 1991, Site 808, *in* Taira, A., Hill, I., Firth, J.V., and others, Proceedings of the Ocean Drilling Program: Initial Reports, 131, College Station, Tex., (Ocean Drilling Program), p. 71-269.

Shipboard Scientific Party (leg 96), 1986, Site 618, *in* Bouma, A.H., Coleman, J.M., Meyer, A.W., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 96, p. 399-421.

Shipboard Scientific Party (Leg 76), 1983, Site 533: Blake Outer Ridge, *in* Sheridan, R.E., Gradstein, F., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 76, p. 35-85.

Shiple, T.H., and Didyk, B.M., 1982, Occurrence of methane hydrates offshore southern Mexico, *in* Watkins, J.S., Moore, J.C., and others, Initial Reports of the Deep Sea Drilling Project: U.S. Government Printing Office, Washington, D.C., v. 66, p. 547-555.

Soloviev, V., and Ginsburg, G.D., 1994, Formation of submarine gas hydrates: Bulletin of the Geological Society of Denmark, vol, 41, p. 86-94.

7.2. Methane Hydrate Phase Boundary Estimates

Methane hydrate phase boundary estimates, Claypool, G.E., and Kaplan, I.R., 1974, The origin and distribution of methane in marine sediments, *in* Kaplan, I.R., ed., Natural Gases in Marine Sediments: New York, Plenum Press, p. 99-139.

Dickens, G.R., and Quinby-Hunt, M.S., 1994, Methane hydrate stability in seawater: *Geophysical Research Letters*, v. 21, p. 2115-2118.

Englezos, p. , and Bishnoy, p. R., 1988, Prediction of gas hydrate formation conditions in aqueous electrolyte solutions: *American Institute of Chemical Engineers Journal*, v. 34, p. 1718-1721.

John, V.T., Papdopolous, K.D., and Holder, G.D., 1985, A generalized model for predicting equilibrium conditions for hydrates: *American Institute of Chemical Engineers Journal*, v. 10, p. 202-205.

Seitz, J.C., and Pasteris, J.D., 1990, Theoretical and practical aspects of differential partitioning of gases by clathrate in fluid inclusions: *Geochemica et Cosmochemica Acta*, v. 54, p. 631-639.

Sloan, E.D., Jr., 1990, *Clathrate Hydrates of Natural Gases*: Marcel Dekker, Inc., New York, 641 p. 15.

7.3. Cited in text

Brooks, J.M., Field, M.E., and Kennicutt, M.C., II, 1991, Observations of gas hydrates in marine sediments, offshore northern California: *Marine Geology*, v. 96, p. 103--109.

Brooks, J.M., Anderson, A.L., Sassen, R., MacDonald, I.R., Kennicutt, M.C., II, and Guinasso, N.L., Jr., 1994, Hydrate occurrence in shallow subsurface cores from continental slope sediments, *in* Sloan, E.D., Jr., Happel, J., and Hnatow, M.A., eds., *International Conference on Natural Gas Hydrates*, *Annals of the New York Academy of Sciences*, v. 715, p. 381-391.

Li Floodgate, G., and Judd, A.G., 1992, The origins of shallow gas: *Continental Shelf Research*, v. 12, p. 1145-1156.

Hyndman, R.D., and Davis, E.E, 1992, A mechanism for the formation of methane hydrate and seafloor bottom-simulating reflectors by vertical fluid expulsion: *Journal of Geophysical Research*, v. 97, No.B5, p. 7025-7041.

Kvenvolden, K.A., Ginsburg, G.D., and Solovev, V.A., 1993, Worldwide distribution of subaquatic gas hydrates: *Geo-Marine Letters*, v. 13, p. 32-40.

Parkes, R.J., Cragg, B.A., Fry, J.C., Herbert, R.A., and Wimpenny, J.T., 1990, Bacterial biomass and activity in deep sediment layers from the Peru margin, v. A331, p. 139-153.

Sloan, E.D., Jr., 1990, *Clathrate Hydrates of Natural Gases*: New York, Marcel Dekker, Inc., 641 p.

7.4. Gas hydrate overviews

Cox, J.L., ed., 1983, Natural Gas Hydrates: properties, occurrence, and recovery: Woburn, Butterworth Publishers, 125 p.

Kaplan, I.R., ed., 1974, Natural Gases in Marine Sediments: New York, Plenum Press, 324 p.

Sloan, E.D., Jr., 1990, Clathrate Hydrates of Natural Gases: New York, Marcel Dekker, Inc., 641 p.

Englezos, p. , 1993, Clathrate Hydrates: Ind.Eng.Chem.Res., v. 32, p. 1251-1274.

8. Appendix- Column descriptions for Database (Database, Plate 1)

This pdf file is text only for OF 96-272. Plate 1 (database) is a separate, downloadable file, either in excel or in adobe format, which prints a poster 44 inches wide by 24 inches tall.

Column A — GEOGRAPHIC AREA

1. General geographic area (yellow fields)

In alphabetical order, this column gives the name of the ocean or sea in which the gas hydrate sample was recovered. This geographic name is, where appropriate, linked by a dash to the name of the physiographic province or another geographic name that serves as an aid to further locate the site. The name of the nearest country, state/province, city, or prominent feature to the site is given in parenthesis. If the sampling was a part of a Deep Sea Drilling Project (DSDP) or Ocean Drilling Program (ODP) activity and only one gas hydrate sample site was in the area, the leg and hole number are also provided.

2. Listing of sites within the aforementioned area (white fields)

Gas hydrate sites are numerated and, in cases where downhole sampling was involved, each separate zone of hydrate recovery is identified. Additional information is given for the site in the form of local names or core identification, as warranted. Note that a site is defined in terms of geographic position (latitude and longitude) and depth, in that individual hydrate zones associated with the sites, are also represented. Accordingly, DSDP or ODP leg and hole number corresponding to the site are provided as they apply.

Column B - CORE/SAMPLE COUNT

The number of distinct gas hydrate occurrences sampled in the specified geographic area

All samples were recovered using over-the-side coring equipment ("gravity" or piston) or downhole samplers, where the former class of samplers was effective only in sampling hydrates in surface sediments. Given that the literature cited does not distinguish multiple hydrate zones in these cores, each core was taken to represent one gas hydrate sample.

Column C- PHYSIOGRAPHIC PROVINCE

Classification of the area or subarea in terms of its physiography

In most instances the classification is only taken to the second order (e.g., continental slope), although modifiers are used where possible (e.g., lower and upper continental slopes have a discernible difference in geologic setting).

Column D — TECTONIC SETTING

A binary assessment of regional tectonism: active or passive (yellow fields)

The terms "active" and "passive" are applied within the context of plate tectonics.

Column E — GEOGRAPHIC POSITION

Latitude and longitude of the gas hydrate sample sites

Column F - WATER DEPTH

Water depth (in meters) for each site

Depths were taken directly from the literature.

Column G — SUBBOTTOM DEPTH

Vertical distance (in meters) from the sea floor ("mudline") to the position of the gas hydrate sample or the top of the sampled gas hydrate zone

If the sediments are assumed to be normally consolidated (i.e, pore pressures are hydrostatic pressures), then this value plus the water depth (Column F) would equal the total hydrostatic pressure at the position of the gas hydrate occurrence; that is, pressure expressed in units of meters of seawater (1 m seawater \approx 10 kPa).

Column H — TEMPERATURE AT HYDRATE:GEOTHERMAL GRADIENT

- 1. Temperature at the level of gas hydrate occurrence or at some other level within the sediment that is relevant to establishing an applicable geothermal gradient**

In cases where hydrate occurrence is at the sea floor, the temperature given is bottom water temperature.

2. The geothermal gradient (in °C/km)

The temperature at a given subsurface level may be estimated if the geothermal gradient is known. Thus, in the absence of downhole temperature data, the subsurface position of the combination of T and P that would be the phase boundary may be estimated using the geothermal gradient.

In conjunction with total pressure, the temperature sets the position of the phase boundary; i.e., data in columns G and H permit determination of the regional gas+water:gas hydrate phase boundary.

Column I — ESTIMATED DEPTH TO PHASE BOUNDARY

The vertical distance (in meters) from the sea floor to the regional phase boundary

The temperature and pressure combinations required, and hence the water plus subseabed depth to the boundary (assuming sediments are normally consolidated) were estimated using information from four references, which are identified by the following superscripts:

C&K – Claypool and Kaplan, 1974. Value shown based on curve for phase boundary in seawater plotted to a pressure of 55 MPa (hydrostatic pressure equivalent to total depth of ≈5,500 m).

D&Q – Dickens and Quinby-Hunt, 1994. Value shown calculated from phase boundary equation for seawater to a pressure of 10 MPa (hydrostatic pressure equivalent to total depth of 1,000 m).

E&B – Englezos and Bishnoy, 1988. Value shown calculated from phase boundary equation for seawater to a pressure of 13 MPa (hydrostatic pressure equivalent to total depth of 1,300 m).

S – Sloan, 1990. Value shown calculated from phase boundary equation for pure water to a pressure of 33 MPa (hydrostatic pressure equivalent to total depth of 3,300 m).

None of the estimates shown in Column I are based on extrapolations: all are within the P, T ranges presented in the cited studies. Results are rounded to 10-m increments.

Column J — BOTTOM SIMULATING REFLECTOR PRESENT?

Yes or No

If yes, subbottom depth to bottom simulating reflector (BSR) at or proximal to the geographic position of the sample is given. If no, BSR may not be present or may not have been detected.

Column K — OBSERVED THICKNESS OF HYDRATE ZONE

Thickness of the interval of gas hydrate occurrence (thickness of relatively uninterrupted sequence of hydrate-bearing sediment)

The thickness of the zone in which hydrates were physically present and ubiquitous, regardless of apparent relative abundance (default units are meters). In cases where gravity-driven coring devices were used, thicknesses given may be conservative estimates because corers may not have been able to penetrate the entire zone.

Subseabed depths to upper and lower zone boundaries (in meters) are shown in parentheses, where known.

Column L— THICKNESS/SIZE OF PURE HYDRATE LAYER/GRAINS

Measured or estimated dimensions, or other characterization, of the mass or size of a sample of pure gas hydrate recovered from the site (hydrate with trace to minor sediment content is considered pure).

Column M — HABIT OR MODE OF OCCURRENCE

Descriptors either used in or based on the cited references with respect to the appearance of the gas hydrate in the field

With regard to the descriptions, no attempt was made to standardize terminology or provide an indication of scale. In addition, no attempt was made to discriminate between terminology applied to the gas hydrate alone versus the aggregate appearance of sediment+hydrate.

Column N — SEDIMENT DESCRIPTION

Descriptions of the sediment associated with the gas hydrate; that is, the host material for the hydrate

These descriptions are largely excerpts from the cited references.

Column O — APPARENT ORIGIN OF INCLUDED GAS

Origin of methane in the hydrate: biogenic or thermogenic.

Column P — OBSERVATIONS AND COMMENTS

Additional information that may be relevant to understanding gas hydrate occurrence at this site or at this subbottom depth

Column Q — REFERENCES

Source of data and information for the row. Some temperature data were estimated from literature or from U.S. Naval Oceanographic Data Center profiles and no specific reference is provided. If reference(s) is in a yellow field, it applies to all samples in the subset; if in a white field, the reference only applies to that specific row.

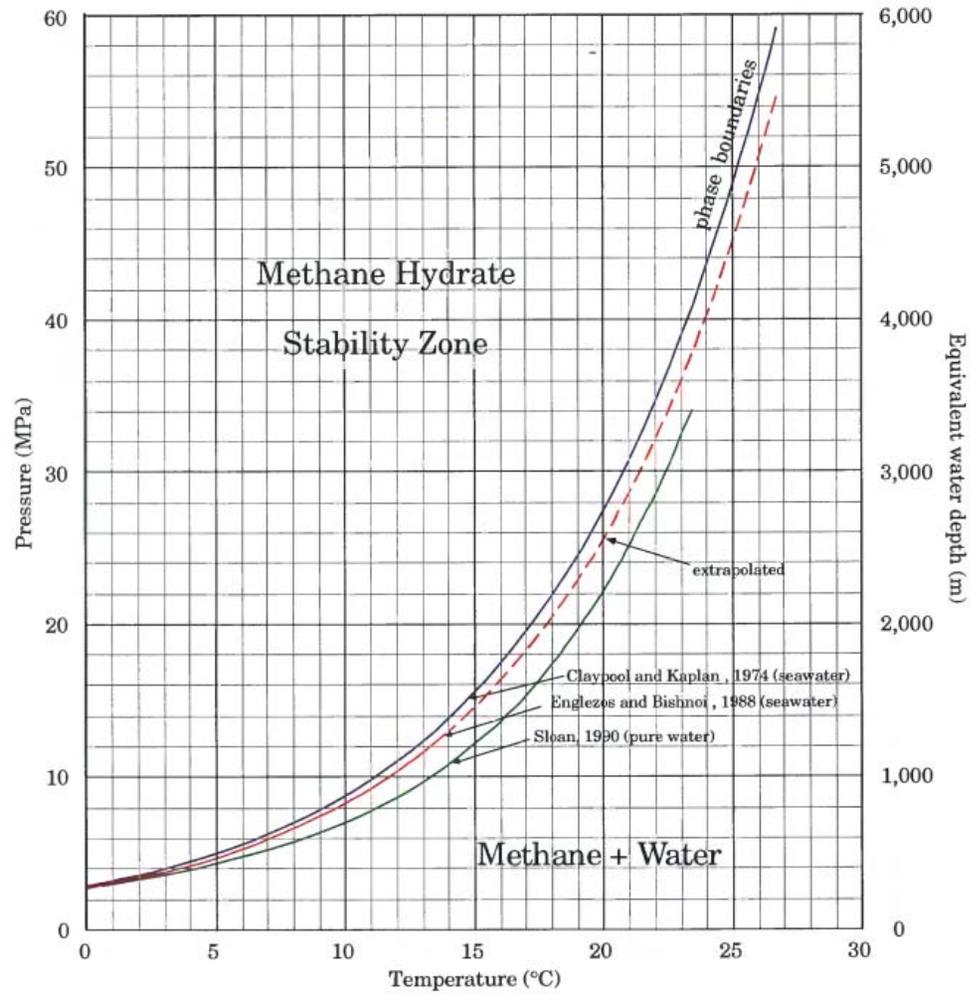


Figure 1. Stability zone for methane hydrate. Note the effect of salts in solution on the position of the phase boundaries.

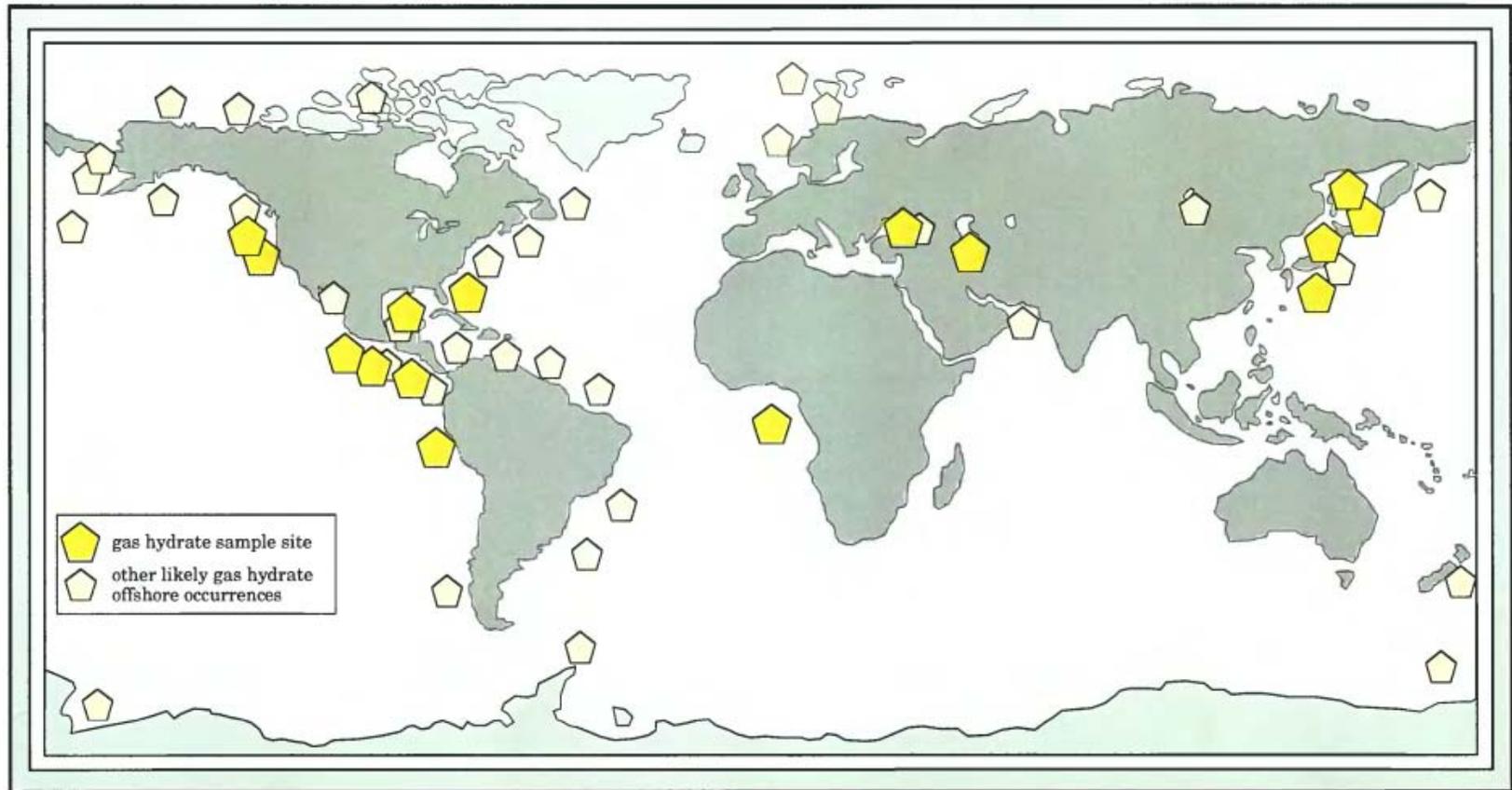


Figure 2. Worldwide distribution of confirmed or inferred offshore gas hydrate-bearing sediments. Sites taken from Kvenvolden and others and Brooks and others.

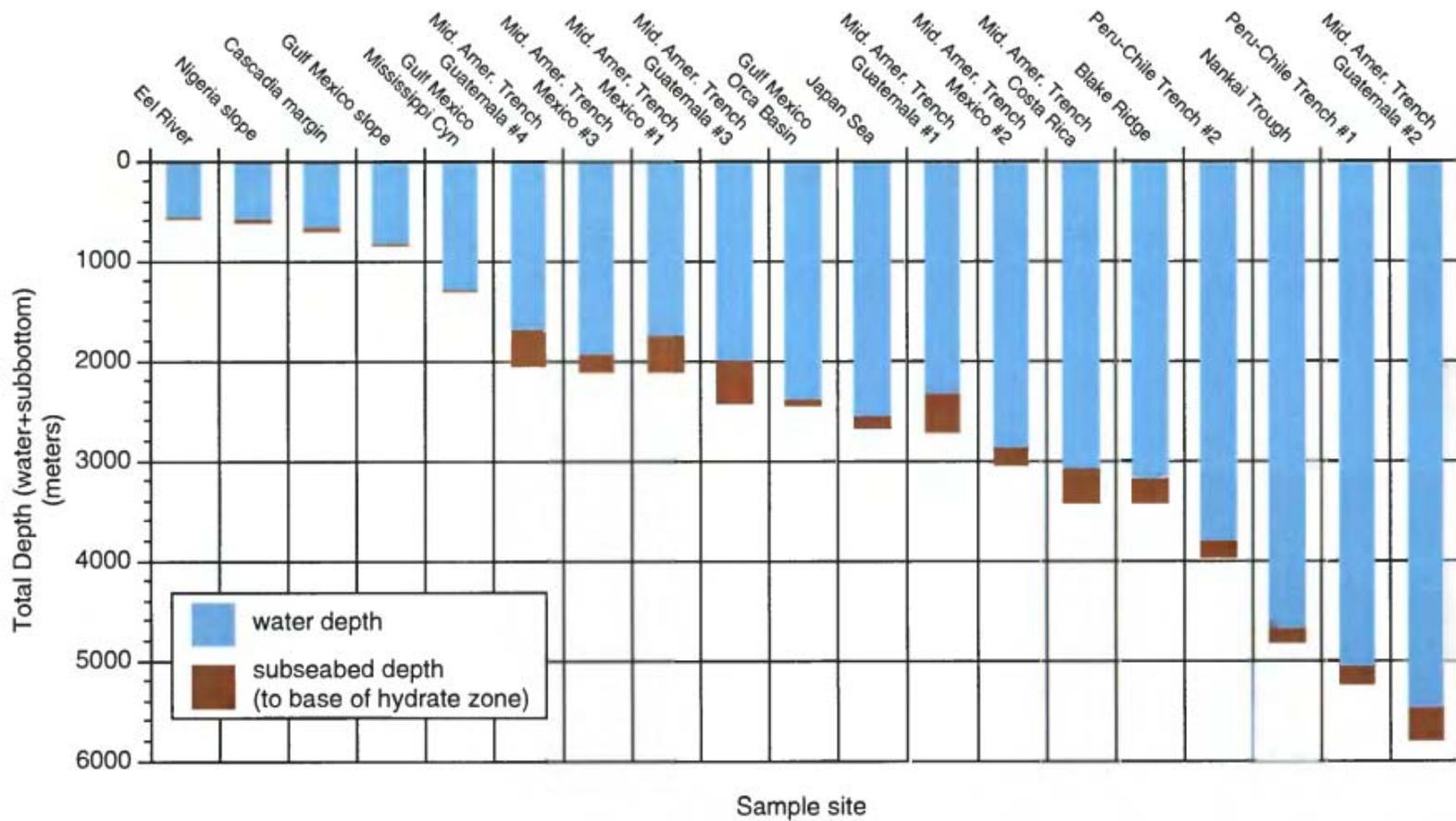


Figure 3. Distribution of recovered gas hydrate samples with respect to total depth (water depth plus subseabed depth). Sites listed refer to sites listed in the database

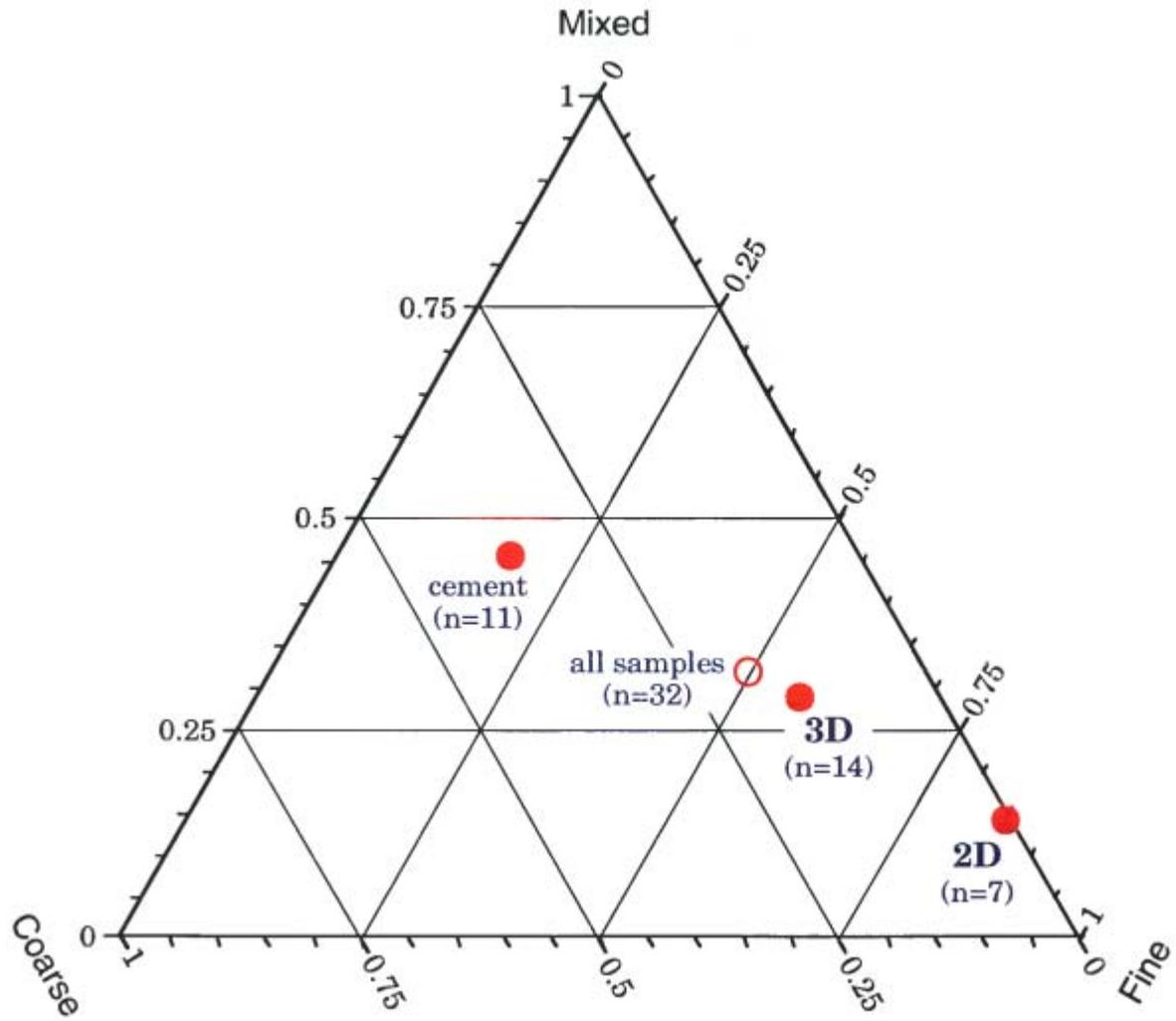


Figure 4. Relative frequency of occurrence of different gas hydrate forms (habit) with respect to sediment type (drilling samples only).

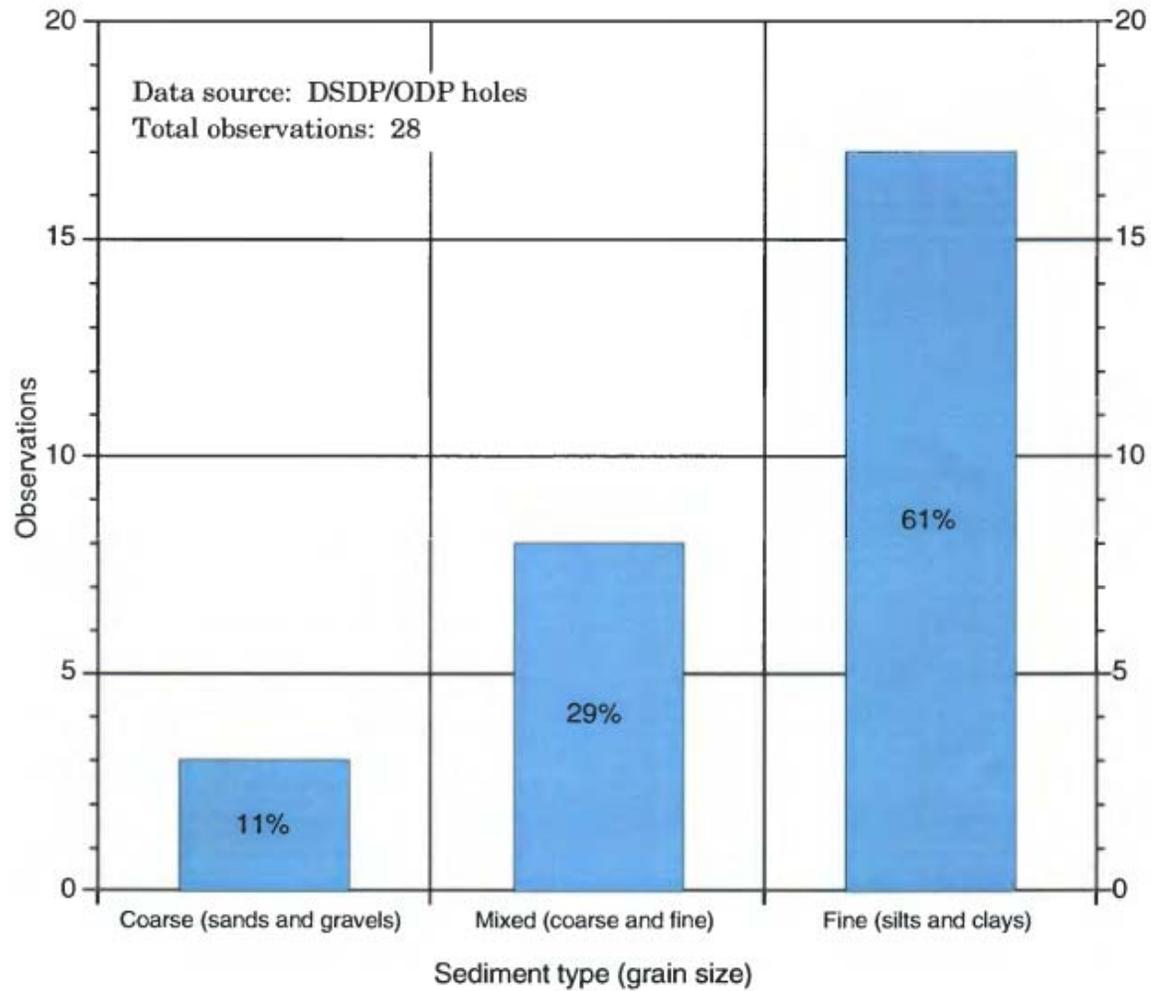


Figure 5. The frequency of occurrence of gas hydrates with respect to sediment texture. Data from sea floor samples are not included. The category "mixed" refers to either the presence of gas hydrate in mixed coarse and fine sediments or to gas hydrate recovered from a zone in which both of these basic sediment textures are present, as described in the literature cited in the database

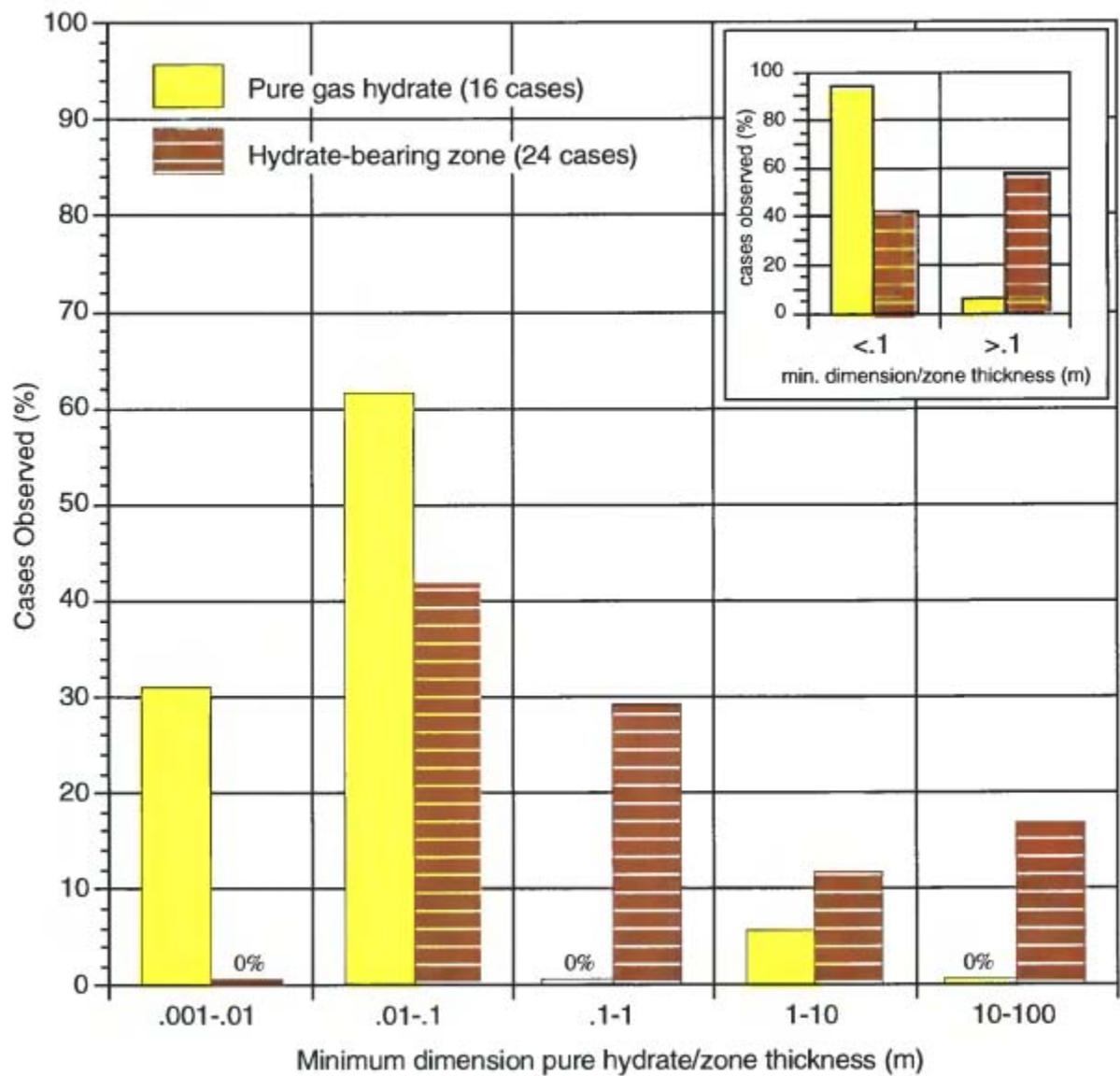


Figure 6. Dimensions of pure hydrate samples in comparison to thicknesses of hydrate zones. The gross trends displayed by the two variables are emphasized in the inset.

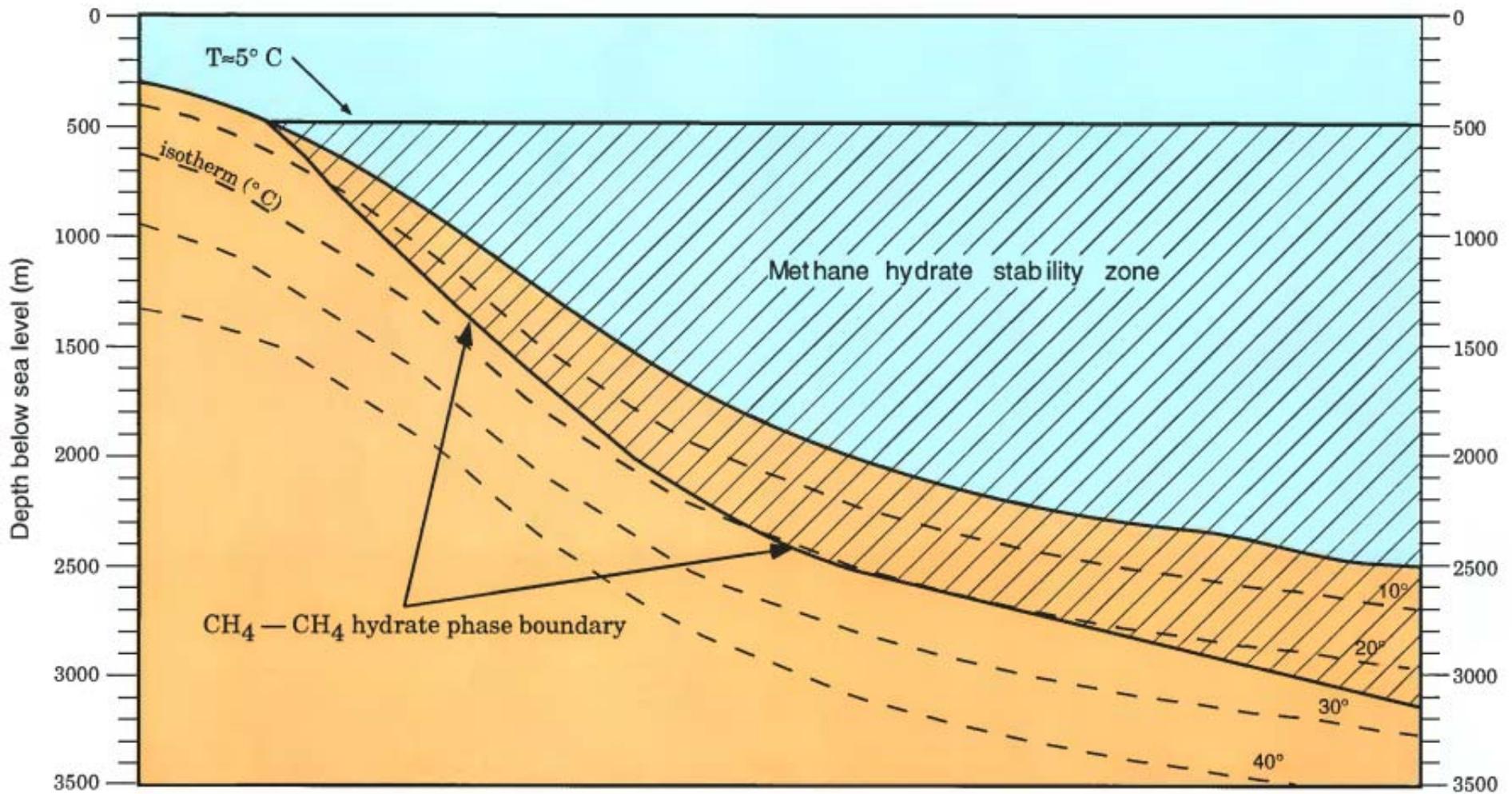


Figure 7. General stability range of methane hydrates on continental margins. Variations exist in high latitudes or where water temperatures on margins are influenced by boundary currents. Plot constructed using a geothermal gradient of $35^{\circ}\text{C}/\text{km}$.

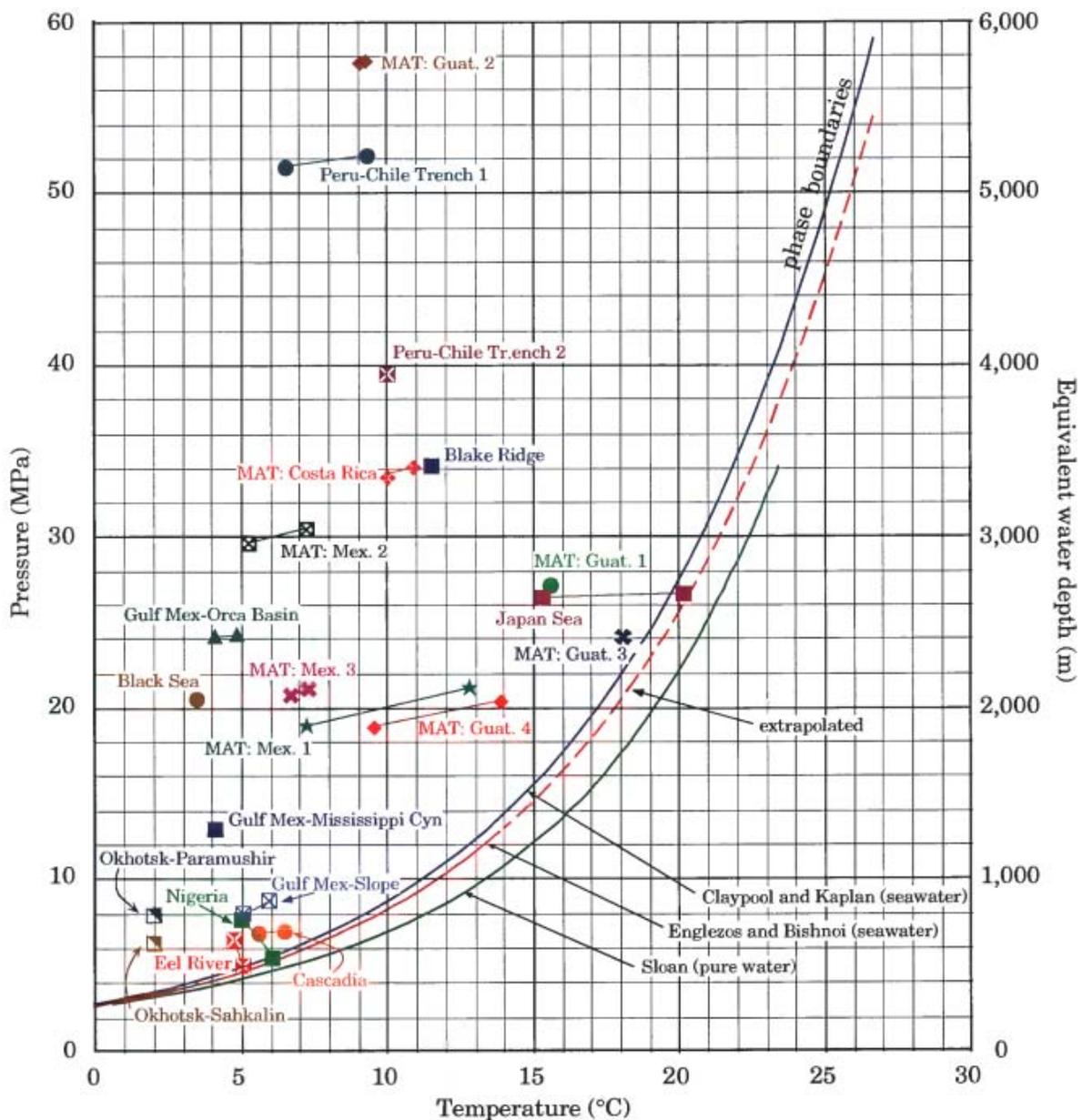


Figure 8. Relationship of estimated in-situ temperatures and pressures of methane hydrate samples to phase boundary. Ranges represent the temperatures and pressures from the uppermost and lowermost hydrate found on a specific site or, in the case of grouped surface samples (Eel River, Nigeria, Gulf of Mexico slope), the estimated variation in T and P over the area of sample recovery. Labels refer to sites listed in database (Appendix). MAT designation refers to Middle America Trench. Construction assumes that sediments are normally consolidated (no excess + pore pressures) and thus reflects hydrostatic pressures only.

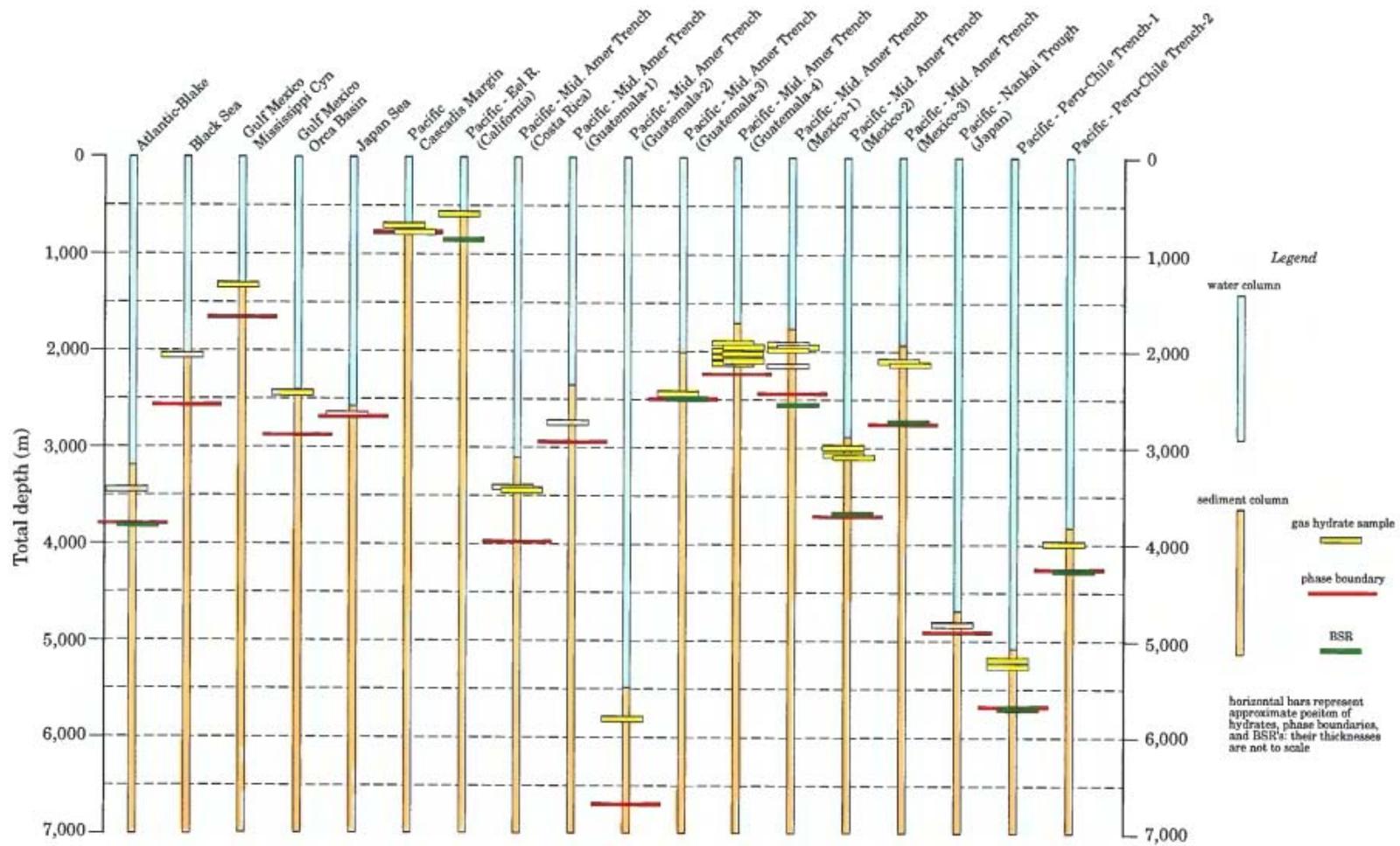


Figure 9. Summary of vertical spatial relationships of sample zones, BSRs, and calculated positions of the regional phase boundary for each site. (See Appendix).

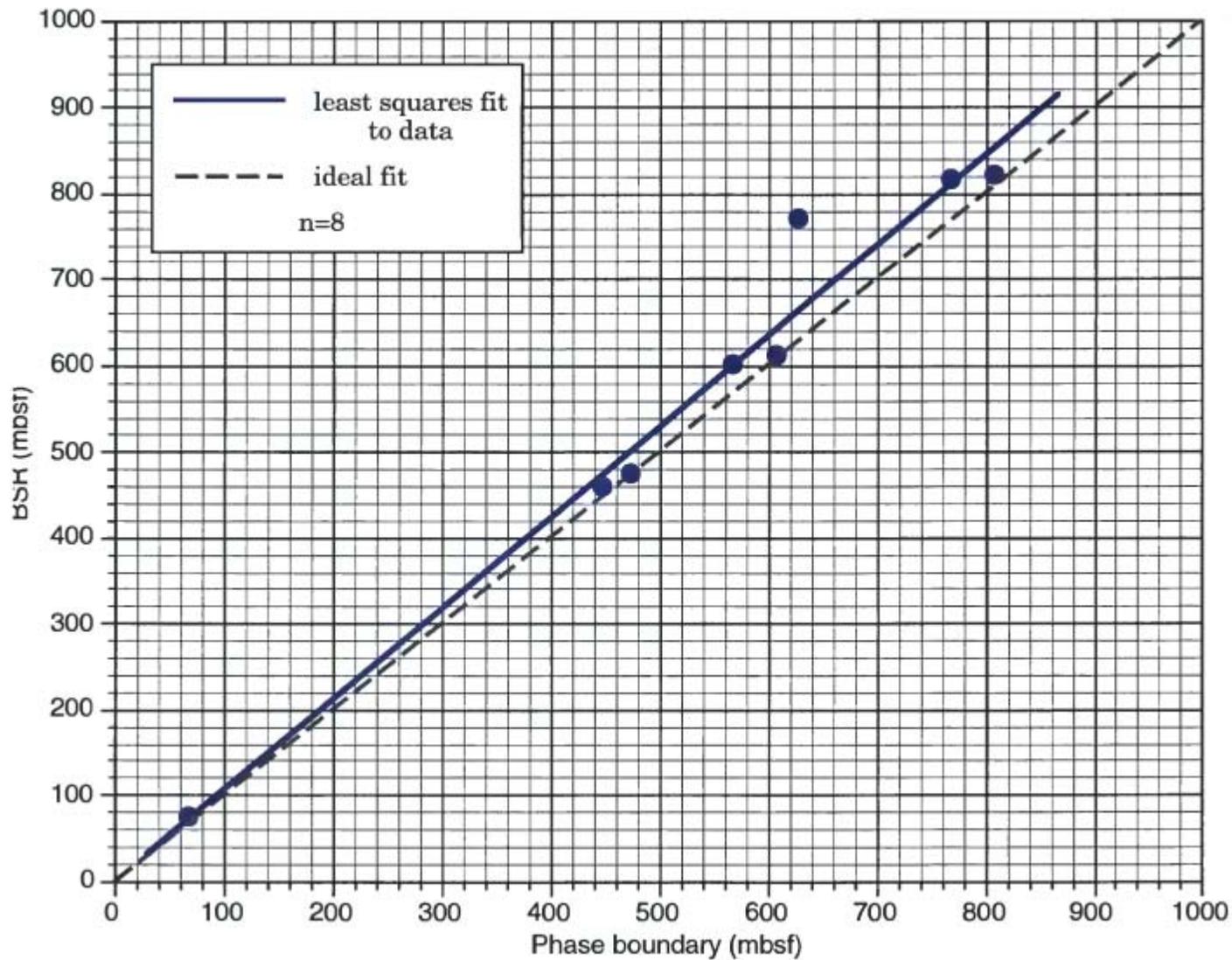


Figure 10. Relationship between position of phase boundary and position of BSR. Depths to phase boundaries based on Claypool and Kaplan; depths to BSR's based on assumed velocities of sound in sediment at each site by authors. (See Appendix.) The term "ideal fit" represents the concept that the BSR originates at the phase boundary.