

THE EVOLUTION OF AN IDEA: FROM AVOIDING GAS HYDRATES TO ACTIVELY DRILLING FOR THEM

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INTRODUCTION

Over the past decade and a half the Ocean Drilling Program (ODP) has contributed to an amazing turn-around in the perception of marine gas hydrates, one of the hottest topics in geoscience today. In 1986, the JOIDES Pollution Prevention and Safety Panel (PPSP) recommended:

"In theory, the gas-hydrate stability zone may be drilled without danger of gas release..., however, a gas-hydrate layer may cap and seal reservoir rocks which are filled with gas.... In view of these considerations...the PPSP policy has been that drilling should not be carried into the strata underlying the gas-hydrate stability zone..."

The same panel softened its view in 1992:

"Indirect evidence for gas hydrate occurrence in deep sea sediments is the bottom-simulating seismic reflection (BSR) that is sometimes present at the base of the gas hydrate stability zone. Previous safety advice was that drilling should not continue beneath the theoretical depth of methane hydrate stability.... Subsequent reinterpretation indicates that quantities of free gas beneath the gas hydrate stability zone should be minor, and that the gas pressure should be controlled at hydrostatic by equilibrium with gas hydrate. Based on this reinterpretation, PPSP has approved drilling beneath visible BSRs in geologic settings that are otherwise considered safe..."

Now, eight years later, the ODP community has an even more enthusiastic view as stated in the COMPLEX Report:

"Ocean drilling revealed the hydrate system, ...recovered hydrates, fluids, and gas as well as tantalizing evidence of their effects on the subsurface environment...and will continue to provide crucial evidence about it.... Thus, there is a challenging new opportunity for a future integrated program of ocean drilling to establish an ocean-wide network of hydrate sampling sites...the only avenue for us to gain insight into how the processes of hydrate formation and release affect the global biogeochemical cycle and how they are related to tectonic processes..."

What has happened, and why has gas hydrate gone from a phenomenon to be avoided to one of the most important initiatives of the future Integrated Ocean Drilling Program (IODP)?

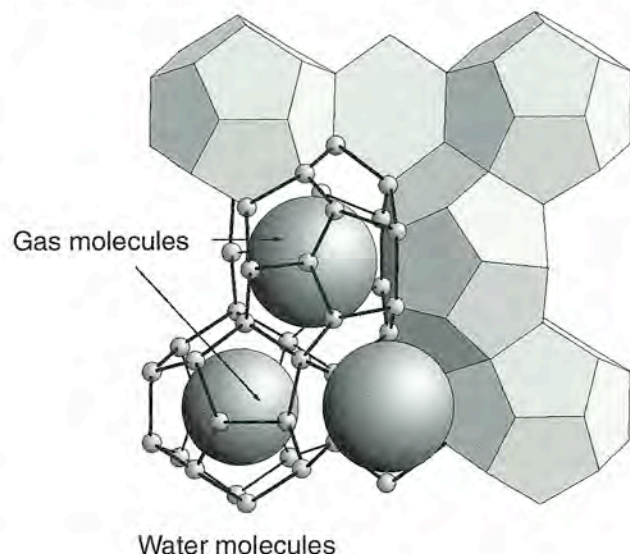
This overview begins with general information on the structure and composition of gas hydrates, and then addresses their stability in the marine environment and

evidence for their existence in sub-seafloor acoustic records and the Cl anomaly pattern. The final discussion is on the role of gas hydrate as a methane store that fuels unique seafloor and sub-seafloor ecosystems, affects global climate, and may provide a potential energy resource for the future.

STRUCTURE AND COMPOSITION

It has long been known that natural gas hydrates occur globally in marine sediments, in permafrost regions, and in the continental ice sheets (Kvenvolden et al., 1993). They are solid compounds similar to ice crystals where cages of water molecules enclose molecules of natural gases (Fig. 1). The gases mostly are methane but also include ethane, propane and butane, as well as carbon dioxide and hydrogen sulfide (Sloan, 1990). Three types of crystal structures are found in nature; type I and II belong to the cubic system, and type H to the hexagonal crystal system (Fig. 1). The formation of gas hydrates depends on the presence of sufficiently high gas content, elevated pressure, and low temperature. Their dominant component, methane (CH_4), is largely a diagenetic product of fermentative decomposition of organic matter or of bacterial CO_2 reduction in sediments. Methane also is sometimes formed, along

Figure 1. Gas hydrate of type I structure. Small spheres are tetrahedrally-linked water molecules which comprise the cages; large spheres are gas molecules. Four (5^{12})-cages are shown, one at each corner composed of twelve five-sided polygons known as pentagonal dodecahedra, and two ($5^{12}6^2$)-cages in the center facing each other, composed of twelve five-sided and two six-sided polygons. The (5^{12})-cages are present in all three gas hydrate structure types.



with higher hydrocarbons by thermocatalytic conversion of organic material in the deeper subsurface. In the latter case, the methane migrates from these deeper sources, often from hydrocarbon reservoirs, into the hydrate stability zone. The largest deposits of gas hydrates are found along continental margins where formation of methane is favored by rapid sedimentation and high contents of sedimentary organic matter providing extensive microbial fermentation.

THE HYDRATE STABILITY ZONE AND THE BOTTOM SIMULATING REFLECTOR

Gas hydrates respond rapidly and completely to changes in pressure and temperature by re-equilibration or dissociation. Compositional changes in the environment also exert a significant role on stability. Salinity reduces it, whereas trace gases enlarge the stability field when the temperature is kept constant (Sloan, 1990). The effects are not linear but increase with total pressure. A five-fold increase in salinity, for example, requires the equilibrium pressure to increase by about 13 bar at 300

m of water depth and by about 40 bar at 700 m of water depth (Fig. 2). This increase is equivalent to a change of >200m in the hydrate stability zone (HSZ). On the other hand, incorporation of about 3 mol-% H_2S at 700 m of water depth lowers the equilibrium pressure by the equivalent of 15 m. These effects lead to considerable uncertainties in the predicted depth of the HSZ, a fact that is not widely appreciated.

Hydrogen sulfide (H_2S) strongly affects the stability of gas hydrates (Fig. 2). Since reports on the H_2S content vary widely, the shift of the HSZ and bottom-simulating reflections (BSRs) can be large. For example, during Leg 146 drilling at the Cascadia Margin, hydrates with from 0.05 to 10 mol-% of H_2S were found; no H_2S was reported from hydrates of the Blake Ridge during Leg 164 drilling, and the H_2S level of Chilean margin hydrates likewise appeared very low during Leg 141. The other extreme comes from a Leg 182 report postulating gas hydrates with 10 to 30 mol-% H_2S in the sediments drilled off the Eucla Margin of South Australia. It is possible that very little H_2S is actually present in the hydrate lattice, and that rather high amounts might be trapped in the pore space. With these uncertainties, technological advances in drilling and maintaining hydrates under *in situ* conditions will continue to be essential. Only then can we gain basic knowledge about their distribution and correlation with the acoustic response of sub-seafloor hydrate deposits.

The presence of gas hydrate in sediments beneath the sea floor is usually identified from a BSR, a negative polarity compressional (p)-wave reflection parallel to the seafloor that is imaged at the base of the hydrate stability zone (HSZ). Previously, the BSR was assumed to result from the contrast between high acoustic impedance of hydrate-filled sediment overlying a lower impedance hydrate-free zone. However, seismic modelling studies, new data, and high-resolution wide-angle multi-channel seismic reflection (MCS) data have shown that the development of a strong BSR requires the presence of certain amounts of free gas beneath the hydrate-cemented sediment (Mienert et al., 2001; Pecher et al., 1996; Bangs et al., 1993; Fig. 3). Leg 164 data support these interpretations; a BSR is present in a zone

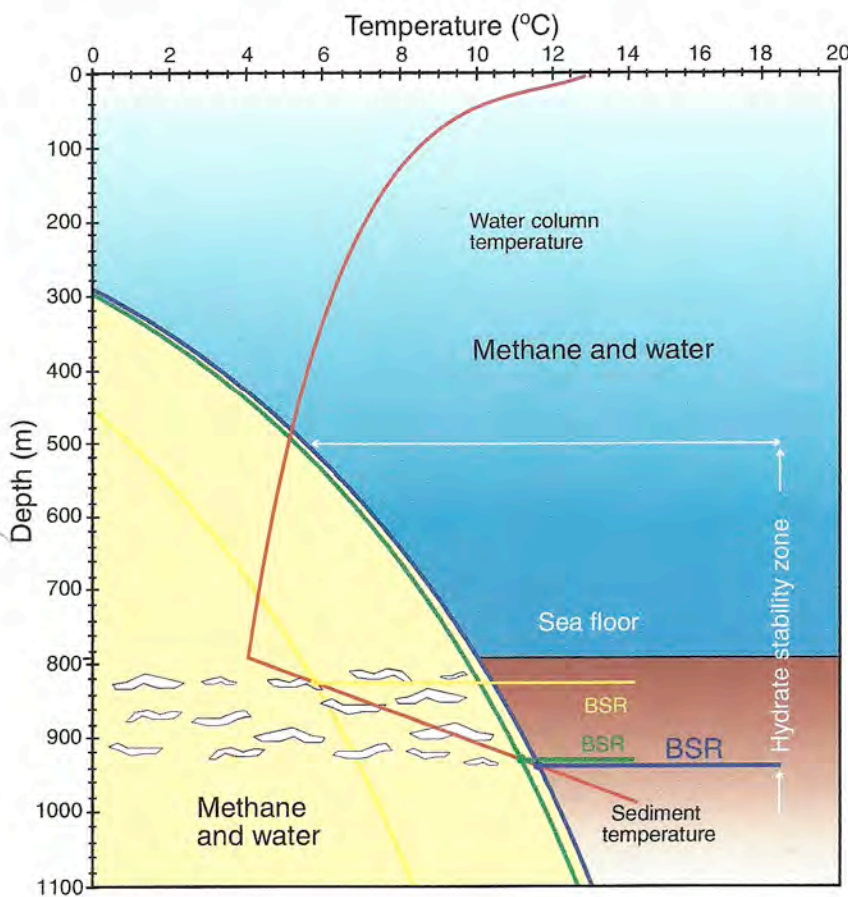


Figure 2. Stability and phase boundaries of gas hydrates superimposed on depth-temperature distribution (red) in the ocean and the upper sediment column. Also shown are the phase boundary of pure methane hydrate at normal seawater salinity (green), the phase boundary of methane hydrate with 3 mol-% H_2S at seawater salinity (blue), and the phase boundary of pure methane hydrate in five times sea water salinity (yellow). Intersections of temperature profiles with the phase boundaries define the hydrate stability zone (HSZ) and the bottom simulating reflection (BSR) for each of the three hydrate compositions.

containing free gas immediately beneath the hydrate, but no BSR is present where free gas is absent (Holbrook et al., 1996). Thus, although the presence of a BSR means that gas hydrates are present, the converse is not true. The absence of a BSR does not mean there are no hydrates.

CHLORIDE-ANOMALY PATTERN AND THE "MISSING SALT"

Direct retrieval of gas hydrates on board ship, without maintaining *in situ* conditions, is usually a matter of pure luck. Hydrate samples that "survive" have begun to dissociate or might be contaminated. Hence, their composition and physical properties can only be characterized in a limited way. Nevertheless, significant advances have been made in understanding marine gas hydrates from the beginning of the Deep Sea Drilling Project (DSDP Leg 67 and Leg 76) and continuing through ODP (Legs 112, 141, 146, and 164, the latter having been dedicated to gas hydrate sampling). Along with actual pieces of recovered gas hydrate, indirect evidence for their presence exists in pore fluids through the well-known artifact of negative Cl anomalies. Gas hydrates were first indicated, later documented, and eventually quantified by chloride anomalies. These anomalies result from the release of hydrate water during core retrieval, causing dilution of the normal pore-fluid salinities and chlorosities. This effect is known as "freshening" among the ODP community.

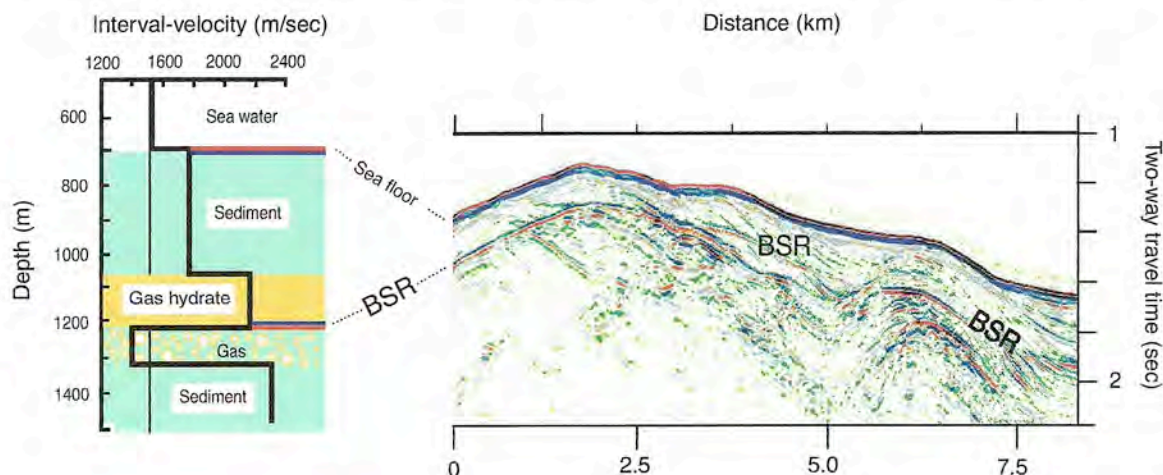
From such freshening of fluids, it is estimated that 10-15% of the available pore space in the Chilean and Cascadia accretionary sediments is occupied by hydrate. On the Blake Ridge, it is estimated to increase from 1.4% at the ridge flank to at least 2.1% at the crest

(Matsumoto, 2000). We still largely rely on this Cl anomaly as the best evidence for the presence of hydrates, although new data from hydrates exposed at the sea-floor suggest that the calculation of the amount of hydrate has been significantly underestimated due to residual chloride trapped within the hydrate pore space (Suess et al., 2001). The same has been observed when synthesizing hydrates in NaCl solutions. It is unknown whether trapped ions also are present in deep hydrates.

Although "freshening" of pore fluids is observed in cores, the opposite (enrichment) should occur *in situ* because the ions of sea salt and the light isotopes of water, ^{16}O and ^1H , are excluded and become enriched in the residual pore fluid. Over the past decade and a half of ODP drilling, convincing evidence for "excess salt" as well as "light isotopes" has remained elusive. On the contrary, as seen above, dissociation of hydrate during core retrieval tends to mask and even reverse any "salt and light isotope" exclusion.

Leg 146 (Kastner et al., 1998) and Leg 164 (Matsumoto, 2000) pore fluid data were used to derive an O isotope fractionation factor, $\alpha = 1.003$, for *in situ* hydrate formation (Fig. 4). This factor agrees with the value estimated from hydrate water analyses and with experimentally derived values (Maekawa and Imai, 2000). Figure 4 illustrates how the fractionation of ^{18}O -to- ^{16}O between pore water and hydrate water derived from dissociation is related to the fractionation under *in situ* conditions, assuming a closed system. Only the latter case represents the "real world". No data have yet been discovered from that situation in the field. Ocean drilling and recovery of hydrated sediment under *in situ* conditions are the only means with which to verify this process.

Figure 3. Schematic seismic velocity distribution of sub-seafloor strata (left) and seismic profile across hydrate and gas-containing strata showing layered and folded structures with cross-cutting bottom simulating reflection (BSR; right). Red=large positive amplitude p-waves, and blue=large negative amplitude p-waves. BSR with negative polarity comes from the contrast between high acoustic impedance of hydrate-filled sediment (>2000 m/sec) and free gas-containing sediment (<1500 m/sec). Sea floor reflection shows positive polarity from contrast between sea water seismic velocity (1500 m/sec) and sediment velocity (about 1800 m/sec).



ANAEROBIC METHANE OXIDATION AND THE GAS HYDRATE CONNECTION

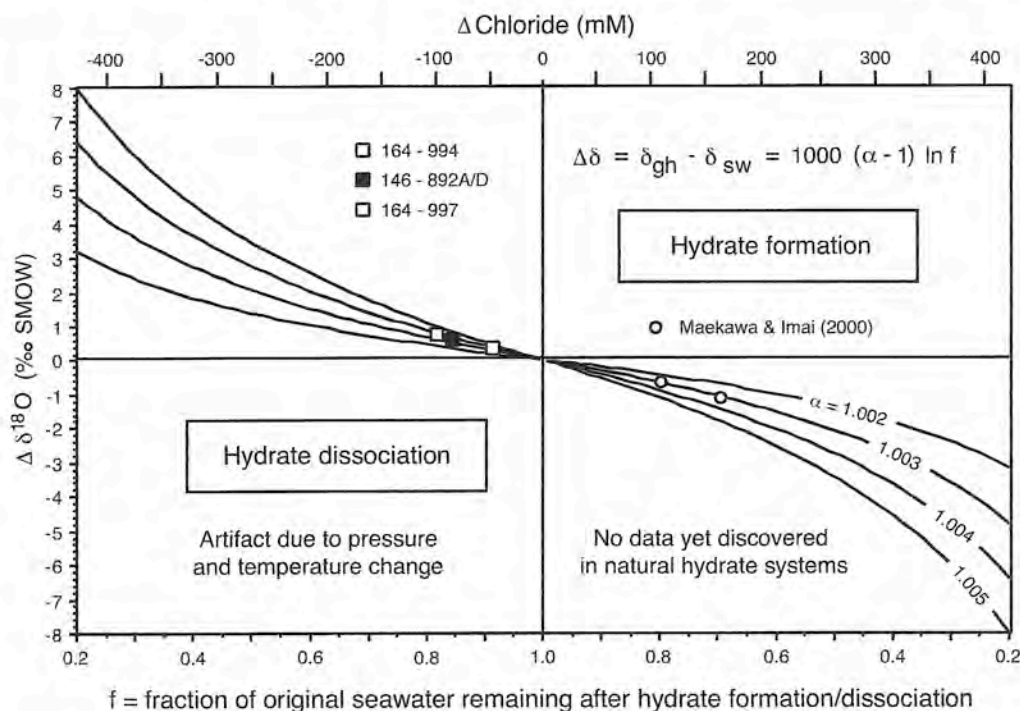
Methane from gas hydrates greatly stimulates microbial activity not only at the seafloor but much deeper than previously believed. High levels of microbial methane oxidation and high cell counts from sediments of the gas hydrate stability zone and underlying free gas zone were among the outstanding results of ODP data collected during Legs 146 and 164. These data suggest that microbes extensively oxidize methane, apparently utilizing sulfate in the absence of oxygen. Such a process has long been suspected by geochemists, based on reaction-transport models of interstitial sulfate and methane (Borowski et al., 2000). The recent first identification of a microbial consortium of methanotrophic archaeobacteria and sulfate-reducing bacteria from gas hydrate-bearing sediments (Boetius et al., 2000), has opened the door for anaerobic methane oxidation (AMO) research. The increasing library of biomarkers, combined with C isotopes information on the molecular level, promise an enormous leap in the basic knowledge of these processes (Elvert et al., 1999).

The significance of this ongoing research, and the essential role of ODP, is dealt with in the chapter on The Deep Biosphere (D'Hondt, this volume). In the context of this article, emphasis is placed on the importance of AMO for the formation of authigenic hydrate-carbonates, limestone buildups at the seafloor known as "chemohermes" (Bohrmann et al., 1998). Other AMO-related features are crusts, concretions, cement, and massive limestone beds in deep continental margin sediments, often referred to as "organic carbonates".

The biogeochemical process underlying this carbonate formation and its intimate association with gas hydrates can be gleaned from the set of reactions shown in Table 1. Gas hydrates provide an almost inexhaustible supply of isotopically "light" methane (shown in red as $^{13}\text{C}/^{12}\text{C}$) which is transformed by the microbial consortium into bicarbonate. The bicarbonate then equilibrates with pore water containing ^{18}O -enriched hydrate water (shown in blue as $^{18}\text{O}/^{16}\text{O}$). This process is unique for the recognition of gas-hydrate involvement because the oxygen isotope signal is "heavier" than expected from normal pore water. This "heavy" water signal originates from hydrate water via dissociation and is recorded by the precipitating CaCO_3 phases along with isotopically "light" calcium carbonate (shown in blue and red). The mineral phases formed are low- and high-Mg calcites with a highly enriched ^{12}C isotope signal of up to -60‰ PDB. Aragonite and dolomite have been reported with similar C isotope signals.

The hydrate-associated carbonates also faithfully preserve biomarker evidence for the individual microbial reactions involved in methane oxidation from gas hydrates. These are shown in red in Table 1 as two types of "lipid biomarker". One group is synthesized by sulfate-reducing bacteria (SRBs), the other by archaeobacteria (Boetius et al., 2000). Biomarkers of archaeobacteria consist of irregular saturated and unsaturated isoprenoids known as crocetane and pentamethylcosane (PMI). They are the dominant compounds obtained from gas hydrate-containing sediments and carbonate precipitates. Crocetane and PMI in such a setting are specific for known methanogenic archaeobacteria, which grow on methane as their carbon

Figure 4. Oxygen isotope fractionation ($\Delta\delta^{18}\text{O}$) between pore water and hydrate water and simultaneous Cl anomaly (ΔCl mM). Hydrate dissociation (left quadrant=artifact) causes Cl dilution and ^{18}O enrichment; hydrate formation (right quadrant=real world) causes Cl enrichment and ^{18}O depletion. The fraction factor, $\alpha=1.003$, was derived from Leg 146 and Leg 164 pore fluid data, and agrees with experimentally derived values.



source rather than forming it as a metabolic product. The sulfate-reducing bacteria of the consortium are recognized by other lipid biomarkers. The association of archaeobacteria- and SRB-derived biomarkers identify the AMO consortium. Both groups of molecular compounds also contain ultra-high enrichments of ^{12}C derived from hydrate methane; $\Delta\delta^{13}\text{C}$ values of between -102 and -124‰ PDB for crocetane and PMI have been reported (Elvert et al., 1999). These unambiguously document the gas hydrate connection.

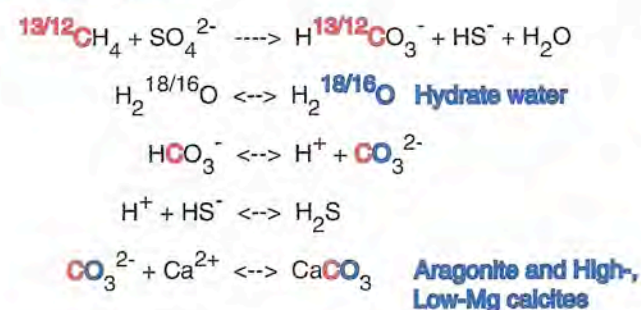
FUTURE ENERGY RESOURCE AND IMPACT ON CLIMATE

Marine as well as permafrost-bound gas hydrates have come under increased world-wide attention. The large volumes of methane stored in these deposits represent a significant fraction of the global methane budget, and may be an almost inexhaustible energy resource for the future (Kvenvolden et al., 1993; Booth et al., 1998).

Massive and catastrophic release of methane hydrates from sub-seafloor deposits are believed to have triggered transient warm climates, and are implicated in the generation of large submarine slides with ensuing tsunamis (Dickens et al., 1999; MacDonald, 1990). One locality from which such a catastrophic release has been identified through ODP drilling is the Blake Spur in the western Atlantic. The evidence is based on chaotic and brecciated sediment fabric from disrupted strata left behind after methane eruption during the Late Pale-

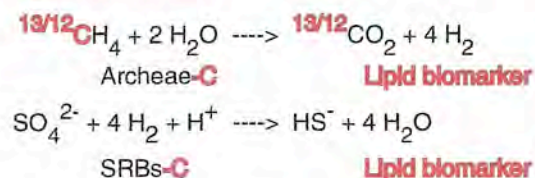
Overall reaction by microbial consortium

Hydrate methane



Possible individual reactions

Hydrate methane



ocene Thermal Maximum (LPTM), a time of extremely warm global climate (Norris and Roehl, 1999).

Generally, release of large amounts of methane implies a positive climate feedback (MacDonald, 1990). Dissociation of hydrate from shelf and upper slope deposits caused by post-glacial warming may further accelerate global greenhouse warming. Conversely, sea-level lowering during initiation of ice-ages may have a negative feedback. This also is caused by dissociation of continental margin hydrates, but with the effect of inhibiting further cooling and lowering of sea level (Paull et al., 1991). Dissociation of hydrates in either scenario could mechanically destabilize continental margin sediments and lead to massive slides.

A third possible way for gas hydrates to affect global climate is by "hydrate floats". These chunks of porous, positively buoyant hydrate constitute an efficient mechanism for rapid transport of methane directly into the atmosphere, where it is climatically active. Large chunks of gas hydrate, newly formed from free methane gas in near-surface sediments, have been observed to detach from the seafloor and float to the surface (Suess et al., 2001). Central to the hypothesis of hydrate floats is the role of the porous hydrate fabric. It consists of macroscopic pores filled with free methane providing the buoyancy. These scenarios remain speculative, however, as the volume of gas stored in the hydrate reservoir, and its physical and chemical properties and behavior during changing environmental conditions, are currently not well understood.

OUTLOOK

Research on natural methane hydrates, in seafloor and deep sub-seafloor settings at active and passive continental margins, is a topic of world-wide interest. IODP is set to play a leading role in the following high priority gas hydrate research topics in the coming decade:

- Recent data indicate the existence of highly specialized ecosystems in seafloor gas-hydrate sites and in hydrates of deeply buried strata, where large quantities of methane carbon are efficiently converted. Characterization and quantification of turn-over rates of methane from gas hydrates is indispensable to understanding the global carbon cycle.
- The quantification of hydrates and free gas is a high priority. The relationship between seismic detection

Table 1. Coupled anaerobic methane oxidation (AMO) and calcium carbonate precipitation as unique process for gas hydrate environment. Hydrate methane= $^{13/12}\text{CH}_4$ and hydrate water= $\text{H}_2^{18/16}\text{O}$ are involved in precipitating "hydrate-CaCO₃-phases". Groups of lipid biomarkers from methane oxidizing consortium (sulfate-reducing bacteria=SRBs and Archeobacteria) contain ultra-high enrichments of ^{12}C ; ($\Delta\delta^{13}\text{C}=-102$ and -124‰ PDB).

and quantity, as well as phase properties of gases and hydrates, is poorly understood. Gas hydrate thermodynamics and kinetics also affect seismic properties.

- The role of hydrate methane as a greenhouse gas has not been adequately considered in global climate models. Data from paleoclimate research suggest that gas hydrates might have played an important role in the world's climate. Gas hydrates are sensitive to the equilibrium of the natural environment. They are stable under low temperatures and/or high pressure but respond rapidly to changes, providing a modulator for the greenhouse gas budget.
- The influence of hydrate on slope stability, the mechanical behavior of sediments and their resulting hazards are not known. However, evidence from the geologic record is mounting that gas hydrate dissociation may often trigger submarine slumps and slides, possibly leading to damage of off-shore structures as well as generating devastating tsunamis.
- The exploitation of gas hydrates as an efficient energy source has been unsuccessful due to the complex technical requirements for economical extraction despite existing offshore and onshore expertise. Potentially serious environmental consequences, and the continued emission of CO₂ when using hydrate as fuel, may ultimately prevent worldwide exploitation.

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