

ACCUMULATION OF SUBMARINE GAS HYDRATES

Gabriel D. Ginsburg and Valery A. Soloviev
Research Institute for Geology and Mineral Resources of the Ocean
1, Angliyskiy prospekt, St.Petersburg, 190121 Russia

Keywords: submarine gas hydrates, accumulation mechanisms, fluid migration

INTRODUCTION

During last fifteen years the authors have been studying the generation and accumulation of submarine gas hydrates. In particular, expeditions have been carried out in the Caspian, Black, and Okhotsk seas (Ginsburg et al., 1990, 1992, 1993), and the Norwegian Sea (1996, unpublished). The results of our investigations have been summarized in a monograph (Ginsburg and Soloviev, 1994). That is the basis of this presentation.

RESULTS AND DISCUSSION

The analysis of the worldwide observational data suggests that submarine hydrates largely occur in local accumulations (Ginsburg and Soloviev, 1994, 1995). All observed submarine gas hydrates are readily divisible into two groups: associated and non-associated with fluid vents. Hydrates of the first group, which have been observed close to the sea floor in the Caspian, Black, Okhotsk and Norwegian seas, the Gulf of Mexico, and in several other sites (altogether in 11 regions, Fig.1) are controlled by fluid conduits: mud volcanoes, diapirs, and faults. As for the second group of gas-hydrates (deep-seated), their control by fluid flow may be usually deduced from an association with indirect borehole indications of fluid flows, such as relatively coarse-grained sediments and anomalies of pore water chlorinity (Figs.2, 3).

The generation, accumulation and disappearance of any water-soluble naturally occurring compound in terms of water availability are governed by solubility variations of this compound. This is true also in regard to gas hydrates. It is extremely important for natural gas hydrate formation that the solubility of methane (which is the major component of natural hydrates) in water in terms of hydrate stability is little affected by the general (hydrostatic) pressure (contrary to "normal" conditions of hydrate instability) but is dictated essentially by the equilibrium pressure of hydrate formation, which is temperature-dependent. Since the equilibrium pressure of hydrate stability is diminished with decreasing temperature, methane solubility in water also decreases (Fig.4, solid line). Because of this, the solubility of methane in pore waters generally decreases towards the sea floor within the submarine gas hydrate stability zone (Fig.5). The higher the geothermal gradient, accordingly the thinner the hydrate stability zone, the sharper is the methane solubility decrease.

Three major mechanisms of methane transport in sediments can be distinguished: dissolved in pore water flows, as free gas flows, and molecular diffusion. Hydrate precipitation from ascending methane-saturated water is thought to be the most straightforward (Ginsburg, 1990; Ginsburg and Soloviev, 1994). The hydrate zone forms a gas-geochemical barrier for methane-saturated water which rises either from below or from within this zone: as the water cools it should precipitate hydrate. The amount of precipitated hydrate obviously corresponds to the excess of dissolved methane (i.e., over the solubility). Clearly the effectiveness of this process depends, in particular, on the rate of water flow and the water temperature; in the case of focused flow of warm water, the thickness of the submarine hydrate zone can decrease to zero. Gas hydrates being precipitated from infiltrated waters are progressively filling the sediment pore space and/or fracture porosity and eventually cement them, producing massive and vein hydrate sediment structures.

Gas hydrates associated with free gas flows discharging on the sea floor were observed in the Gulf of Mexico (Brooks et al., 1994) and in the Okhotsk Sea (Ginsburg et al., 1993). Clearly, the gas seeping through the hydrate stability zone has no time to crystallize as a hydrate. After a hydrate film forms at the gas-water interface, each succeeding portion of free gas, prior to hydration, has to penetrate this film. Thus the rate of hydrate formation in the vicinity of free gas flows is limited by the rate of this penetration (i.e., the rate of molecular diffusion), and hydrates are accumulated primarily from the water-dissolved gas: a solid (hydrate) phase grows at a distance from free gas. The lateral outward diffusion of methane of the ascending gas flow appears to be governed by the difference between chemical potentials of gaseous and dissolved methane at common depths. The above difference is deduced from the difference between the pressure of a free methane close to the hydrostatic pressure and the vapour pressure of dissolved methane, which in terms of pore water saturation should be close to the equilibrium pressure of gas hydrate formation (compare P_h and P_{eq} on Fig.6). Since this difference decreases with increasing subbottom depth, hydrate accumulations associated with ascending free gas flows are assumed to taper off downward. Accumulations of this type at great water depths should be more extensive than shallow ones (other factors being equal) because the considered difference increases with deepening water. It is self-evident that this model simplifies the matter. In fact, the heat release caused by hydrate formation enhances the outward methane transport and extends the diffusion aureole around ascending gas flow. Within this aureole the hydrates are thought to result not only from outward diffusing methane

but also from upward diffusion, the intensity of which is controlled by high gradients of concentration and vapor pressure of water-dissolved methane in the hydrate zone (in terms of methane-saturated water); these gradients greatly exceed values outside the hydrate zone (Figs.5 and 6).

A similar pattern of methane diffusion and gas hydrate accumulation should also characterize the vicinity of ascending flows of gas-saturated water. In particular this is possible around the water flows which are too warm for hydrate precipitation. High gradient of temperature nearby these flows provides favorable conditions for rapid gas hydrate accumulation.

It is generally believed that diffusion plays only a destructive role in the history of hydrocarbon accumulations. In contrast, Egorov (1988) has put forward the concept of "directional diffusion recondensation". This implies the diffusional transfer of hydrocarbons which saturate water in the presence of a temperature-controlled solubility gradient. According to this concept, the formation and accumulation of a hydrocarbon phase in the region of lower temperature results from such a transfer. We suggest that directional diffusion recondensation is just the process which governs gas hydrate accumulation in the vicinity of free gas and gas-saturated water flows, as well as within and above the sediment sections where biochemical methane is intensively generated. Relatively impervious sediments may act as a cap in this process. DSDP-ODP data offer examples of gas hydrate occurrences close to the boundary between relatively coarse- and fine-grained sediments (Ginsburg and Soloviev, 1994).

Thus, gas hydrates accumulate from water solutions, no matter whether methane is delivered into the reaction zone, by infiltration or diffusion. The important distinction between two modes of hydrate accumulation in sediments (aside from the process rate) lies in the source of hydrate water. In the case of hydrate precipitation from infiltrated gas-saturated water this source is flow itself; in the case of diffusional methane delivery the hydrate water is extracted from sediment pore water in-situ.

We have proposed the term segregation to designate the mechanism of hydrate accumulation from diffusing gas and from water being extracted from sediments (Ginsburg and Soloviev, 1994). A continuous delivery of methane and the associated formation of hydrate generates a migration of pure water into the reaction zone from the adjacent sediments or sea water. This mechanism of water migration is thought to be diffusion-osmotic. Hydrate inclusions of a different shape are formed during this process due to the dewatering of surrounding sediments if the latter are compacted. The shape of inclusions is obviously caused by the factors controlling the fields of gas and water chemical potentials. In particular the subhorizontal lenticular-bedded hydrate sediment structure observed in association with submarine gas vents in the Okhotsk Sea (Ginsburg et al., 1993) may result from the subhorizontal extension of isotherms.

As a result of water redistribution during segregational gas hydrate accumulation, the total water content of hydrate-bearing sediments may turn out to be higher than that of the adjacent nonhydrated ones, as has been observed in the Okhotsk Sea (Ginsburg et al., 1993). A water content of sediments directly proportional to their hydrate content has been demonstrated in the Caspian Sea (Ginsburg et al., 1992). Hence the hydrate accumulation in sediments may imply not only gathering of gas but also of water. Due to hydrate water abundance, a sediment may become fluidized upon decomposition of hydrate.

Diffusion is known to be an ubiquitous process in marine sediments. Since a hydrate of any origin is subject to subsequent decomposition and possible diffusional recondensation of the released hydrate methane, segregational hydrates are thought to be more common than those precipitated by infiltrated water.

We mentioned two kinds of inhomogeneity of the geological medium exerting influence upon gas hydrate accumulation: permeability variations, which control fluid conduits and gas hydrate caps, and geothermal inhomogeneity (geothermal gradient), which predominantly governs gas solubility in water. In addition two other kinds of inhomogeneity - hydrochemical and lithological can have a pronounced effect on this process. It is well-known that water-dissolved salts inhibit (prevent) gas hydrate formation, i.e. hydrates form more readily from fresh water. Therefore, a gradient of water salinity within the hydrate zone under gas-saturation conditions must provoke a diffusional flux of methane into fresh water, where this arriving methane should be hydrated. Such a situation may occur near boundaries of water flows. It is necessary to emphasize here that the solubility of methane in the fresh gas-saturated water is known to be higher than in saline water, whereas the corresponding methane fugacity, which actually should be considered as a driving force of diffusion, is higher in saline water (Handa, 1990).

A lithological (or in more exact terms, a porometric) inhomogeneity implies, in particular, a distinction of sediment pore size (we do not consider here a shape of sediment pores and their specific properties, which of course also affect gas hydrate accumulation). The pore medium influences the hydrate equilibrium (thermodynamic effect) and the kinetics of hydrate formation. The thermodynamic effect essentially is as follows: a pore surface is hydrophilic and

therefore lowers the pore water chemical potential. As a result, a higher thermodynamic concentration of methane is required for the formation of hydrate. In principle, this effect is similar to the influence of salts dissolved in water. This surface effect was studied by many authors and had been found negligible in terms of natural sediment water content. The kinetic effect lies in the fact that a pore size may be less than a gas hydrate critical nucleus size at a given temperature. In this case, for hydrate formation to start, more significant overcooling or oversaturation is required (Chersky and Mikhailov, 1990). We suggest that the essence of both effects (thermodynamic and kinetic) can be understood by examination of hydrate formation in adjacent sediments having different pore sizes. It is evident that the hydrate formation in coarse-pored sediments has an advantage over fine-pored ones - the same gas concentration in water may turn out to be sufficient to form hydrates in the former case and insufficient in the latter. What this means is hydrate can accumulate rather in relatively large pores in the course of sediment compaction and/or biochemical gas generation.

CONCLUSIONS

Submarine gas hydrates mostly occur locally and are linked to fluid flows. They accumulate from methane-saturated water, in the course of pore water infiltration and methane diffusion. Apart from the methane availability the accumulation of hydrates is controlled by physical factors such as temperature gradient, pore water salinity gradient and lithological variability. The hydrates precipitate at lower temperatures and from less saline water; relatively coarse-grained sediments make better hydrate reservoirs than fine-grained sediments.

REFERENCES

- Brooks, J.M., Anderson, A.L., Sassen, R., MacDonald, I.R., Kennicutt II, M.C. and Guinasso, N.L., Jr., 1994. Hydrate occurrences in shallow subsurface cores from continental slope sediments. In: E.D. Sloan, Jr., J. Happel and M.A. Hnatow (Eds.), *Int. Conf. on Natural Gas Hydrates*. Annals of the New York Acad. Sci., 715: 381-391.
- Cherskiy, N.V. and Mikhailov, N.E., 1990. Size of equilibrium critical nuclei of gas hydrates. *Doklady Akademii Nauk SSSR*, 312(4): 968-971 (in Russian).
- Egorov, A.V., 1988. Diffusional Mechanisms of Hydrocarbons Primary Migration and Accumulation in Offshore Sedimentary Basins, Thesis. Institut Okeanologii Akademii Nauk SSSR, Moscow, 218pp. (in Russian).
- Gieskes, J.M., Johnston, K., Boehm, M., 1985. Appendix. Interstitial water studies. Leg 66. In: von Huene, R., Aubouin, J. et al. *Init. Repts. DSDP, 84: Washington, D.C.*: 961-967.
- Ginsburg, G.D., 1990. Submarine gas hydrate formation from seeping gas-saturated underground waters. *Doklady Akademii Nauk SSSR*, 313(2): 410-412 (in Russian).
- Ginsburg, G.D. and Soloviev, V.A., 1994. Submarine Gas Hydrates. *VNIIOkeangeologia, St.Petersburg*, 199 pp. (in Russian, with English abstract).
- Ginsburg, G.D. and Soloviev, V.A., 1995. Submarine gas hydrate estimation: theoretical and empirical approaches. *Proc. 27th Annu. OTC., Houston, Texas, USA, 1-4 May 1995*: 513-518.
- Ginsburg, G.D., Kremlev, A.N., Grigor'ev, M.N., Larkin, G.V., Pavlenkin, A.D. and Saltykova, N.A., 1990. Nitrogenic gas hydrates in the Black Sea (twenty-first voyage of the research vessel "Evpatoriya"). *Soviet Geology and Geophysics (Geologia i Geofizika)*, 31(3): 8-16.
- Ginsburg, G.D., Guseynov, R.A., Dadashev, G.A., Ivanova, G.A., Kazantsev, S.A., Solov'yev, V.A., Telepnev, E.V., Askeri-Nasirov, R.Ye., Yesikov, A.D., Mal'tseva, V.I., Mashirov, Yu.G. and Shabayeva, I.Yu., 1992. Gas hydrates of the Southern Caspian. *Int. Geol. Rev.*, 34(8): 765-782.
- Ginsburg, G.D., Soloviev, V.A., Cranston, R.E., Lorenson, T.D., Kvenvolden, K.A., 1993. Gas hydrates from continental slope offshore from Sakhalin Island, Okhotsk Sea. *Geo-Marine Letters*, 13: 41-48.
- Handa, Y.P., 1990. Effect of hydrostatic pressure and salinity on the stability of gas hydrates. *Journ. Phys. Chem.*, 94(6): 2652-2657.
- Makogon, Yu.F. and Davidson, D.W., 1983. Influence of excessive pressure on methane hydrate stability. *Gazovaya promyshlennost'*, 4: 37-40 (in Russian).
- Namiot, A.Yu., 1991. Solubility of Gases in Water. Reference Textbook. Nedra, Moscow, 167 pp. (in Russian).
- von Huene, R., Aubouin, J. et al., 1985. *Init. Repts. DSDP, 84: Washington, D.C.*
- Watkins, J.S., Moore, J.C. et al., 1981. *Init. Repts. DSDP, 66: Washington, D.C.*

FIGURES

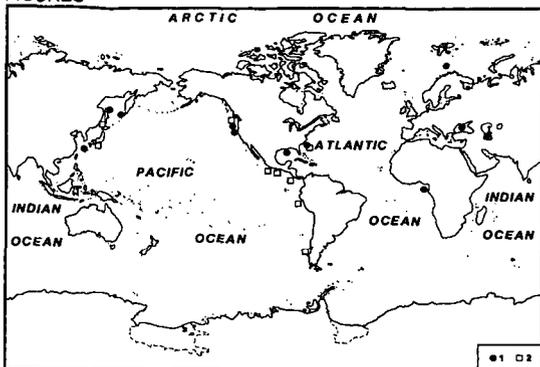


Fig.1. Worldwide locations of observed submarine gas hydrates. Updated after Ginsburg and Soloviev, 1994. 1, 2 - sea floor seepage-associated and non-associated gas hydrates, respectively.

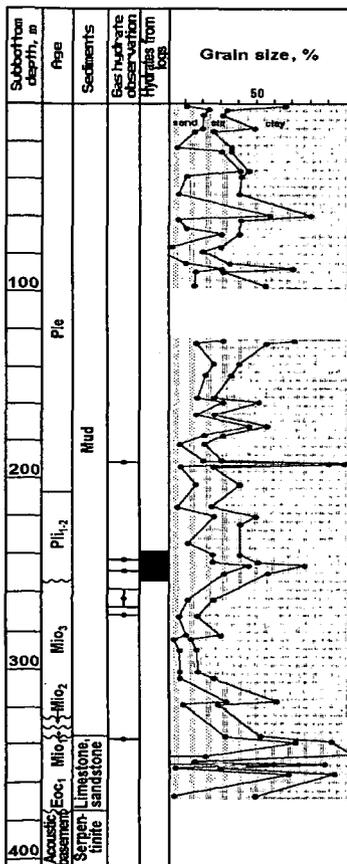


Fig.2. Gas hydrate shows and sediment grain size in geological section at DSDP Site 570, Middle America Trench. Compiled from von Huene, Aubouin et al., 1985.

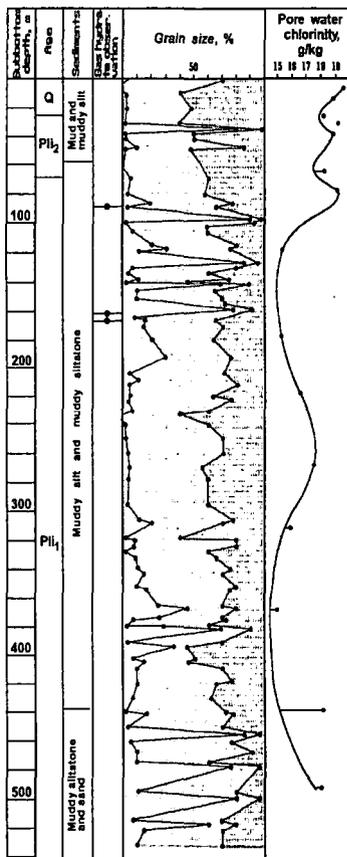


Fig.3. Gas hydrate shows, sediment grain size, and pore water chlorinity in geological section at DSDP Site 491, Middle America Trench. Compiled from Watkins, Moore et al., 1981, and Gieskes et al., 1985. The chlorinity curve is drawn using sulfate as a measure of sample contamination with the sea water. For symbols of sediment grain size see Fig.2.

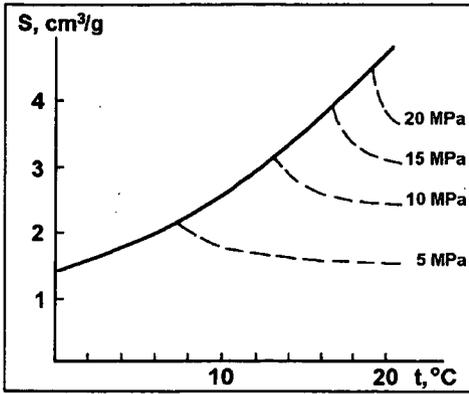


Fig. 4. Solubility of methane (S) in pure water plotted against temperature (t): isobars of instability in terms of gas hydrate instability (set of dashed lines), and solubility in equilibrium with hydrate (solid line). Compiled using the data of Makogon and Davidson (1983) and Namiot (1991).

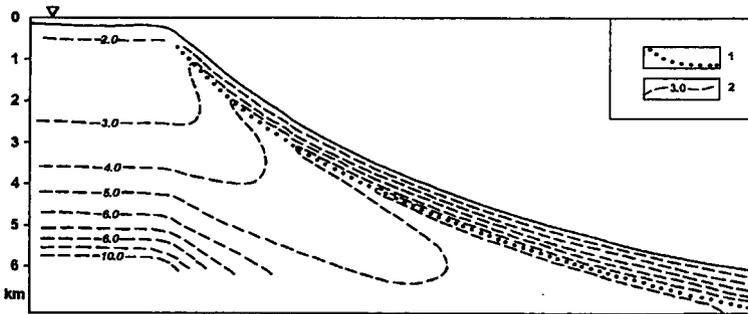


Fig. 5. Vertical cross-section demonstrating solubility of methane in water under thermobaric conditions of continental margins (after Ginsburg and Soloviev, 1994). The dashed lines are isolines of solubility numbered in STP cm³/g. Dotted line is the base of thermobaric gas hydrate stability zone. Compiled using the data of Makogon and Davidson (1983) and Namiot (1991). Accepted assumptions: water is pure; bottom water temperature is 5°C for water depths down to 500 m, and 2°C at greater depths; geothermal gradient is 30°C/km; hydrobaric gradient is 10 MPa/km.

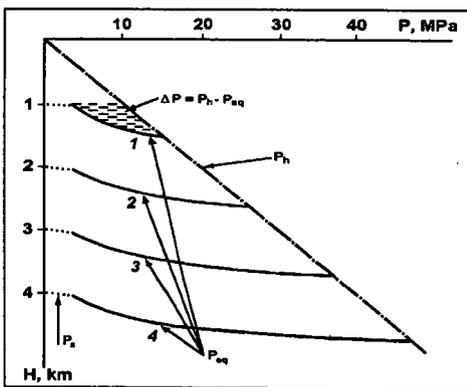


Fig. 6. Relationship between different kinds of pressure (P) affecting diffusion of methane in subbottom conditions. H is total depth = water depth + subbottom depth. P_h is conventional hydrostatic pressure. P_{eq} is equilibrium pressure of methane hydrate; curves 1-4 relate to water depths 1, 2, 3, 4 km, respectively. P_s is saturation pressure of dissolved methane within sulfate reduction zone. Accepted assumptions: water is pure, gas is pure methane (see also Fig. 5). The P_{eq} curves are the usual PT gas hydrate equilibrium curves but the temperature axis is replaced by the depth axis based on the accepted assumptions.