Marine Gas Hydrate Research at IFM-GEOMAR: An Overview on History and Recent Developments

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Abstract

Research on marine gas hydrate and the methane cycle has a tradition at IFM-GEOMAR. In summer 1996 during a cruise with RV SONNE offshore Oregon (USA) scientists of the former GEOMAR recovered the largest amount of gas hydrate from the seafloor. This discovery stimulated research on marine gas hydrates in Germany and induced funding of scientific programs such as LOTUS and OMEGA with numerous innovative technologies within the special program GEOTECHNOLOGIEN of BMBF and DFG. The primary objectives of ongoing and future research are to achieve a comprehensive knowledge of:

- gas hydrate distribution and quantity;
- variation and regulation of gas hydrate formation and dissociation as well as of the related fluid flow;
- functioning of chemosynthetic communities in methane oxidation, carbonate precipitation and methanotrophy as biological barrier against methane emission and
- delineating the escape routes of methane to the hydrosphere and atmosphere.

Within the nationally funded COMET program we study in detail the complex transport processes and biogeochemical reactions in hydrate-bearing surface sediments to better understand the working and efficiency of the benthic filter in different environments. We use advanced lander technology complemented by unique experiments in a novel pressure lab, numerical modelling, and isotopic analysis of fluids and authigenic precipitates to quantify rates of hydrate turnover. Mechanisms of hydrate dissolution and gas bubble transport are further investigated in a newly designed pressure laboratory. Authigenic carbonates and their isotopic composition are analyzed to reconstruct the changing rates of hydrate turnover on

geological time scales. Fluxes of methane into the water column and the atmosphere are studied by using hydroacoustic techniques and the stable isotopic composition of dissolved methane.

Gas Hydrate Exploitation and Future Climate Change

So far, most of these programs work under the broader rationale of understanding how methane flux may act as a force in climate change and from a carbon-cycling perspective, whereas the possible exploitation as a future energy reserve has received only very little attention in Europe. In contrast, a number of national research programs were recently launched in such countries as Japan, Canada, South Korea, Taiwan, India and China to investigate methane gas hydrates as a future energy resource.

We believe that hydrate exploitation could be feasible and might help to meet the growing energy demand of European countries. Nevertheless, we also demand that new approaches have to be developed to minimize the effects potential hydrate exploitation will have on atmospheric greenhouse gases and climate change. Harvesting and using the hydrate energy resource needs to be done on a CO₂-neutral basis, e. g. without increasing the emission of CO₂ into the atmosphere. In the following, we provide background information on methane gas hydrates and present a few ideas that should be considered in a future European strategy for gas hydrate research and exploitation.

1. Occurrence and abundance of gas hydrates

Methane gas hydrates are solids composed of water and methane molecules. They are only stable under low temperature and high pressure conditions and occur in seafloor sediments deposited at the continental slope and rise and in permafrost soils. At the typical range of bottom water temperature prevailing in many European waters $(0 - 4^{\circ}\text{C})$, sedimentary hydrates accumulate at water depths larger than ~400 m and are usually found in the upper ~300 m of the sediment column pending on local geothermal gradients and water depth. Below this sediment depth, temperatures are usually too high so that methane occurs as free gas rather than as solid hydrate.

Hydrates precipitate only if the methane concentration in the pore fluids exceeds the very high saturation value (~0.1 Mol CH₄ dm⁻³). In surface sediments methane is lost by microbial oxidation and by diffusion into the overlying bottom waters. The upper ~50 m of most sediment deposits are thus essentially hydrate-free. Only at mud volcanoes and other sites where methane-charged fluids, gases, and muds rapidly ascend to the surface, do gas hydrates accumulate at or close to the seafloor. These near-surface hydrate deposits are much more dynamic than hydrates deposited at greater sediment depth dissolving and emitting methane into the overlying bottom water and continuously being replenished by methane ascending from the underground.

Deep-sea drilling at a number of continental margin sites (Blake Ridge, Hydrate Ridge, Nankai Trough) have revealed that subsurface hydrates usually occur in discrete sediment layers with a thickness of up to several metres. These layers are preferentially composed of coarse-grained and permeable sediments and are usually covered with fine-grained impermeable layers. In some of these hydrate-bearing strata up to 50 % of the pore volumes is filled with gas hydrates.

The global abundance of gas hydrate is poorly constrained. Until recently it was generally accepted that about $10 \times 10^{+18}$ g of methane carbon (equivalent to $21 \times 10^{+15}$ m³ of methane gas at standard conditions) reside in gas hydrates [1]. Oceanic gas hydrates deposited in seafloor sediments are believed to be much more abundant than continental hydrates. The latter are only found in high-latitude permafrost regions and are estimated to contribute $0.4 \times 10^{+18}$ g C to the total hydrate inventory, excluding the vast but unknown reserves in Antarctica [1].

New offshore drilling results prompted a revised and significantly lower estimate of oceanic gas hydrates [2]. According to these data the oceanic hydrate inventory falls in the range of $0.5 - 2.5 \times 10^{+18}$ g C whereas new models of methane and gas hydrate accumulation at the seafloor suggest that modern ocean sediments should harbour about $3 \times 10^{+18}$ g methane carbon in the form of gas hydrates and $2 \times 10^{+18}$ g carbon in methane bubbles [3]. The total carbon mass in all conventional fossil fuel deposits (coal, oil and natural gas) is approximately $5 \times 10^{+18}$ g [1]. Hence, energy resources could be significantly expanded if new techniques

could be developed to exploit the vast inventory of methane at the seafloor and in permafrost regions.

2. Natural methane emissions from gas hydrates: Past, present, and future

Gas hydrates deposited in shallow sediments are highly soluble and constantly release dissolved methane into the overlying bottom waters. According to the Intergovernmental Panel on Climate Change (IPCC), $10 \times 10^{+12}$ g CH₄/yr are currently released from hydrates into the ocean and atmosphere. Most of this methane is oxidized by microorganisms residing at the seafloor and in ocean waters so that only a small fraction escapes into the atmosphere.

Ancient seafloor carbonates show a number of negative excursions in their stable isotopic composition (δ^{13} C). These excursions are believed to document massive hydrate dissociation events in the geological past. The most recent of these events happened about 55 million years ago [4]. This was associated with a strong warming of oceanic bottom waters which may have induced melting of gas hydrates at the seafloor so that massive amounts of 13 C-depleted methane were released into the ocean and atmosphere. Models show that the reconstructed release of $1.4 - 2.8 \times 10^{+18}$ g CH₄ over a period of about 10,000 years induced a massive increase in atmospheric greenhouse gases (CH₄, CO₂).

Methane emissions from gas hydrates may be strongly amplified by future climate change. Recent modeling showed that the total inventory of sedimentary gas hydrates would be reduced by 85 % or 2.5 x 10⁺¹⁸ g C in response to 3°C of ocean warming [3]. The timing of future hydrate dissociation remains to be resolved [5]. It is likely, however, that permafrost regions and sedimentary gas hydrates deposited at high latitudes will be the first to melt as future warming will proceed most rapidly in these regions. If melting would be completed within 1000 years, the annual flux of methane carbon into the ocean and atmosphere would be 2.5 x 10⁺¹⁵ g C/yr. This flux is much higher than the current anthropogenic methane emission and falls into the same order of magnitude as the present man-made CO₂ flux into the atmosphere. Thus, the current anthropogenic CO₂ emission via fossil fuel-burning and cement production is about 7 x 10⁺¹⁵ g C/yr while 1 x 10⁺¹⁴ g CH₄/yr are emitted as methane gas from industrial production according to the IPCC. The emission of greenhouse gases into the atmosphere will hence be prolonged into the distant future by gas hydrate

dissociation long after humankind has developed alternative means of energy production. In other words, partial pressures of greenhouse gases in the atmosphere will not be stabilized but will continue to rise over the coming centuries and millennia if gas hydrates are indeed as abundant and labile as currently believed.

3. Production of methane gas from natural gas hydrate deposits

The Messoyaka field located in the eastern Siberian permafrost area is the only hydrate deposit which has been exploited so far. Currently about 0.2 x 10⁺¹² g C/yr are produced at this onshore moderate-sized field while commercial methane production from offshore deposits has not yet started. Methane gas locked in hydrates can be produced by pressure reduction, temperature increase, and the injection of chemicals that cause hydrate dissociation [6]. Each of these methods has its merits and limitations depending on local conditions (water depth, hydrate concentration, presence or absence of free gas, etc). New and interesting laboratory studies suggest that CO₂ could be used to destabilize methane gas hydrates. In such a case, artificial CO₂-hydrates would be formed to replace natural CH₄-hydrates. The former hydrates could be used as a long-term sedimentary repository for anthropogenic CO₂. Reaction rates and the total yield of the CO₂ replacement reaction in natural gas hydrate deposits would depend on a variety of factors such as particle size and gas transport, which need further investigation.

It is very likely, however, that hydrate production is economically feasible only where large amounts of hydrate occur in high concentrations. These conditions are fulfilled in many offshore deposits where hydrates accumulate in coarse-grained sediment layers. It may also be possible to exploit near-surface hydrates accumulating in offshore mud volcanoes which may harbour as much as $10^{+13} - 10^{+15}$ g methane carbon in the form of gas hydrates [7].

From an environmental perspective, methane should be preferentially produced from labile hydrate deposits. In this case, the exploitation of hydrates would help to minimize ongoing natural methane emissions and mitigate future emissions caused by global warming. Hence, onshore and offshore deposits located at high latitudes should be primary targets because they will probably dissociate in the near future anyway. Mud volcanoes which are abundant in European waters could also be explored; methane is emitted at high rates from these

geologically active structures [8] and their emissions might be mitigated by appropriate exploitation techniques. The replacement of natural CH₄-hydrates by artificial CO₂-hydrates could be a promising and CO₂-neutral approach for the production of methane from deeper and more stable offshore deposits located at mid-latitudes and great water depths. It may also be feasible to extract hydrogen gas (H₂) from methane leaving the carbon at the seafloor and providing fuel for a future H₂-base energy production.

4. Elements of a future European program on gas hydrate research

A European program should be initiated to explore the potential of methane gas hydrates as future energy reserve considering also the fate of gas hydrates on a warming world. Based on the background information given above this program could address the following objectives:

- Quantify the distribution and amount of gas hydrates in sediments deposited along the European continental margin.
- Identify the sensitivity of permafrost and offshore hydrates to global climate change.
- Study hydrate accumulation and natural methane emissions at European mud volcanoes.
- Explore new sites and techniques for the sustainable production of methane from onshore and offshore hydrate deposits.
- Investigate the effects of sedimentary hydrate exploitation on benthic biota, slope stability and seafloor gas emissions.

A CO₂-neutral harvesting of gas hydrates would be of benefit not only to Europe but to all mankind and German scientists and SMEs are preparing at present national proposals in this direction covering the methods shown in Figure 1.

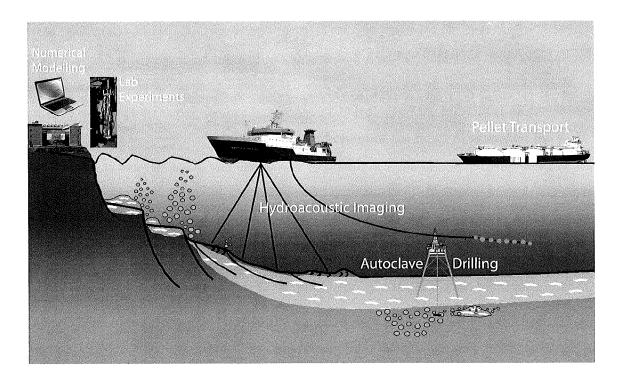


Fig. 1: Envisioned methods for the exploration and transport of gas hydrates.

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Peter Linke

Peter Linke has a record of more than 20 years of scientific work on deep-sea benthos starting in the Sonderforschungsbereich 313 with investigations on bentho-pelagic coupling. In 1993 he joined the department of Environmental Geology at the former GEOMAR where fluid circulation at active margins and the quantification of the input of gases and fluids into the hydrosphere was a major objective. Within this group, he gained expertise in the investigation of biogeochemical processes associated with fluid flow phenomena at various subduction zone (Aleutean, Cascadia, Makran, Peru, Costa Rica margin) and hydrothermal vent (Aegean Sea) settings. This includes process-oriented investigations by combining geological, geochemical and biological approaches and by using modern *in-situ* techniques, in particular Lander and ROV technologies. He worked as principal investigator and coordinator in various multidisciplinary DFG-, BMBF- and EU-funded projects and was chief scientist of several major cruises. At present he coordinates the COMET project within the special program GEOTECHNOLOGIEN by BMBF and DFG which addresses the complex physico-chemical and biogeochemical control parameters on marine methane fluxes and turnover rates from gas hydrate-bearing sediments into the water column and the atmosphere.