Ice On Fire – Methane Emissions to the Atmosphere

Is There a Hazard Lurking on the Sea Floor?

The stories told by seafarers over the centuries about burning icebergs were long considered superstition until they were finally confirmed near the end of the last century. The "burning icebergs" are caused by pieces of methane hydrate, a compound of ice and methane deposited in the sediments of the seabed, occasionally floating to the sea surface. All it takes is for them to be struck by lightning and we really can see burning ice. Around 10,000 billion tonnes of methane are bound in the form of gas hydrates in the sediments of the world's oceans. In the EU project CRIMEA, EAWAG is investigating the occurrence of methane in the Black Sea.

Methane hydrate looks like ordinary ice, but when it comes into contact with air, it decomposes, separating into methane gas and water. This compound of frozen water and methane belongs to what are known collectively as gas hydrates (see box and Fig. 1), and is found mainly in marine sediments and polar permafrost. There are particularly large methane hydrate fields on the continental shelves of the oceans, where the water is between 500 and 2000 m deep [1]. The methane hydrate could be shaken free of its bonds by an undersea earth tremor, resulting in enormous amounts of methane escaping into the atmosphere. Since methane, along with carbon dioxide, is one of the major greenhouse gases (see box), the consequences of this for the climate could be serious. There is a lot of evidence to suggest that such a catastrophe has occurred once already, 55 million years ago, resulting in a dramatic global warming event [2].

Methane Sources in the Black Sea

Even small changes in environmental conditions – such as a slight rise in the deep-water temperature, or a variation in sea level causing a pressure change – can result in methane being released from methane hydrate. This process should not be underestimated, considering that the concentration of methane in the atmosphere has doubled over the past 150 years, and is now 1.7 ppm (ppm = parts per million), i.e., 1.7 parts methane per million parts air. Along with methane hydrate, there are also other undersea methane sources which, through microbial and geochemical processes, cause methane to be released from the sediments, increasing the methane concentration in the atmosphere.

Thousands of active methane sources have already been located in the northwestern part of the Black Sea, where plumes of bubbles rising from them have been detected by hydro-acoustic techniques. During our CRIMEA research expeditions alone, we have discovered approximately 2800 new sources. Measurements of the methane flux through the water surface over the Georgian Shelf of the Black Sea have shown that between 1.7 and 7.0 liters of methane per m^2 are being released there per day. Extrapolating this over the entire Black Sea, we estimate that around 70,000 tonnes of methane are escaping annually into the atmosphere. However, it is still unclear what happens to the methane on its journey through the water column.

Gas Hydrates

Definition, Deposits, Origin

Gas hydrates are non-stoichiometric, crystalline substances consisting of gas and water. Water molecules form cage structures in which the gas molecules are enclosed (Fig. 1). Gas hydrates are therefore also called inclusion compounds, or clathrates (Latin: clatratus = cage). All in all, there are five different cage structures known. About 90% of the naturally occurring gas hydrates contain methane. In addition, there are hydrates of carbon dioxide and hydrogen sulfide. Methane hydrate is formed at low temperatures and high pressures, and the methane gas necessary for its formation originates from the anaerobic decomposition of organic material by bacteria. Given long periods of time, this continuous process can result in surprisingly large quantities of methane hydrate.

A Future Source of Energy?

Gas hydrates contain much more energy than all the reserves of natural gas, coal, and oil put together, and therefore represent a potential future energy source. The technical problems involved in exploring for methane from gas hydrates have not been solved yet and will occupy technologists for some years to come. Should it come to an industrial exploitation of methane, we must bear in mind that the burning of methane leads to the emission of carbon dioxide, the most important greenhouse gas (after water vapor).

Greenhouse Gases

Greenhouse gases are those gases which absorb the infrared radiation that the earth re-radiates into the atmosphere. This process is also known as the Greenhouse Effect, and is the cause of global warming. The major greenhouse gases in addition to methane are water vapor, carbon dioxide, nitrous oxides, and ozone. The effect of the various greenhouse gases varies greatly and depends on their specific warming potential. Although methane occurs only in very small concentrations in the atmosphere, its role should not be underestimated, as it is about twenty times more potent as a greenhouse gas than carbon dioxide. Without greenhouse gases, the earth would be uninhabitable, as the mean temperature of its surface would be –18 °C instead of today's 15 °C.

The CRIMEA Project

This is one of the questions researchers from ten European research institutes and universities – including EAWAG – are seeking to answer within the framework of the CRIMEA project (Contribution of high intensity gas seeps in the Black Sea to methane emission to the atmosphere). CRIMEA specifically aims to:

- map the methane sources in the Black Sea,
- quantify the escaping fluids and gases,
- describe the active methane-decomposing bacteria on the seabed and in the water column,
- quantify the methane turnover, and
- characterize the physical, biological, and chemical processes involved during the rise of the methane to the sea surface.

The First Black Sea Expedition

In June 2003, we undertook the first Black Sea expedition on the Ukrainian ship "Prof. Vodyanitsky". Our objectives included investigating two different methane sources, one at a depth of 90 m and the other at 1980 m. The existence of these sources could be identified using what is known as gas bubble imaging. For comparison purposes, measurements were also conducted at two reference sites with no methane sources. The Black Sea is 80 m deep at the shallower of the two reference sites, and 1660 m deep at the other.

The Path of Methane through the Water Column

The first step involved finding answers to two questions [3]: how high are the methane concentrations immediately above the emission sites, and how does the methane behave during its rise through the water columns of differing lengths? To answer these questions, a special probe, a rosette sampler, was used to take water samples above the two methane sources and at the two reference sites. The rosette is comprised of 12 10-liter sampling bottles which can be closed off by a signal from the ship at different depths.

Preliminary results show that the methane concentrations are highest directly above the two emission sites (Fig. 2A + B). The concentrations change very little during the first 40 m above the shallow site, and during the first 1500 m above the deeper site. At the deep methane source, a significant decrease in methane concentration only occurs in the upper 500 m of the water column.

EAWAG

To obtain the water samples we used a rosette sampler with 12 sampling bottles which could be closed off at different depths by a signal from the ship.

We had expected to find much lower methane concentrations at the reference sites than at the emission sites. In the shallow zone this is in fact the case: there the methane concentrations at the reference site were on average 10 times lower than in the water column above the methane source (Fig. 2A). The methane concentrations found over the deep emission site, however, do not differ significantly from those found over the corresponding reference site. This was surprising, and we wondered whether our measuring technique, which involved the detection of methane using a gas chromatograph with a flame ionization detector, was capable of distinguishing such a low concentration difference.

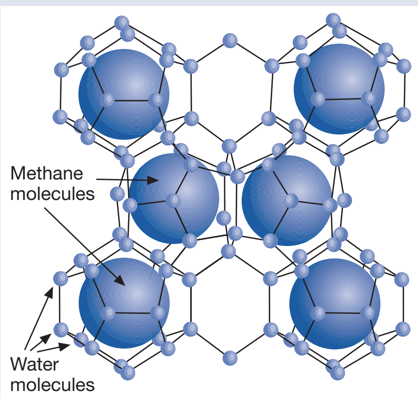


Fig. 1: Structure of methane hydrate.

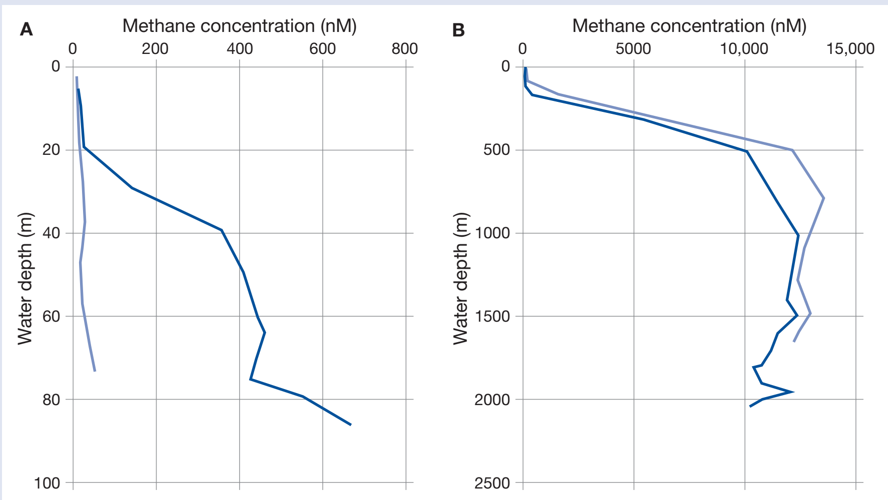
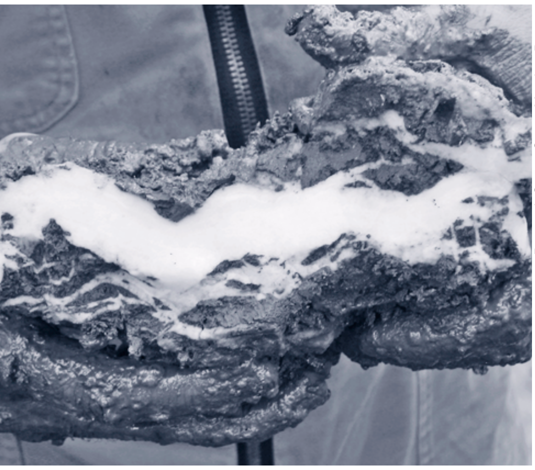


Fig. 2: Methane concentrations in the water columns above two methane sources (dark-blue curves) and the respective reference sites with no methane emission (light-blue curves). (A) in the shallow zone, (B) in the deep-water zone.



Research Center Ocean Margins, Bremen

Methane hydrate in a sediment sample.

We therefore used a second measuring technique that involves determining the distribution of the noble gas neon in the water column (see box). Normally, we would expect the neon concentration to be approximately the same throughout the deep water of the Black Sea. An anomalously low neon concentration in the water above a methane source would therefore suggest the occurrence of gas exchange between the rising methane bubbles and the water column. The concentration differential between the gas bubbles and the water column would cause some of the neon dissolved in the water to diffuse into the gas bubbles, and a corresponding amount of methane to diffuse out of the gas bubbles into the water column (Fig. 3). We did indeed find a lower neon concentration in the water column above the deep methane emission site than at the reference site, which, integrated over time, corresponds to a 20 % higher methane concentration above the methane emission site.

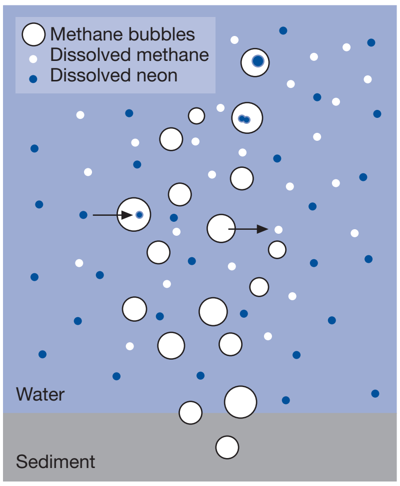


Fig. 3: Gas exchange between methane bubbles rising from a methane source and the surrounding deep water. Some of the neon dissolved in the water diffuses into the gas bubbles because of the concentration difference, and a corresponding amount of methane diffuses from the gas bubbles into the water.

Are Bacteria Decomposing the Methane?

A second step involved determining whether the methane is being decomposed by bacteria on its journey through the water column [4]. The continuous decrease in the methane concentration from the seabed to the water surface (Fig. 2A + B) suggests that this may be the case. Methane-oxidizing bacteria belong to the euryarchaeota, one of the two subgroups of the archaea bacteria. In the upper water layers, methane is oxidized to carbon dioxide by aerobic methane-oxidizing bacteria using oxygen. In the anaerobic conditions prevailing in the deep water, however, methane is oxidized using sulfate. This process is carried out by a specially adapted bacterial community: sulfate-reducing bacteria reduce sulfate to sulfide, and archaea oxidize methane to carbon dioxide.

Molecular biological methods make it possible to identify individual groups of bacteria, and to calculate the proportions of the total number of bacteria in the water samples belonging to each of these groups. We counted on average 25 % more archaea cells at the emission sites than at the reference sites. This result shows that methane-oxidizing bacteria are present above both the deep and shallow methane sources, and convert methane to carbon dioxide. Whether the methane from the sources we analyzed reaches the sea surface, and from there is able to get into the atmosphere, still needs to be investigated. The latest model calculations indicate that little or no methane from sources deeper than 100 m below the sea surface escape to the atmosphere [5]. We are currently processing the samples that have been brought back from the Black Sea expedition in 2004. The CRIMEA project runs until the beginning of 2006; by then we hope to have built up a comprehensive picture of the fate of this methane.

The Neon Method

Neon gas is present in air. In addition, neon is able to dissolve in water by gas exchange at the air-water interface. The neon concentration in the water depends on its equilibrium concentration, which is determined by the environmental conditions, such as water temperature and salinity, that prevail at the time of gas exchange. Since the Black Sea is stably stratified and neon is chemically inert, the concentration of neon in the deep water is constant. Any deviation from this constant concentration indicates that some additional physical process is at work.

The CRIMEA project is funded by the European Union and the Swiss Federal Office of Education and Science.

Carsten Schubert is a geologist and heads the "Biochemistry" group in the Department of Surface Waters. His chief areas of research are the anaerobic oxidation of methane and ammonia in marine and limnetic systems, and the decomposition of organic carbon in sediments.

Co-authors: Edith Durisch-Kaiser, Lucia Klauser, Christian Holzner, Dan McGinnis, Rolf Kipfer, Johny Wüest, Bernhard Wehrli.

[1] Kvenvolden K.A. (1988): Methane hydrates and global climate. Global Biogeochemical Cycles *2,* 221–229.
[2] Norris R.D. & Röhl U. (1999): Carbon cycling and chronology of climate warming during the Palaeocene/Ecocene transition. Nature *401,* 775–778.
[3] Schubert C.J., Kaiser E., Kuypers M.M.M., Wehrli B. (2004): Methane formation and oxidation in the Black Sea. Geophysical Research Abstracts, Vol. 6, 02867.
[4] Kaiser E., Schubert C.J., Wehrli B. (2003): Anaerobic oxidation of methane in the water column of the Black Sea. Geochimica et Cosmochimica Acta *67,* A193–A193 Suppl.
[5] McGinnis D.F., Wüest A., Schubert C.J., Klauser L., Lorke A., Kipfer R. (2005): Upward flux of methane in the Black Sea: Does it reach the atmosphere? In: Environmental Hydraulics and Sustainable Water Management (eds. Lee & Lam). Taylor and Francis Group, London p. 423–429.