Methane hydrate is an intriguing naturally occurring substance with a distinctive structure and the potential to be an energy resource, a natural hazard and a contributor to catastrophic climate change. **David Long** and **Peter Jackson** review the evidence.

## Hydrate: fossil fuel or lurking menace?

Methane hydrate is a solid substance that superficially resembles ice but, has an unusual structure in which methane molecules are 'caged' by water molecules. This cage allows the methane molecules to be held close together, much closer than in a free gas. One cubic metre of solid hydrate can hold the equivalent of 164 cubic metres of methane gas and 0.8 cubic metres of water at standard temperature and pressure. However, methane hydrate, like many other clathrates (substances where the molecules of a gas are trapped within a lattice of different molecules without any chemical bonding), is not stable at normal temperatures and pressures. Methane hydrate requires higher pressures and, generally, lower temperatures to exist.

Initially, gas hydrate in the natural environment was looked on as little more than a curiosity. However, the possibility that a huge volume of methane might be bound up in the gas-hydrate reservoir began to be considered by geoscientists. They began to recognise hydrate dissociation effects in shallow sediment cores and detected bottom-simulating reflectors (BSRs) beneath wide areas of the sea floor. BSRs are a large negative change in the acoustic impedance subparallel to the sea floor and are thought to represent the base of the hydrate stability zone beneath which free (methane) gas exists. Vast reserves have been claimed for methane hydrate but these estimates have moderated in recent years to between 1000 and 10 000 gigatonnes of carbon in natural methane hydrate. This is about 30 to 300 times the

amount of methane in the present atmosphere, where it is a powerful greenhouse gas. It is also comparable to other fossil fuels as a carbon store. As well as being found in water depths generally greater than 500 metres on virtually every continental margin, hydrates associated with permafrost have been encountered in Siberia, Alaska and the Canadian Arctic. Therefore there is much interest in developing ways to exploit this source of hydrocarbons.

However, natural hydrates may also be considered a hazard as changes to their environment that lead to their dissociation will have impacts both locally and globally. Hydrates occur within the upper few hundred metres of the sea bed so disturbance by drilling or the installation of foundations during development can cause the hydrate to melt, releasing gas around pipework and foundations and making them susceptible to ground failure. Alternatively gas seepage to the sea floor within the hydrate stability zone has been known to form hydrate over sea-bed installations including the blow-out preventer. This gas seepage may be from the breakdown of hydrates below the sea bed, or more deeply sourced methane forming hydrates as it rises up a conduit.



Burning methane hydrate sample.

Hydrate dissociation and changes in the geotechnical properties of the host sediment may be a cause of instability on continental slopes. Many of the world's largest submarine landslides occur in areas where methane hydrates have been found, or suspected, on the basis of BSRs. To change the stability regime of hydrates over large areas in the short term requires global changes in sea level or temperature. In the longer term regional uplift will produce similar effects.

Because it is about 25 times more effective as a greenhouse gas than carbon dioxide, methane from the global hydrate reservoir reaching the atmosphere could also significantly modify the global climate. During a cooling part of the glacial cycle, the lowering of the global sea level by 100 metres or more will change the pressure conditions on any offshore methane hydrates.

Hydrates cropping out on the sea floor will melt; this will probably occur gradually with methane becoming dissolved in the oceans. However melting will also occur at the base of the methane hydrate stability zone, in response to geothermal heat flow, leading to the build up of free gas. This will change the strength of the sediments and can lead to submarine landsliding. When such events occur it is thought that the volumes of methane gas released will be so large that they will reach the atmosphere. This is likely to constrain the glacial cooling thereby providing negative feedback.

However, in the warming part of the glacial cycle, rising sea level and higher temperatures are likely to melt permafrost that is trapping methane hydrate. The rise in temperature will feed down into the hydrate, leading to the release of methane direct to the atmosphere. Thus there is the potential to develop a positive feedback system in which gas hydrate release rapidly responds to, and accentuates, global warming. Also in the change from glacial to interglacial conditions, ocean currents may change causing the sea floor at high latitudes to be warmed, which could also release methane, for instance as a result of submarine slides. This link between



Hydrate stability zone map for UK.

methane release and rising temperatures has led to the 'clathrate gun hypothesis' in which hydrates are intimately involved with the global warming at the end of each ice age.

An alternative hypothesis is that climate change, including major sea-level rise, began before increases in methane in the atmosphere and that the higher methane concentrations in the atmosphere were the result of increased vegetation, particularly in swampy areas.

Sudden changes in atmospheric composition elsewhere in the geological column have also been attributed to hydrate dissociation, for example at the Paleocene–Eocene boundary, and even contributing to the Cretaceous– Palaeogene and Permian–Triassic boundary extinctions. The Palaeocene–Eocene Thermal Maximum was a short period (between 10 000 and 20 000 years) when terrestrial temperatures rose by 5°C and intermediate- to deep-ocean water temperatures increased between 6 and 8°C. This was accompanied by distinct changes in the carbon isotope ratios. It implies that approximately 2000 to 4000 gigatonnes of carbon was released into the ocean-atmosphere system, with the melting of methane hydrates the most likely source. Similarly large quantities of methane hydrates were released following global submarine failures triggered by bolide impact at the Cretaceous-Palaeogene boundary. Such rapid changes are comparable with anthropogenic inputs and may provide a model for the consequences of climate change attributed to present-day activities of mankind.

## For further information, contact:

David Long, BGS Edinburgh, Tel: +44(0)131 650 0363 e-mail: dal@bgs.ac.uk