

The Importance of Clathrates in the Karstprocesses

(Theoretical Considerations on the Analogy of Methane Hydrates)

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Abstract: The clathrates are generally known as methane hydrates and are results of the thermodynamic processes, when a guest molecule is trapped in the frozen ice cage. In the case of the methane hydrates the methane as a non-polar molecule is trapped by the frozen ice in deep sea environment. The cages are formed by several polar water molecules with hydrogen bond. These are also formed and documented in the permafrost zone. The guest non-polar molecules are not only methane in clathrates, but several other molecules like CO₂ and SO₂. In the case of glaciokarst when the ice melts, these guest molecules release and may generate a more aggressive water. These acidic waters can be responsible in the for the intensive karstic processes, in cave generation.

Keywords: clathrates; guest molecules, permafrost, karstic processes

Date of Submission: 03-11-2023

Date of Acceptance: 17-11-2023

I. Introduction:

The Latin word *clathratus* means "caged", and the name refers to the structure of ice-methane compound combinations, where tiny cages formed by ice crystals trap guest molecules (Solan, 2003). The most common guest non-polar molecules are methane, ethane, propane, isobutane, *n*-butane, nitrogen, carbon dioxide, hydrogen sulphide (Mahajan et al, 2007). In other words, clathrate hydrates are crystalline inclusion compounds consisting of a three-dimensional hydrogen-bonded water host molecule and one or more guest molecules, one surrounding the other in a cage-like lattice (Nagy 2013). It is known that in the permafrost region, even today, significant amounts of CH₄ occur as methane hydrate.

The guest molecules include not only methane, but also molecules that are mostly water-soluble or dispersible. These include CO₂, SO₂.

The question arises: what kind of guest molecules would we find trapped in the permafrost and partially and repeatedly frozen-thawing ice of the wider Carpathian Basin during the Ice Age? We speculate that CO₂, SO₂ molecules could be trapped in the surface ice, just as methane is trapped in the deep seas. The melt waters of the ice released the entrapped molecules, which made the melt waters much more acidic and thus could have led to more aggressive karst-water and karstification.

Five factors contribute to the solubility of karst phenomena. These are:

- large quantities of melt water;
- the pressure of this melt water;
- low water temperature (increases the CO₂, SO₂ concentrations);
- the flow rate of the water (faster flow, faster dissolution);
- the insulating effect of ice, which keeps the water temperature low.

Added to this, the insoluble fraction of limestone has a frictional, dragging effect, which forms the physical erosion of caves.

The clathrates

Clathrates are crystalline compounds that form a cage and can trap a guest molecule in it when frozen (Nagy 2013). The most commonly mentioned clathrate is - partly inappropriately - the methane hydrate feared by environmentalists, of which there are more in the bottom sediments of deep oceans and seas than all known hydrocarbon deposits. The risk is that global warming could release most of these into the atmosphere, further accelerating the rate of warming. In fact, there is a significant accumulation in the permafrost zone, where, with the periodic rise of low temperatures, many methane eruptions have occurred naturally and are still occurring. These methane clathrates have been the focus of research by a number of oil companies, but to date there is no

published information that industrial-scale production is being carried out from these sediments. They are even called "burning ice", because they burn with a red-hot flame when ignited (Nemes 2015).

Methane clathrates are no stranger to gas production professionals, as in cooler temperatures, especially in winter time, we are seeing a lot of pipeline freezes, and methanol treatment could soon restart methane production. In fact, methane clathrate can even appear in the gas separators and must be removed to resume production. This shows that the formation of clathrates depends on the thermodynamic conditions i.e., where favourable p and T conditions prevail, the Gay-Lussac (i.e. Amontons) isochoric law applies. In hydrates, water molecules are linked by hydrogen bonds, the water molecules are 180pm apart and can form a ring structure in the presence of other molecules (Figure 1).

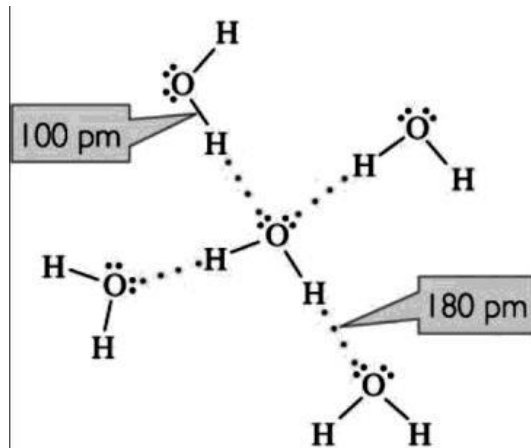


Fig.1. The hydrogen bonds, where the H bridges link the water molecules with a distance of 180pm

When a methane tetrahedral molecule enters the system, its hydrogen molecules interact weakly with the oxygen molecules of water in a weak van der Waals bond. This is called Debye induced polarisation. Even the simplest methane-water structure, the methane molecule, has free internal rotation (Suenram et al, 1994).

If we imagine the four extreme positions in the rotation of a methane molecule as a tetrahedron (Figure 2), the vertices each form a pentagon and together they form a dodecahedron (Figure 3). Its peaks are the oxygen atoms of the water and interact with them in a weakly induced polarization interaction with the hydrogen of the confined methane.

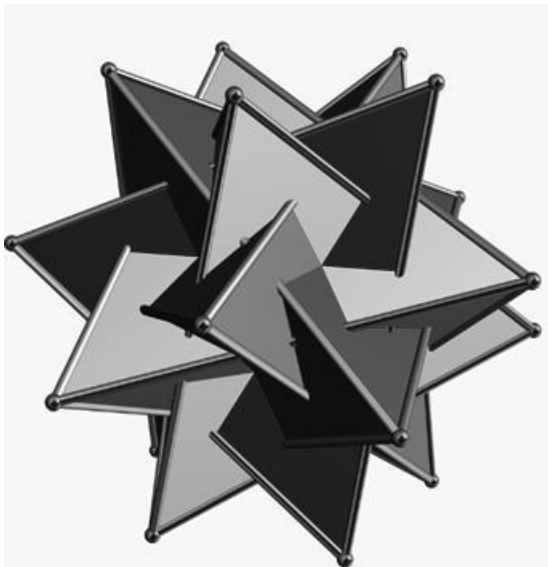


Fig. 2. The four extreme position of the methane tetrahedron rotation, which vertices form pentagons and together a dodecahedron

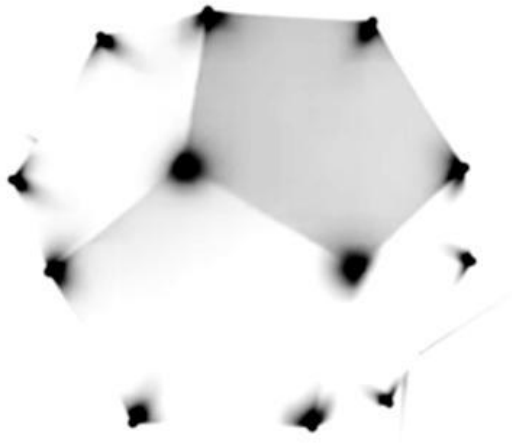


Fig. 3. The vertices of the dodecahedron represent the oxygen of the water molecules, which creates an induced polarisation (Debye effect) with the hydrogen of the methane.

This state is locked by freezing, since the dodecahedron is the regular polyhedron with the largest volume and the smallest edge length, filling 66.5% of the volume of the sphere around the dodecahedron.

The environment in which clathrates form

Based on their spatial distribution, methane clathrates occur in two geological environments: Deep-sea environments and permafrost areas. Rüppel's (2011) diagram (Figure 4) shows the gas hydrate stability in oceanic sediments and in permafrost areas. In both cases, the solid curve shows the phase boundary, the dashed line the temperature profile and the GHS the area bounded by the curves represents the gas hydrate stability zone. As shown in Figure 4A, for the marine environment, the GHS extends to a depth of about 1100 m, with the seafloor at 800 m. Theoretically, gas hydrates are also stable below this depth i.e. in the uppermost approximately 200-300 m of seafloor sediments (where the geothermal gradient curve intersects the phase boundary curve). Free gas may also occur below the gas hydrate-bearing sediments and may be incorporated into the GHS. Depending on the geothermal gradient of the sediment and ocean temperature, the gas hydrate stability zone is about 300-500 m thick at continental margins and can be more than 1000 m thick in deep-sea sediments.

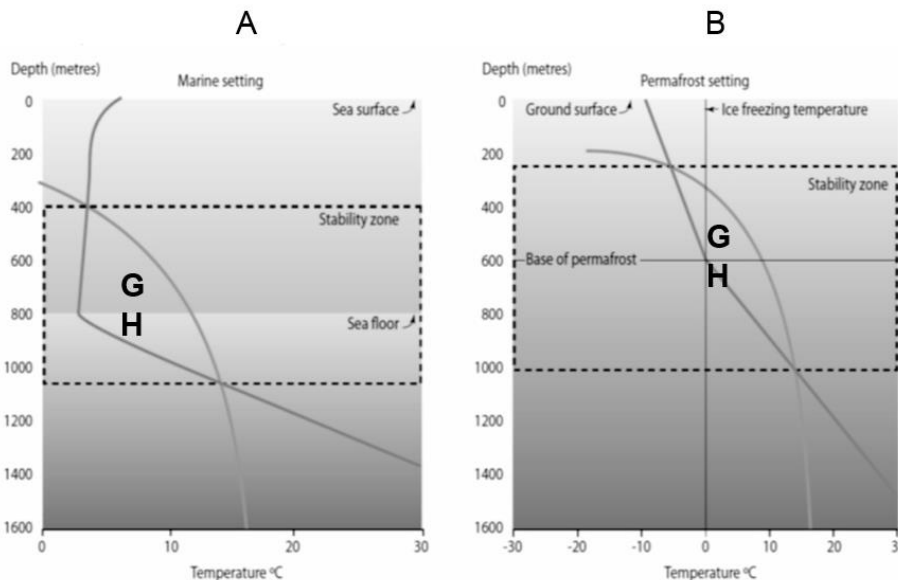


Fig. 4. The Gas Hydrate Stability Zone (GHS) from the marine (A)- and permafrost (B) environment (redrawn after Rüppel 2011)

Figure 4B: Geothermal gradient versus depth for the permafrost situation shows that the hydrate zone can extend from the surface of the permafrost sediments to depths of several hundred metres. For us, the latter figure 4B is important, because during the Quaternary glaciation, a large number of molecules of different types could have been trapped in the ice.

Molecules trapped in clathrates

In the case of clathrates, methane hydrates are the most commonly heard of, although there are many other guest molecules that are "caged" in the system and play a major role, especially in permafrost and glaciokarst phenomena.

One of the conditions for the formation of clathrate is that the water molecules form a lattice and the guest molecules fit into the cavities of the water molecular lattices based on their size and shape. Experience to date suggests that ~130pm (~1.3Å) ionic radius is this limit. The methane tetrahedral molecule is just this size (Figure 5), ($1.087 \text{ \AA} + 0.27 \text{ \AA} = 1.36 \text{ \AA}$)

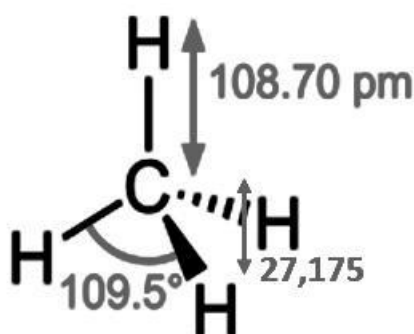


Fig. 5. The methane molecule size

The second prerequisite is that no chemical reactions, e.g. hydrolysis, occur between the guest and the water molecule, and that the hydrogen in the guest molecule does not break the hydrogen bonds in the water. The molecules that meet these two conditions, apart from methane, are CO_2 , SO_2 , N_2 the noble gases, and many other hydrophobic molecules.

The most important for karstification are CO_2 , SO_2 , molecules, which are released by subsequent dissociation making the meltwater more acidic-aggressive and significantly influencing the karstification phenomenon.

Some literature on the chemical composition of ice and meltwater

In his article, VASILCHUK (2006) provides a whole series of data from different glacial environments, where he gives the chemical composition of the ice and even mentions the importance of clathrates, which may be a clue to the former air composition. What is striking is the relatively high SO_4^{2-} content¹, which may not have come from the air, but from sediments, rocks, or possibly from contact with seawater. The author reports a wide range of H_2SO_4 contents from the Antarctic region, with concentrations of 10-36% from present-day ice and 16% from the glacial period.

On the Chukotka Peninsula (NE Russia), 4.9-26.3 mg/l SO_4^{2-} was identified from late Pleistocene permafrost ice, and significantly higher amounts of HCO_3^- in the range of 7.3-92 mg/l.

In western Siberia, from the Yamal Peninsula and Duvanny (North Yakutia), while the sulphate content of Holocene and modern ice varied between 4-11 mg/l, Pleistocene ice was found to contain 0.1-66 mg/l of sulphate; HCO_3^- amounts varied from 7 to 628 mg/l. Also on Belyi Island in western Siberia and in the northern region of the Gydan Peninsula, 5-94 mg/kg SO_4^{2-} and 12-24 mg/kg HCO_3^- were measured in Holocene ice samples.

Ice samples (moraine and pinnacle ice) from the McMuro (New Zealand) self show extreme sulphate values, with moraine ice reaching a maximum of 321 mmol/l with an average of 6.54 mmol/l compared to pinnacle ice which has a maximum of 2.82 mmol/l (de Mora et al 1994). VASILCHUK does not discuss in the article which of these were or could have been trapped in clathrates, but he rightly assumes their existence, devoting a separate subsection to this possibility.

II. Discussion, summary

The discovery and study of clathrates has focused attention on the phenomena of permafrost and glaciokarst, i.e. guest molecules embedded in ice cages during Quaternary glaciation. The release of sulphur dioxide and carbon dioxide from clathrates can significantly increase the aggressiveness of meltwater. In glaciers, the release of molecules from clathrates can also occur continuously as meltwater is generated from the ice or as glaciers retreat. In the former case, the increase in aggressivity may be associated with the meltwater pathway generating caves with karst phenomena; in the latter case, it may occur over the entire area covered by the former glaciers.

¹ The author gives the ice composition based on ions (anions-cations).

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Zoltán UNGER. "The Importance of Clathrates in the Karstprocesses." *International Journal of Engineering Science Invention (IJESI)*, Vol. 12(11), 2023, PP 21-25. Journal DOI- 10.35629/6734