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Investigation on clathrates localised in the Eastern Mediterranean mud volcanoes

Introduction

Clathrates, or more commonly called Gas/Methane hydrates, are ice-like crystalline solids formed from a mixture of water and natural gas, usually methane. They occur in the pore spaces of sediments, and may form cements, nodes or layers.

Clathrates are usually found in deep sea sediments on the continental slope, or off the coast in Polar Regions. They can also occur in glaciers. The two main factors that keep the clathrates in a stable condition are temperature and pressure. For example, gas hydrate will remain stable at a temperature of 10°C if the pressure does not fall below about 100 atm, which is roughly equal to 1000m underwater. A less important factor controlling the stability of methane hydrate is salinity. Methane hydrate will dissociate at 5°C lower in NaCl-saturated water than in normal seawater.[1] Because methane hydrate has an average composition of CH_4 5.75H2O, the volumetric ratio between methane and water is roughly 164. That is, $1m^3$ of gas hydrate yields 164 m^3 of methane gas and only 0.8 m^3 H_2O at stp.

This explains why Gas hydrates are economically important. There exist enormous quantities of it, about 10,000 Pg, and provides us with a long-lasting energy resource. However, the gas is up to 30 times as powerful as CO_2 in the atmosphere and is therefore a great contributor to the greenhouse effect. Any accident that may occur during exploitation of the gas will have major consequences to the global climate. It is important to note that gas hydrates act as a seal to trap free methane gas below. Earthquakes, fluctuations in temperature of sea water, or a drop in sea level, will destabilise the seal, causing a major submarine landslide to occur together with a tsunami and vast amounts of methane will be released into the atmosphere. Such landslides have been spotted as ‘scars’ located on the continental slope and rise around the world.

Of course, methane is also released naturally from gas hydrates such as in the Eastern Mediterranean Sea. A large number of mud volcanoes exist there of which some are nearly entirely composed of gas hydrates, such as the dormant Milano dome. However, another studied active dome, the Napoli dome, seems to be void of gas hydrates. Because it is not possible to go down 2000m below sea level to check for the presence and amount of gas hydrates, researchers have analysed the ocean water nearby the domes for the amount of NaCl present. Results show that “it seems…that the low salinities in the pore waters at Milano Dome are caused by the presence of significant amounts of methane hydrates in combination with brine-dominated in situ pore waters.”[2] At the Napoli Dome salinities show to be much higher in the nearby pore waters. Remarkably, seismic profiles have shown that gas hydrates exist at 0.1m down to 40m in the sediment at the Milano Dome.

[1] Page 569 P3 l2-3 from J. De Lange and H.J. Brumsack
[2] Page 571 l4-7 from J. De Lange and H.J. Brumsack

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Because researchers cannot 'measure' the amount of Gas hydrates present in the Eastern Mediterranean, from a series of assumptions reasonable estimates can be calculated. Furthermore, the release rate of methane can be deduced, some related chemical reactions, and the O_2 concentration before and after the release of methane. Finally, it would be interesting to investigate how much the global temperature would rise if all this methane were to enter the atmosphere instantly.

Method

See Appendix A for a detailed workout of the exercises on Gas Hydrates in the Eastern Mediterranean Sea.

Results

The quantity of Gas Hydrates in the Eastern Mediterranean has been calculated for two extremes over a calculated area of 30,000 km^2, i.e. the concentration of mud volcanoes on the Med. ridge. The low extreme takes into consideration that only 50% of the sediment volume consists of GH and only 10% of the mud volcanoes contain GH. The calculation yields 61km^3 of GH. The high extreme takes into consideration 80% and 50% respectively, yielding an amount of 490km^3 of GH.

The calculation for the release rate of methane for the low extreme gives a value of 2.02E10 m^3 yr^{-1} gas CH_4 = 9.10E11 mol yr^{-1} For the high extreme this is, 8.06E11 m^3 yr^{-1} gas CH_4.= 3.64E13 mol yr^{-1} When calculating both extremes, the progressive diffusion of heat into the sediment was 5 and 25cmyr^{-1} respectively for the low and high extremes.

Exercise 3 asks for two possible extreme cases of methane removal from seawater to the atmosphere. Both equations are shown below:

Microbially mediated oxidation

$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$

Release into the atmosphere

$HS^- + 2O_2 \rightarrow H^+ + SO_4^{2-}$

The amount of oxygen consumed by the flux of the low extreme case is calculated to be 1.82E12 mol O_2. For the high extreme case this is 7.28E13 mol O_2.

From these results the original oxygen levels can be calculated before GH were released. For the low extreme the answer came to be 205 µmol L^{-1} O_2. For the high extreme it is 580 µmol L^{-1} O_2, whereas the current O_2 concentration is at roughly 195 µmol L^{-1} O_2 in the deep sea.

The temperature results for both extremes obtained from the calculation in exercise 4 are 2°C and 12°C for the low and high extremes respectively.

Discussion

It proves to be very difficult to obtain a reliable estimate for the concentration of mud volcanoes over an area. Unfortunately, a difference in this calculation causes the rest of the calculations to differ as well. Therefore it is hard to reproduce the exact same results by anyone else, unless when using computers, that is.

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The two temperatures obtained in the last exercise are based upon the sudden release of all gas hydrates located in the Eastern Mediterranean directly into the atmosphere. A maximum increase of about 12°C globally is, however, very concerning. It will cause an exacerbated greenhouse effect which in turn will totally destabilise the global climate, during which numerous species may become extinct. Some extra assumptions had to be made such as that the GH reservoir has only an outgoing flux and that the release of methane enters the atmosphere directly. Therefore, chances of such an occurrence are nihilistic especially because it is not likely that all gas hydrates will suddenly be released.

Overall, there is a great difference between the low and high extremes calculated each time. Especially, exercise 3 shows that the high extreme case, GH certainly consumes much more oxygen than the low extreme. This is of great importance to deep-sea life that depends on the availability of O_2. The presence of gas hydrates in the Mediterranean Sea could also affect people living at the coastline. If much methane is released suddenly and so much that the deep waters will be depleted of oxygen, etc, the food chain in the Mediterranean may suffer as vital species down the food chain become extinct. Local fishing companies especially in locations where people depend on fish export will suffer from the extinction of certain fish species. On the other hand, if the gas hydrates could be exploited successfully, this means big business for nearby countries and will profit from this new resource.

Conclusions

- The quantity of methane stored in the Eastern Mediterranean varies from 61 to 490km^3.
- The release rate of methane varies from 9.10E11 mol yr^{-1} to 3.64E13 mol yr^{-1}.
- The amount of O_2 consumed by methane varies from 1.82E12 mol O_2 to 7.28E13 mol O_2.
- The concentration of O_2 before the release of CH_4 varies from 205 µmol L^{-1} O_2 to 580 µmolL^{-1} O_2.

Calculations show that a release of CH_4 to the atmosphere generates a significant increase in global temperature 2°C up to 12°C. When not assuming that CH_4 directly enters the atmosphere it could still, however, upset marine life due to depletion of O_2, especially in the deep sea.

References

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