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Noble gases and radiocarbon in natural gas hydrates

Gisela Winckler

Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

Werner Aeschbach-Hertig, Johannes Holoher and Rolf Kipfer

Institute of Isotope Geology and Mineral Resources, ETH, Zurich, Switzerland

Department of Water Resources and Drinking Water, EAWAG, Dübendorf, Switzerland

Ingeborg Levin and Christian Poss

Institut für Umweltphysik, Universität Heidelberg, Germany

Gregor Rehder and Erwin Suess

GEOMAR, Forschungszentrum für marine Geowissenschaften, Kiel, Germany

Peter Schlosser

Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

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[1] In samples of pure natural gas hydrates from Hydrate Ridge, Cascadia Margin, virtually no helium and neon components are present providing evidence that the light noble gases are not incorporated into the structure of natural methane hydrates. In contrast, the hydrates contain significant amounts of argon, krypton and xenon. These gases show a distinct fractionation pattern, with the heavier ones preferentially incorporated into the gas hydrate structure. The hydrate methane is devoid of ^{14}C indicating that there is no contribution of a recent (^{14}C -active) organic carbon reservoir to the hydrate carbon pool. On the basis of the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ signature, it appears that microbial CO_2 -reduction is the dominant CH_4 production pathway. *INDEX TERMS*: 4825 Oceanography: Biological and Chemical: Geochemistry; 4820 Oceanography: Biological and Chemical: Gases; 4860 Oceanography: Biological and Chemical: Radioactivity and radioisotopes; 3022 Marine Geology and Geophysics: Marine sediments—processes and transport

1. Introduction

[2] Over the last decade natural methane hydrates have become a major focus of earth science because they represent an enormous reservoir of carbon and, potentially, are a significant energy resource. At the same time, they possibly are a climate-sensitive reservoir of greenhouse gases as well as a potential cause of submarine slope destabilization. Gas hydrates are crystalline, ice-like substances composed of rigid cages of water molecules that enclose guest gas molecules. The gas component of natural hydrates is mainly methane.

[3] Formation of gas hydrates requires moderate to high pressures, low temperatures and substantial amounts of methane. Consequently, methane hydrates are widespread in permafrost regions and seafloor sediments along continental margins. Shallow marine gas hydrates are known to form where gaseous methane or methane-rich fluids are advected to the seafloor from deeper organic-rich sediments [Kastner *et al.*, 1998; Suess *et al.*, 1999]. However, many features of gas hydrate dynamics remain unknown. The location and source of the methane reservoir, the time scale

and p/T-condition of the gas hydrate formation process, and the age of current hydrate deposits, are poorly defined.

[4] For the present study we recovered large amounts of an exposed methane hydrate from Hydrate Ridge, Cascadia Margin. The samples were analyzed for noble gases as well as for $\delta^{13}\text{C}$, $\delta^2\text{H}$ and ^{14}C of CH_4 . Since noble gases are chemically inert, changes in their elemental ratios occur only by physical processes and thus represent a useful tool to detect complex geochemical processes that are not directly accessible to observations as has been shown for example for hydrothermal systems and natural hydrocarbon reserves (e.g. [Winckler *et al.*, 2000]). The analysis of stable carbon and hydrogen isotopes of the dominant guest molecule methane allows to establish its origin [Whiticar *et al.*, 1986], and the radiocarbon signature reflects if recent organic carbon contributes to the source of the methane.

[5] Up to now, only one experimental noble gas study of gas hydrates has been presented in the literature, using samples from ODP leg 164 at Blake Ridge [Dickens and Kennedy, 2000]. In this study major sampling problems, i.e. introduction of air to the samples during shipping and storage, were encountered and masked the noble gas signals to some degree [Dickens and Kennedy, 2000]. Our study relies on a different sampling procedure, even possible with conventional shipboard techniques, that appears to be less susceptible to contamination than the ODP study.

2. Geological Setting and Sampling

[6] The Hydrate Ridge is a 25 km long and 15 km wide ridge in the accretionary complex of the Cascadia Margin off Oregon [Suess *et al.*, 2001]. The summit of Hydrate Ridge appears to be paved by outcropping hydrates. A TV-guided sediment grab was deployed on these outcrops, recovering large amounts of gas hydrates [Bohrmann *et al.*, 2000]. Typically, hydrates removed from the sediment become unstable in the water column and disintegrate into water and gas during their recovery. However, the large volume (0.7 m^3) sampled by a TV-grab leads to a good insulation and preservation, minimizing the probability of gas loss prior to sampling. Six samples for the noble gas analysis were taken from two TV-grab stations SO143-21-1 and SO143-71-1 at a water depth of 786 m [Bohrmann *et al.*, 2000]. Sections of about 30 cc from the inside of larger pieces of pure hydrate (Figure 1) were separated and immediately transferred into a vacuum tight stainless steel sampling container. The outer portions, which might have lost original gas

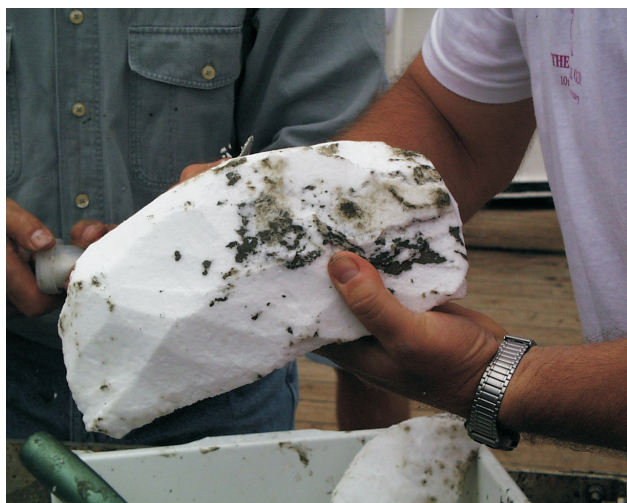


Figure 1. Gas hydrate sample from Hydrate Ridge.

and were likely contaminated by ambient air, were completely cut off. After a small part of the hydrate had decomposed, the valve on top of the container was opened for a brief time in order to flush out any residual atmospheric gases by the flow of pressurized methane. As the methane flow was viscous, this process is not expected to result in a significant fractionation of the elements. After final closure of the valve the gas hydrate completely decomposed into water and gas resulting in final total pressures between 3 and 19 bars inside the container (Table 1). In case of the low total pressure samples GH2 and GH5, the valve might have been opened too late when the major part of the gas hydrate had already decomposed. Approximately 1 to 3 cc STP of the gas in the headspace of the containers were analyzed for noble gases at the noble gas laboratory at the ETH Zürich following the procedures described by [Beyerle *et al.*, 2000]. Aliquots from the same samples were analyzed for $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of CH_4 at the Institut für Umweltphysik, Heidelberg, and for radiocarbon at the AMS facility at Groningen.

3. Results and Discussion

[7] The noble gas compositions, along with the total pressure inside the containers, are listed in Table 1. Figure 2 shows the noble gas concentrations, normalized to their atmospheric abundance. The data show three main features:

1. The noble gas signatures can be divided into groups A (GH 2,5) and B (GH 4, 3, 11, 6). Samples GH2 and GH5, with the lowest total pressure inside the container, show the highest partial pressures for all noble gases. Group B with high total pressures between 10 and 19 bar shows relatively constant partial pressures for the noble gases that are lower than for group A. These samples contained high amounts of non-decomposed gas hydrate when the valve was finally closed. Therefore, they are considered to best represent the composition of the gas hydrate.

Table 2. Carbon and hydrogen isotopic signature of CH_4

Sample ID	Station SO 143	$\delta^{13}\text{C}_{\text{CH}_4}$ [‰ vs PDB]	$\delta^2\text{H}_{\text{CH}_4}$ [‰ vs SMOW]	^{14}C [pmc]
GH2	21-1	-66.7 ± 0.1	-191 ± 10	0.22 ± 0.12
GH5	71-1	-69.1 ± 0.1	-180 ± 10	0.22 ± 0.12
GH3	21-1	-67.1 ± 0.1	-193 ± 10	n.d.
GH11	71-1	-69.7 ± 0.1	-189 ± 10	0.29 ± 0.12

2. Virtually no He and Ne component is present in any of the analyzed gas hydrate samples. The strikingly low He and Ne concentrations confirm that the air inside the container was efficiently removed by the applied procedure.

3. In contrast to He and Ne, we found significant amounts of Ar, Kr and Xe in the gas hydrates. The normalized abundances of these heavier noble gases increase with their mass.

[8] Carbon and hydrogen isotope ratios were measured on four of the samples and are listed in Table 2. The $\delta^{13}\text{C}$ (vs. PDB) and $\delta^2\text{H}$ (vs. SMOW) values range between -66.7 and -69.7 ‰, and between -180 and -193 ‰, respectively. None of the three samples analyzed for ^{14}C showed a significant radiocarbon activity.

[9] To discuss the fractionation pattern between the different noble gases, the concentration ratio between each noble gas and Ar is normalized to the respective ratio in the atmosphere (Figure 3)

$$F^x = \frac{\left(\frac{C_x}{C_{\text{Ar}}}\right)_{\text{sample}}}{\left(\frac{C_x}{C_{\text{Ar}}}\right)_{\text{air}}}$$

Thermodynamic conditions for the stability of gas hydrates are strongly dependent on the size and shape of the gas molecules and their capability to fit in the cavities of the structure. In principle, the gas molecules must be small enough to fit into the cavities of the lattice but large enough to lend stability to the structure. Helium and neon belong to a group of substances that have van der Waals diameters smaller than 0.35 nm that have been shown to generally not form gas hydrates, presumably because the molecules are too mobile to remain trapped in the cavities and hence cannot stabilize the hydrate lattice [Dyadin *et al.*, 1999]. The virtual absence of He and Ne in the gas hydrates presented in this work is in excellent agreement with theoretical expectations and, for the first time, provides experimental evidence that these light noble gases are not incorporated in the crystal structure of natural methane hydrates.

[10] The heavier noble gases Ar, Kr and Xe have linear dimensions >0.38 nm, and are among the smallest guest molecules that are able to form hydrates. Consequently, traces of Ar, Kr and Xe are readily incorporated into the crystal structure during genesis of the hydrate. As shown in Figure 3, the heavier noble gases reveal a distinct elemental fractionation pattern, characterized by an enrichment that increases with the atomic mass ($\text{Xe} > \text{Kr} > \text{Ar}$), with fractionation factors up to 23 for Xe. The heavier noble gases are also clearly enriched with respect to ASW (ambient seawater), which is supposed to represent the noble gas signature of the porewater from which the hydrate is

Table 1. Noble gas concentrations in cc per cc total gas (which is nearly pure methane)

Sample ID	Station SO 143	Pressure [bar]	He [10^{-10} cc/cc]	Ne [10^{-9} cc/cc]	Ar [10^{-5} cc/cc]	Kr [10^{-8} cc/cc]	Xe [10^{-9} cc/cc]
GH2	21-1	3.3	90.6 ± 0.3	61.5 ± 2.4	53.2 ± 1.2	29.7 ± 0.6	93.4 ± 0.8
GH5	71-1	5.7	14.7 ± 0.1	14.2 ± 3.2	41.4 ± 1.5	20.2 ± 0.8	62.1 ± 0.6
GH4	71-1	10.4	3.2 ± 0.2	3.4 ± 1.2	5.9 ± 1	2.4 ± 0.4	3.06 ± 0.09
GH3	21-1	12.1	9.6 ± 0.3	4.1 ± 1.3	5.0 ± 1.3	1.84 ± 0.5	2.68 ± 0.08
GH11	71-1	19.0	11.6 ± 0.3	2.5 ± 0.7	6.9 ± 1.3	4.17 ± 0.6	14.6 ± 0.3
GH6	21-1	n.d.	7 ± 4	4.1 ± 2.5	3.5 ± 0.9	2.4 ± 0.5	8.2 ± 0.1
Air			52400	18180	934	114	87

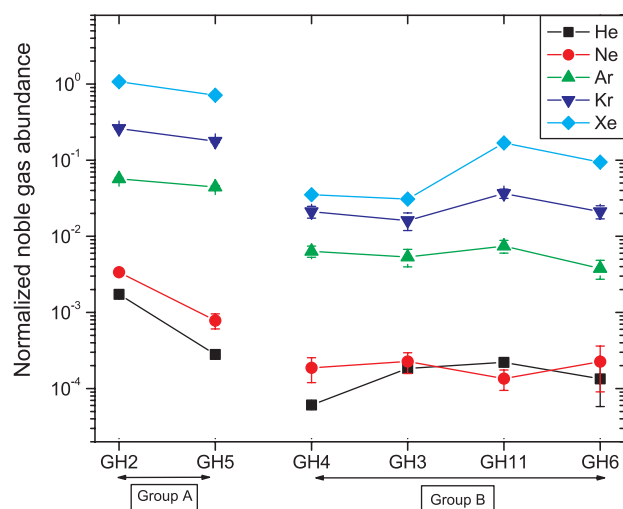


Figure 2. Noble gas concentrations normalized to their respective atmospheric abundance. The samples are ordered by increasing total pressure inside the container.

formed. Presumably, this reflects mass-dependent preferential incorporation of the heavier noble gases in the gas hydrate lattice. Such fractionation may be explained by two different processes:

1. Elemental fractionation of noble gas mixtures during CH_3Cl hydrate formation has been reported by *Barrer and Stuart* [1957] and *Barrer and Edge* [1967] who investigated the potential industrial use of gas hydrates to concentrate components of gas mixtures. These authors concluded from their laboratory studies that the clathration of gas during hydrate formation is selective towards the heavier molecular species and that the degree of fractionation increases with decreasing temperature. The preferential enrichment of the heavier noble gases in our data from Hydrate Ridge is consistent with this thermodynamic effect. However, quantitative conclusions on the basis of our results are tentative as there are no laboratory data available on noble gas fractionation during methane hydrate formation.

2. Alternatively, the fractionation pattern in our data could reflect noble gas fractionation in the source fluid from which the methane hydrate is formed. Submersible and video observations have shown the crest of the Hydrate Ridge to be a dynamic system characterized by solid hydrates, fluid expulsion and methane gas plumes [*Suess et al.*, 2001]. Pore water interacting with a free gas phase is expected to be depleted in its noble gas content with the heavier noble gases being less affected due to their progressively increasing solubilities and lower diffusion coefficients. Consequently, a hydrate phase formed from such a reservoir would show a corresponding fractionation pattern. However, the relatively high Xe concentrations of the hydrates analyzed do not support a substantial noble gas depletion of the water forming the hydrate.

[11] The current knowledge and scarce experimental data, both from natural gas hydrates and from laboratory studies on methane hydrates, do not allow distinction between these two processes and the quantification of their relative contributions. An ultimate test to differentiate between the two potential scenarios would be to sample and analyze the complementary reservoirs for noble gases: the free gas phase, e.g. the bubbles emanating from the seafloor, and the pore waters. If stripping by a gas phase was responsible for the observed enrichment of the heavier noble gases, the gas phase should show the reverse fractionation pattern ($\text{Ar} > \text{Kr} > \text{Xe}$), while the pore water would be expected to have the same trend for Ar, Kr and Xe as the hydrates. On the other hand, if the fractionation was

due to the thermodynamics of the hydrate formation from the undisturbed (ASW-type) pore water, the remaining water phase should have the reverse fractionation pattern. If thermodynamic fractionation during hydrate formation was responsible for the observed noble gas fractionation pattern, and the temperature-dependent fractionation factors were known from laboratory studies, then in principle the noble gas distribution in gas hydrates could be used as a proxy for the temperature during hydrate formation.

3.1. Comparison With Data From Blake Ridge

[12] Our He and Ne data differ significantly from the data from Blake Ridge [*Dickens and Kennedy*, 2000] where high He fractionation factors of up to 350 and low radiogenic $^3\text{He}/^4\text{He}$ ratios have been reported, similar to He data of gas hydrate recovered from a mud volcano environment [*Prasolov et al.*, 1999]. Based on our results and theoretical considerations [*Dyadin et al.*, 1999] it appears unlikely that significant amounts of He reside as guest molecules in the hydrate lattice, even if the hydrate-forming gas contains a large He fraction. Probably, high He abundances in hydrate samples indicate the presence of an additional gas reservoir. We suggest that the He may have originated from gas vesicles trapped and sealed in the interstices of the hydrate during its formation or from contributions of ^4He -rich pore water incorporated in sediments that stick with the sampled hydrate. The heavier noble gases from Blake Ridge show a weaker fractionation pattern, which is probably due to a higher degree of contamination by air.

3.2. Carbon and Hydrogen Isotopes

[13] The $\delta^{13}\text{C}$ signature of the samples between -66.7 and -69.7‰ identifies the methane to be of microbial origin [*Whiticar et al.*, 1986] without a significant contribution of athermogenic source. The additional $\delta^2\text{H}$ signature allows to distinguish between the two basic microbial methane production pathways, acetate fermentation and CO_2 reduction. Combined, the data reflect the end-member of methanogenesis from CO_2 reduction. Our data are in agreement with an earlier study at Hydrate Ridge [*Kastner et al.*, 1998] and similar to the isotopic signature that has been found at Blake Ridge [*Paull et al.*, 2000] and the Okhotsk Sea [*Ginsburg et al.*, 1993] implying that CO_2 microbial reduction is the dominant CH_4 production pathway in these gas hydrate systems. In all samples, the methane is deficient in ^{14}C . The ^{14}C activity yields information on the integrated time span from burial of the organic

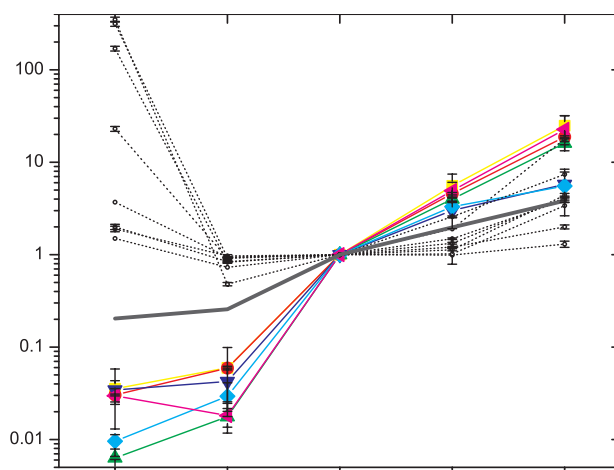


Figure 3. Noble gas fractionation factors. Also included are data from Blake Ridge [*Dickens and Kennedy*, 2000] and for ambient seawater ($T = 4.7$ C, $S = 34.2$).

matter, production of CO₂, production of methane to the formation of the methane hydrate and thus allows quantification of the potential contribution from a recent carbon reservoir. We may clearly exclude a contribution of a relatively recent (¹⁴C-active) organic carbon reservoir. Therefore, the organic matter from which the methane of the hydrates originated, must have been buried more than ~50 ka ago. Our data do not support an in-situ source of methane within the upper sediment interval. They clearly show that not only the deeper hydrates but also the shallow outcropping hydrates found at Hydrate Ridge are fed from a deeper ¹⁴C-dead methane source and that there is no near-surface process nor a recent carbon pool involved.

4. Conclusions

[14] Our findings open up a new application for He isotope studies at other gas hydrate sites. Helium components found in gas hydrates, as at Hakon Mosby Mud Volcanoe [Prasolov *et al.*, 1999] and at Blake Ridge [Dickens and Kennedy, 2000], presumably represent residual gas vesicles that are trapped in the hydrate structure (rather than as guest molecule) or porewater contributions and, thus, may yield direct information about the methane gas source.

[15] Hydrate formation seems to fractionate the heavier noble gases. The preferential incorporation of the heavier noble gases into the hydrate (Xe > Kr > Ar) is in accordance with theoretical considerations which also predict a temperature-dependence of the fractionation process [Barrer and Edge, 1967]. Therefore, noble gas distributions in gas hydrates may have the potential to be used as a proxy for the temperature during hydrate formation. At present, the lack of laboratory data on the preferential incorporation of noble gases in methane hydrates limits the quantitative interpretation of our heavy noble gas results. To exploit the full potential of the noble gases, we suggest laboratory formation of gas hydrates under controlled conditions and determination of noble gas fractionation factors under quasi-realistic natural conditions. At the same time, our study shows the need for intensified sampling, including the hydrate, the pore water and the free gas phase. Noble gas analysis of these three phases should distinguish the influence of purely thermodynamic vs geochemical factors on the noble gas pattern.

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G. Winckler and P. Schlosser, Lamont-Doherty Earth Observatory, Columbia University, 61 Route 9W, Palisades, NY 10964, USA. (winckler@ldeo.columbia.edu)

W. Aeschbach-Hertig, J. Holoher, and R. Kipfer, Isotope Geology, ETHZ, NOC 61, ZH 8092, Zürich & Department Water Resources and Drinking Water, EAWAG, ZH 8600, Dübendorf, Switzerland.

I. Levin and C. Poss, Institut für Umweltphysik, INF 229, 69120, Heidelberg, Germany.

G. Rehder and E. Suess, GEOMAR, 24148, Kiel, Germany.