

## **OBSERVATIONS OF MASS FRACTIONATION OF NOBLE GASES IN SYNTHETIC METHANE HYDRATE**

**Andrew G. Hunt<sup>1</sup>, John W. Pohlman<sup>2</sup>, Laura Stern<sup>3\*</sup>, Carolyn Ruppel<sup>2</sup>, Richard J. Moscati<sup>1</sup>, Gary P. Landis<sup>1</sup>, and John Pinkston<sup>3</sup>**

**1. U.S. Geological Survey  
Denver Federal Center, Bld 21, MS 963  
Denver, CO 80225  
USA**

**2. U.S. Geological Survey  
384 Woods Hole Rd  
Wood Hole, MA 02543  
USA**

**3. U.S. Geological Survey  
345 Middlefield Rd., MS 977  
Menlo Park, CA 94025  
USA**

### **ABSTRACT**

As a consequence of contemporary or longer term (since 15 ka) climate warming, gas hydrates in some settings are presently dissociating and releasing methane and other gases to the ocean-atmosphere system. A key challenge in assessing the susceptibility of gas hydrates to warming climate is the lack of a technique able to distinguish between methane recently released from gas hydrates and methane emitted from leaky thermogenic reservoirs, shallow sublake and subseafloor sediments, coalbeds, and other sources. Carbon and deuterium stable isotopic data provide only a first-order characterization of methane sources, while gas hydrate can sequester any type of methane. Here, we investigate the possibility of exploiting the pattern of noble gas fractionation within the gas hydrate lattice to fingerprint methane released from gas hydrates. Starting with synthetic gas hydrate formed under careful laboratory conditions, we document complex noble gas fractionation patterns in the gases liberated during dissociation and explore the effects of aging and storage (e.g., in liquid nitrogen), as well as sampling and preservation procedures. The laboratory results confirm a unique noble gas fractionation pattern for gas hydrates, one that shows promise in evaluating modern natural gas seeps for a signature associated with gas hydrate dissociation.

*Keywords:* gas hydrates, noble gas, climate change, methane source, seep

### **INTRODUCTION**

Recent studies provide some of the best indications to date that methane hydrate may be dissociating due to recent warming of intermediate ocean waters (e.g., Spitsbergen Margin [1]) or marine inundation of permafrost and warming since 15 ka (e.g., East Siberian Shelf [2]). At such sites, constraining the component of methane emissions attributable directly to gas hydrate dissociation is critical. Such information provides a baseline for comparison with future observations of local change and can be upscaled to better inform estimates of methane emissions from gas hydrates for IPCC [3] assessments. Unfortunately, stable isotopic techniques cannot distinguish

between methane that was recently sequestered in gas hydrates and microbial or thermogenic methane that has most recently been stored in gaseous form in sediments. Noble gases, preferentially partition by molecular weight in the gas hydrate lattice, but do not have such a predictable relationship in other gas populations. Noble gas signatures might therefore be used to fingerprint gas streams derived from methane hydrate dissociation.

Selective enclathration of noble gases in synthetic gas hydrates has been recognized since the work of Barrer and Ruzicka [4] and Barrer and Edge [5]. These studies demonstrated that xenon (Xe) and

---

\* Corresponding author: Phone: 650-329-4811 Fax 650-329-5163 E-mail: [lstern@usgs.gov](mailto:lstern@usgs.gov)

krypton (Kr) were enriched relative to argon (Ar) in hydrate-derived gases and also inferred that helium (He) and neon (Ne) could be removed from Ar at low temperature [5]. In their study of naturally occurring methane hydrate, Chersky and Tsarev [6] noted that He was not incorporated into the gas-hydrate crystal structure and was instead enriched in the residual gas associated with the hydrate formation. Ginsburg et al. [7-9] also noted low He concentrations from hydrate-derived gases from the Okhotsk, Caspian, and Black seas.

More recent studies present contradictory results regarding the reliability of using this mass-based noble gas fractionation as a fingerprinting tool for hydrate-derived methane emissions. Dickens and Kennedy [10] present data obtained from Blake Ridge (ODP Leg 164), and Winckler et al. [11] present data from Hydrate Ridge, Cascadia Margin. These studies are unique in that they focused on the analysis of natural samples obtained far below and near the seafloor, respectively.

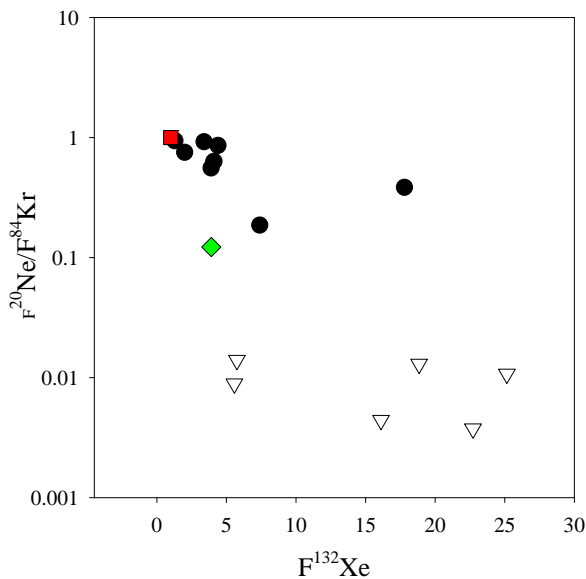


Figure 1. Plot of  $F^{20}\text{Ne}/F^{84}\text{Kr}$  vs.  $F^{132}\text{Xe}$ . Black symbols are from Ref [10] and ODP Leg 164. White data are from Ref [11] and Hydrate Ridge. Red denotes an atmospheric sample, and green is air saturated seawater at 2°C.

The two data sets produced by [10] and [11] are shown in Figure 1. Noble gas data is presented as F values, where  $F_i$  equals the ratio of component  $i$  ( $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{84}\text{Kr}$  or  $^{132}\text{Xe}$ ) to argon-36 ( $^{36}\text{Ar}$ ) of the

sample normalized to the atmospheric ratio of component  $i$  to  $^{36}\text{Ar}$ . The ratio of  $F^{20}\text{Ne}$  to  $F^{84}\text{Kr}$  (equivalent to the ratio of  $^{20}\text{Ne}$  to  $^{84}\text{Kr}$  normalized to atmosphere) is plotted against  $F^{132}\text{Xe}$  from the methane hydrate samples from each investigation.

The plot includes four components of noble gas isotopes ( $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$ ) to examine degrees of mass fractionation relative to  $^{36}\text{Ar}$ . Winckler et al. [11] assume an air-like isotopic composition of the noble gas components (data originally reported as total elemental composition).

Dickens and Kennedy [10] report a relatively small shift of  $F^{20}\text{Ne}/F^{84}\text{Kr}$  values from an atmospheric composition end member with increasing  $F^{132}\text{Xe}$ . Winckler et al. [11], however, reported higher  $F^{132}\text{Xe}$  and lower  $F^{20}\text{Ne}/F^{84}\text{Kr}$  values that suggest extensive loss of light isotopes relative to atmospheric and air saturated sea water (ASSW), a trend that would support the observations and speculations of Barrer. This mass fractionation is further demonstrated in the  $F^4\text{He}$  values reported by Winckler et al. [11] ( $F^4\text{He}$  from 0.006 to 0.097) as compared to Dickens and Kennedy [10] which suggest appreciable amounts of  $^4\text{He}$  ( $F^4\text{He}$  from 1.5 to 350). Winckler and coworkers speculate that the Dickens and Kennedy data reflect contamination by air during sampling and storage in liquid nitrogen ( $\text{LN}_2$ ) prior to analysis, whereas the shipboard techniques used by Winckler et al. avoided that problem. However, that explanation does not account for the extreme He enrichments displayed by the Dickens and Kennedy data.

The purpose of our study is to investigate the systematics of noble gas mass and isotopic fractionation during the formation and dissociation of gas hydrate in controlled laboratory conditions, and, furthermore, to evaluate whether handling and storage procedures have an effect on the measured compositions.

## METHODS

The experiment is designed to evaluate the effects of general encapsulation of noble gases in the synthetic hydrate structure and subsequent storage in  $\text{LN}_2$ . The experiment produced two splits of synthetic hydrate, one control and one experimental. The control sample was left in the synthesis apparatus and dissociated directly after

synthesis (Noble 1). The second experimental hydrate was removed from the synthesis apparatus and stored in LN<sub>2</sub> for later dissociation (Noble 2-2).

### Synthesis procedure

Methane hydrate was synthesized by a modified version of previously-published methods involving the warming and static conversion of a measured mass of small grains (< 250 μm) of H<sub>2</sub>O ice to gas hydrate in an atmosphere of pressurized gas [12-13]. Modifications include pre-mixing of two commercially available gases, a reagent-grade CH<sub>4</sub> spiked with 200 ppm He and pressurized air with uniform noble gas content. To obtain reproducible amounts of noble gases in the final source gas, we mixed the gases within the 900 cm<sup>3</sup> reservoir of our synthesis assembly to ~30 MPa at an approximate ratio of 85:15 methane-to-air. After mixing and cooling the gas to 250K, two pre-chilled sample chambers were packed with identical masses of granular ice. The samples were attached to the synthesis apparatus and evacuated to remove air from between the ice grains. After equilibrating the source gas and sample chambers at ~20 MPa, the chamber was warmed from 250K at a rate of ~ 7 K/hr to ~ 287 K, conditions deep within the methane hydrate stability field and well above the H<sub>2</sub>O ice melting point. Previous work has demonstrated most hydrate formation occurs during the first heating stage [13]; however, additional heating cycles were performed to ensure full reaction.

### Dissociation procedure

The control sample was dissociated by isolating the pressurized sample from the synthesis apparatus and placing it in a low-temperature Hart fluid bath. All portions of the transfer system were fully evacuated prior to sample introduction. Pressure in the synthesis apparatus was reduced to just above 0.1 MPa to relieve excess gas pressure while preventing the infiltration of atmospheric air. The dissociated gas was transferred into collection tubes. For the LN<sub>2</sub> storage experiment, the sample was cooled with LN<sub>2</sub> to ~ 130K at a modest pressure within the methane hydrate stability field. The chilled sample was depressurized, removed from the sample vessel, wrapped in Al foil, and stored in LN<sub>2</sub>. After 9 months, the LN<sub>2</sub>-stored sample (Noble 2-2) was placed into the pressure vessel and attached to the dissociation station. Following brief evacuation to

remove air from the chamber, the experimental samples was dissociated in a similar manner as the control sample.

For multiple-step dissociations, sample temperature was initially kept sufficiently low to ensure slow and controlled dissociation and then warmed through the ice point to release the residual gas. For all samples, temperature was controlled by the Hart fluid bath and monitored with a thermocouple embedded in the center of the sample. The dissociated gas was collected into a series of 50-cc stainless steel cylinders (rated to 1800 psi) and small Cu tubes (loaded to 5 to 15 psi). Numerous valves and pressure gauges on the dissociation station permitted careful monitoring of pressure throughout each collection and full evacuation of various portions of the system, as necessary. Gas collections in the Cu tubes were then shipped to the USGS Noble Gas Laboratory in Denver, CO for subsequent noble gas analysis.

## RESULTS AND DISCUSSION

### Hydrate step dissociation data

Data from the step dissociation of the control sample (Noble 1) are presented in Figure 2A. The plot of F<sup>20</sup>Ne/F<sup>84</sup>Kr versus F<sup>132</sup>Xe from the control sample displays a distinct trend toward elevated F<sup>132</sup>Xe and lower F<sup>20</sup>Ne/F<sup>84</sup>Kr values during the dissociation process. According to Barrer [4-5], Ar, Kr, and Xe components are released from lattice sites of the methane hydrate, but He and Ne have small enough effective ionic radii that they should be absent. While the concentration of Ne is low, it is not absent. The dissociation trend in Figure 2A reflects preferential loss of the trace Ne relative to Kr, as well as preferential loss of Ar relative to Xe during dissociation. Because the sample was purged between dissociation steps, we are confident the trend is not a fractional loss of headspace gas with increasing dissociation steps, but rather a release of gas from hydrate. Overall, the trend suggests preferential loss of the smaller nobles and retention of the larger nobles during gas hydrate dissociation.

A simple two component mixing model quantifies the percent loss of the final headspace gas during dissociation. The dashed lines in Figure 2A are the calculated percent of final headspace gas released during each dissociation step.

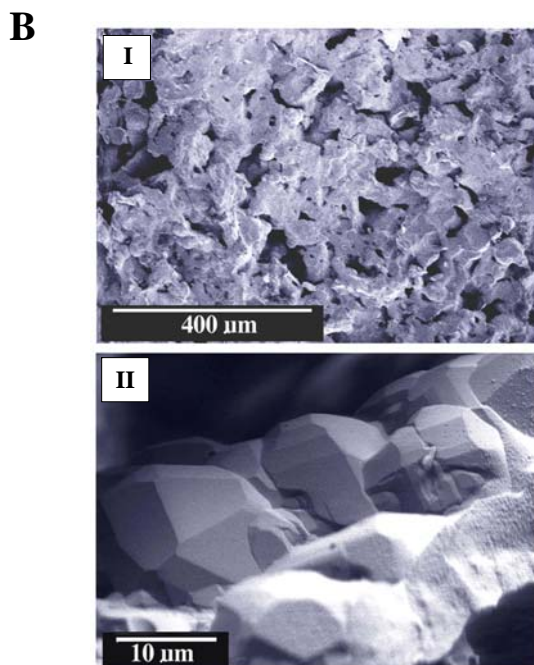
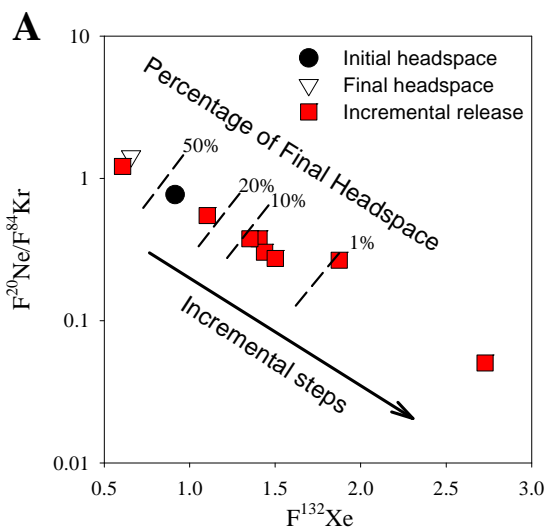


Figure 2. A. Plot of  $F^{20}\text{Ne}/F^{84}\text{Kr}$  versus  $F^{132}\text{Xe}$  for multi-step dissociation of Noble 1 experiment. B. Cryogenic scanning electron microscopy images of methane hydrates synthesized with the same techniques as employed for these experiments. Image I shows the overall appearance and granular nature of the material, which has 30% intergranular porosity. Close-up Image II shows that individual grains are dense and typically 20 to 50  $\mu\text{m}$  diameter.

There are at least two possible explanations for the trend of Ne-depletion and Xe-enrichment during step-dissociation (Fig. 2A). The step measurements release all gases trapped within the bulk hydrate (composition equivalent to the final headspace gas), which consists of non-lattice and lattice-bound voids.

Cryogenic scanning electron microscopy of synthetic hydrate (Figure 2b) shows numerous non-lattice voids where gas could be trapped. If the non-lattice voids contain Ne and are Kr-enriched, the release of gas from the non-lattice sites along with a constant lattice-bound composition would produce the trend observed in Figure 2A. During the initial venting of the sample prior to dissociation (see Methods) audible “sample crackling” occurred and might indicate loss of non-lattice pore space gas from the hydrate. However, stoichiometry tests of synthetic hydrate indicate negligible storage of methane in non-lattice pore space [14], which also suggests insignificant storage of He and Ne in the non-lattice hydrate volume fraction.

An alternative explanation is that the He and Ne components are loosely held in hydrate lattice sites. If gas from lattice and non-lattice hydrate sites is the source of the initial and final headspace gas components, there should be uniformity in the composition light noble gases (He and Ne). The concentration data from the Noble 1 dissociation shows that  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  concentrations are fairly constant at  $30.4 \pm 3.1 (\times 10^{-9})$  and  $1.1 \pm 0.2 (\times 10^{-9})$  ccSTP/cc, respectively, throughout step dissociation, while  $^4\text{He}$ ,  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  concentrations decrease. A plot of  $F^{20}\text{Ne}$  versus  $F^4\text{He}$  (Figure 3) shows that  $^4\text{He}$  and  $^{20}\text{Ne}$  from the late dissociation stage steps do not resemble the gas composition of the initial or final headspace gases.

This release pattern indicates a preferential loss of the light masses relative to the heavy masses and suggests diffusional release of the light gases (He and Ne) during dissociation. This would explain why the  $F^4\text{He}$  and  $F^{20}\text{Ne}$  ratios decrease throughout the dissociation process (Fig. 3). Furthermore,  $F^4\text{He}$  decreases at a greater rate than  $F^{20}\text{Ne}$ , which suggests He, the smallest noble gas, is lost preferentially to Ne. If Ar is diffusing from the system it cannot be determined from the data.

Decreasing concentrations of  $^{36}\text{Ar}$  during step dissociation may be an effect of mixing with the headspace gas and the hydrate end member gas.

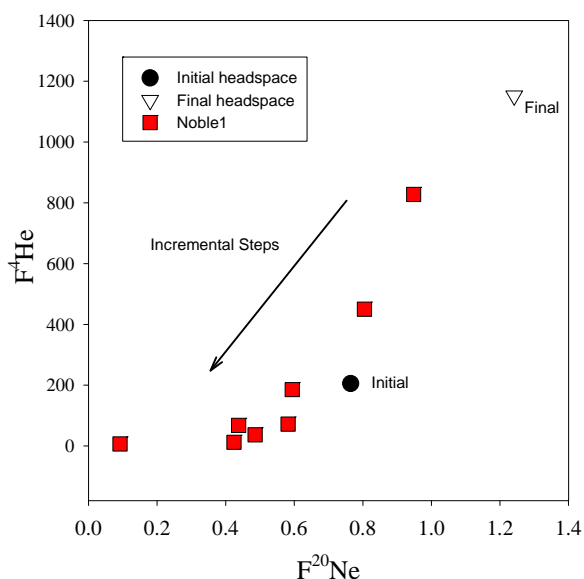


Figure 3.  $F^4\text{He}$  versus  $F^{20}\text{Ne}$  for Noble 1 step dissociation experiment.

### Storage effects

The amount of noble gases in the samples stored in  $\text{LN}_2$  for 9 months (Noble 2-2) were generally lower than the control sample (Noble 1), which

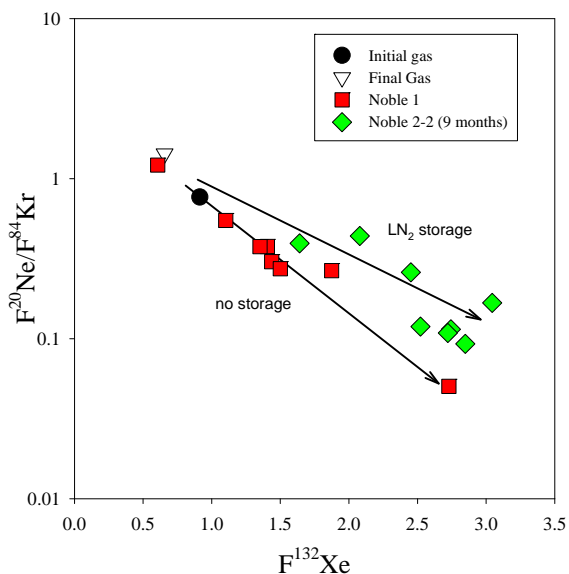


Figure 4.  $F^{20}\text{Ne}/F^{84}\text{Kr}$  versus  $F^{132}\text{Xe}$  for samples stored in  $\text{LN}_2$ .

suggests a net loss of gas during storage. As was observed in the control experiment, Ne and Xe (relative to Kr and Ar, respectively) were also preferentially lost during storage (Figure 4). A notable difference between the results of the control and storage experiments is the relatively greater retention of Ne and He and in the storage experiment.

The offset between control and storage data in Figure 4 provides strong evidence for retention of Ne during storage relative to Kr. He and Ne loss may be suppressed at  $\text{LN}_2$  temperatures and increased when raised to temperatures associated with the dissociation process.

Lattice and non-lattice gas may also have been lost during the transfer from synthesis vessel to  $\text{LN}_2$  and back to the dissociation vessel. However, the step dissociation patterns and large amounts of He and Ne noted in the analyses preclude complete loss of the gases with storage even through loss by diffusion. Possible diffusive losses of the  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  concentrations are similar to the control sample in Noble 1. Overall  $F^{132}\text{Xe}$  and  $F^{84}\text{Kr}$  for the  $\text{LN}_2$  storage samples are uniform, with  $F^{132}\text{Xe}$  of  $2.6 \pm 0.3$  and  $F^{84}\text{Kr}$  of  $1.67 \pm 0.2$ . A trend of increasing  $^{20}\text{Ne}$  is evident in the  $F^{20}\text{Ne}/F^{84}\text{Kr}$  values from the stored sample which deviates from the  $F^{20}\text{Ne}/F^{84}\text{Kr}$  trend of the control sample (Fig. 4). If the trend of increasing  $F^{20}\text{Ne}/F^{84}\text{Kr}$  values during  $\text{LN}_2$  stored is extended to a longer time scale (e.g., years instead of months) values similar to those reported by Dickens and Kennedy [10] are possible (see Fig. 1). Thus, long term storage of gas hydrate in  $\text{LN}_2$  could have more detrimental effects on the noble gas composition of gas hydrate.

### CONCLUSIONS

Mass fractionation of noble gases in synthetic methane hydrate samples follows the observations of Winckler et al. 2002 [11] in that there is enrichment of Kr and Xe relative to Ar. Low values of  $F^4\text{He}$  and  $F^{20}\text{Ne}$  are noted in both the natural and synthetic hydrates, but the hydrates may tend to store these gases in lattice defects that could retain He and Ne. These effects are important factors to consider when evaluating noble gas data from natural gas hydrate samples and when using noble gas data to fingerprint seep gas emissions.  $\text{LN}_2$  storage does affect the noble gas composition of gas hydrate stored over a 9-

month period, but this change may not be significant over shorter time scales.

#### ACKNOWLEDGEMENTS

Partial support for this research was provided by Interagency Agreements DE-FE0002911 and DE-NT0006147 between the U.S. Geological Survey Gas Hydrates Project and the U.S. Department of Energy's Methane Hydrates Research and Development Program. We thank T. Lorenson for help with dissociation of some samples.

#### REFERENCES

- [1] Westbrook, G. K., Thatcher, K.E., et al. *Escape of methane gas from the seabed along the West Spitsbergen continental margin*. Geophysical Research Letters, 2009, 36: p. L15608. doi:10.1029/2009GL039191.
- [2] Shakhova, N., Semiletov, I., Salyuk, A., Yusupov, V., Kosmach, D., and Gustafsson, O., *Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf*. Science, 2010, 327: p. 1246-1250. doi:10.1126/science.1182221.
- [3] Intergovernmental Panel on Climate Change (IPCC). *Climate Change 2007: The Physical Basis*, 2007, Cambridge University Press: New York.
- [4] Barrer, R.M. and Ruzicka, D.J. *Non-stoichiometric clathrate compounds of water. Part 2. Formation and properties of double hydrates*, Trans. Faraday Society, 1962, 58, 2239
- [5] Barrer, R.M. and A.V.J. Edge, *Selective clathration during the formation of gas hydrates*. Separation Science, 1967. 2(2): p. 145-154.
- [6] Chersky, N.V. and Tsarev V.P., *Osobennosti nakopleniya helija v rajonakh rasprostraneniya mnogletnei merzloty. V Kn. "Geologicheskoe stroenie, perspektivy neftegasonosnosti Jakutskoj ASSR", 1972, JF SO AN SSSR pp 124-132 (in Russian)* cited in Prasolov, E.M., et al., *Helium and other noble gases in gas-hydrate sediments of the Hakon Mosby Mud Volcano*. Geo-Marine Letters, 1999. 19: p. 84-88.
- [7] Ginsburg, G.D., et al., *Filtrogenic gas hydrates in the Black Sea*. Soviet Geology and Geophysics, 1990. 31: p. 8-16.
- [8] Ginsburg, G.D., et al., *Gas hydrates of the Southern Caspian*. International Geology Review, 1992. 13: p. 41-48.
- [9] Ginsburg, G.D., et al., *Gas hydrates from the continental slope, offshore Sakhalin Island,*

*Okhotsk Sea*. Geo-Marine Letters, 1993. 19: p. 57-67.

- [10] Dickens, G.R. and B.M. Kennedy, *Noble gases in methane hydrate from the Blake Ridge*, in *Proceedings of the Ocean Drilling Program; volume 164; scientific results; gas hydrate sampling on the Blake Ridge and Carolina Rise; covering Leg 164 of the cruises of the drilling vessel JOIDES Resolution, Halifax, Nova Scotia, to Miami, Florida, sites 991-997, 31 October-19 December 1995*, C.M.R. Miller, Ruth, Editor. 2000, Texas A & M University, Ocean Drilling Program, College Station, TX, United States (USA).
- [11] Winckler, G.A.-H., Werner; Holocher, Johannes; Kipfer, Rolf; Levin, Ingeborg; Poss, Christian; Rehder, Gregor; Suess, Erwin; Schlosser, Peter, *Noble gas and radiocarbon in natural gas hydrates*. Geophysical Research Letters, 2002. 29(10): p. 4.
- [12] Stern, L. A., Kirby, S. H., and Durham, W. B., *Peculiarities of methane clathrate hydrate formation and solid-state deformation, including possible superheating of water ice*. Science, 1996, 273 (5283): p. 1843-1848.
- [13] Stern, L.A., Circone, S., Kirby, S.H., and Durham, W.B. *Scanning Electron Microscopy (SEM) investigations of laboratory-grown gas hydrates formed from melting ice, and comparison to natural hydrates*. American Mineralogist, 2004. 89 (8-9): p. 1162-1175.
- [14] Circone, S., Kirby, S. H., and Stern, L.A. *Direct measurement of methane hydrate composition along the hydrate equilibrium boundary*. J. Physical Chemistry B, 2005. 109 (19): p. 9468-9475.