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16. NOBLE GASES IN METHANE HYDRATE FROM THE BLAKE RIDGE[1]

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ABSTRACT

Fractionation of the noble gases should occur during formation of a Structure I gas hydrate from water and CH_4 such that CH_4 hydrate is greatly enriched in Xenon. Noble gas concentrations and fractionation factors (F[^{4}He], F[^{22}Ne], F[^{86}Kr], and F[^{132}Xe] as well as R/R_a) were determined for eight gas hydrate specimens collected on Leg 164 to evaluate this theoretical possibility and to assess whether sufficient quantities of Xe are hosted in oceanic CH_4 hydrate to account for Xe "missing" from the atmosphere. The simplest explanation for our results is that samples contain mixtures of air and two end-member gases. One of the end-member gases is depleted in Ne, but significantly enriched in Kr and Xe, as anticipated if the source of this gas involves fractionation during Structure I gas hydrate formation. However, although oceanic CH_4 hydrate may be greatly enriched in Xe, simple mass balance calculations indicate that oceanic CH_4 hydrate probably represents only a minor reservoir of terrestrial Xe. Noble gas analyses may play an important role in understanding the dynamics of gas hydrate reservoirs, but significantly more work is needed than presented here.

INTRODUCTION

The "Missing Xenon Problem" is an outstanding geochemical puzzle that relates to observed concentrations of noble gases in the Earth's atmosphere. After considering addition of radiogenic Ar and loss of He, elemental ratios of noble gases in the atmosphere are similar to those in the solar system (as determined from meteorites) with the notable exception of a 10- to 20-fold deficiency in Xe (e.g., Canalus et al., 1968; Pepin, 1992; Tolstikhin and O'Nions, 1994). Thus, for several decades, it was believed that Xe missing from the atmosphere was stored in some repository of the upper geosphere; that is, a large reservoir exists near the Earth's surface that contains abundant Xe without significant enrichment of other noble gases. However, despite numerous investigations of potential Xe-rich reservoirs (e.g., ice caps, shale, siliceous ooze, etc.), no repository has been identified that can account for Xe missing from the Earth's atmosphere (Podosek et al., 1981; Wacker and Anders, 1984; Bernatowicz et al., 1984, 1985; Matsuda and Matsubara, 1989). An alternative explanation for the "Missing Xenon Problem" is that Xe was lost through a specific sequence of processes early in the evolution of our Earth (e.g., Tolstikhin and O'Nions, 1994).

Clathrate hydrates of gas ("gas hydrates") are crystalline compounds in which cages of water molecules host molecules of gas. Vast quantities of CH_4 hydrate are located in pore space of sediment along continental margins and in permafrost regions (Kvenvolden, 1993; Dickens et al., 1997). Although noble gas concentrations had never been determined in samples of CH_4 hydrate (experimental or natural) before this study, theoretical considerations suggest that formation of CH_4 hydrate should involve significant fractionation of the noble gases such that the solid hydrate lattice will become greatly enriched in Xe relative to other noble gases (Nikitin, 1937; Barrer and Stuart, 1957; Davidson, 1973; Verkhovsky et al., 1988). Previous discussions of the "Missing Xenon Problem" have not considered the amount of Xe and other noble gases potentially stored in CH_4 hydrate.

Leg 164 was devoted to understanding the composition and distribution of gas in a large gas hydrate reservoir located on the Blake Ridge off the southeast coast of the United States (Fig. 1; Paull, Matsumoto, Wallace, et al., 1996). Here we present results of a pilot study to examine the noble gas composition of natural CH_4 hydrate specimens collected from boreholes drilled during this leg. Initial goals of this research were twofold: (1) to test whether expected noble gas fractionation actually occurs during the formation of natural CH_4 hydrate, and (2) to assess whether the deficiency of Xe in the atmosphere can be accounted for by storage of Xe in oceanic CH_4 hydrate. Although we address both issues, the main thrust of our discussion is to suggest that noble gases may provide an important means to distinguish between multiple pathways for the genesis of CH_4 hydrate in marine sediment.

THEORETICAL BACKGROUND

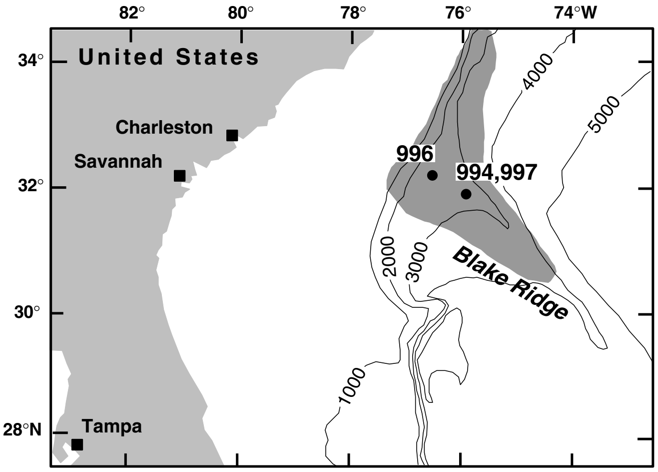

Figure 1. Location of the Blake Ridge showing Sites 994, 996, and 997 (from Paull, Matsumoto, Wallace, et al., 1996). Shaded area shows region with seismic evidence for gas hydrate. Bathymetric contours are in meters.

Three types of clathrate structures have been identified: Structure I, Structure II, and Structure H (Von Stackelberg and Muller, 1951; Davidson et al., 1984; Ripmeester et al., 1987). Each of these clath-

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rate structures contains small and large cavities between cages of water molecules. The type of clathrate structure formed from water and gas depends on the size ("van der Waals diameter") of the gas molecules (Davidson et al., 1984; Handa and Tse, 1986; Ripmeester and Ratcliffe, 1990).

Many pure gases that have average molecular van der Waals diameters between 410 and 580 pm (e.g., CH_4, CH_3Cl, SO_2, and Xe) form Structure I clathrates with two cavities of average diameter of 782 pm and six cavities of average diameter of 866 pm per unit cell (Davidson, 1973; Davidson et al., 1984; Handa and Tse, 1986). In the case of impure gas, trace gases that can fit into Structure I cavities will be incorporated into the clathrate lattice during gas hydrate formation (e.g., Davidson, 1973). This incorporation of trace gases involves fractionation such that the composition of gas in hydrate, gas dissolved in water, and the original gas may be significantly different. The degree of fractionation between any two gases during Structure I clathrate formation should depend largely on temperature and the difference between average van der Waals diameters for molecules of the two gases (Barrer and Stuart, 1957; Davidson, 1973).

Several authors (Nikitin, 1937; Barrer and Stuart, 1957; Davidson, 1973) have demonstrated experimentally or theoretically that formation of a Structure I clathrate in the presence of noble gases will cause large fractionation between the noble gases. Such fractionation is exemplified in Table 1, which lists experimental and "theoretical" Kr/Ar, Xe/Kr and Xe/Ar enrichment factors during formation of CH_3Cl hydrate (from Davidson, 1973, p. 231). Note that enrichment factors indicate preferential enrichment of the heavier noble gas into Structure I gas hydrate (Xe > Kr > Ar) and that fractionation increases with decreasing temperature. Nikitin (1937) reported that small quantities of He and Ne, along with relatively large quantities of Ar and Rn (Rn > Ar >> Ne > He), were incorporated into the clathrate lattice during SO_2 hydrate formation. Barrer and Stuart (1957) and Davidson (1973) omit discussion of He or Ne (as well as Rn) fractionation (presumably because diameters of He and Ne molecules are too small to fit into Structure I cavities so that their fractionation values are very small to zero). To our knowledge, no experimental or theoretical data have been presented for noble gas fractionation during CH_4 hydrate formation.

SAMPLE COLLECTION

Samples collected for our noble gas investigation were gas aliquots from Leg 164 shipboard gas hydrate dissociation experiments at Sites 994, 996, and 997. These experiments are detailed by Paull, Matsumoto, Wallace, et al. (1996, p.18, 19, 112, 113, 249–255, 257, and 286–288).

"Massive" specimens of gas hydrate were recovered in sediment cores by the advanced hydraulic piston core (APC) or extended core barrel (XCB) at Sites 994, 996 and 997 (Paull, Matsumoto, Wallace, et al., 1996). Several of these specimens were hand picked from cores and immediately placed in a storage container with liquid nitrogen for preservation. Stored samples then were transferred into a gas hydrate dissociation chamber. This chamber (Fig. 2) consists of a small (23 cm^3) pressure vessel connected to a gauge block assembly and a gas sampling port. The chamber (with the hydrate specimen inside) was evacuated for 1 s at room temperature. Gas hydrate specimens were then allowed to dissociate at room temperature. After thermal equilibration and complete dissociation, pressure inside of the chamber was recorded and a gas split was collected for shipboard gas chromatography (GC). Remaining gas was released into an evacuated stainless steel gas cylinder for shore-based analyses, including our investigation. The volume of water released during hydrate dissociation and the Cl^- content of this water was determined after opening the chamber. The volume of gas released during hydrate dissociation was calculated from recorded pressures, temperatures, and the ideal gas law.

Table 1. Experimental and theoretical enrichment factors for noble gases during formation of CH_3Cl hydrate.

Noble gas pair M, M′	Temp. (°C)	Experimental	Theoretical
Kr, Ar	0	3.4	4.1
	–30	5.3 ± 2.0	
Xe, Kr	0	2.9	5.7
	–30	4.2 ± 1.2	
Xe, Ar	0	ND	23
	–30	24 ± 3	

Notes: From Davidson, 1973. Enrichment factors signify the amount that gas M will be enriched relative to gas M′. Theoretical enrichment factors were determined according to occupation of similar lattice vacancies, which may not be the case for different noble gases (from Davidson, 1973). ND = not determined.

Gas released from seven gas hydrate specimens were examined in our study (Table 2). For six hydrate specimens, nearly all gas remaining after removal of the split for shipboard GC analyses could be placed inside of a stainless steel container. However, the hydrate specimen recovered from Core 164-997A-42X released a sufficient quantity of gas (1250 cm^3) to transfer significant amounts of gas into two stainless steel containers. Gas in these two containers, labeled A and B, are successive splits of an original gas quantity that were taken at high and low pressure, respectively. All eight gas samples in stainless steel containers were analyzed for noble gases (Table 2).

Original specimens of gas hydrate are from different depths in the sediment column and from distinct fluid flow regimes (Table 2). In particular, specimens from Sites 994 and 997 were collected at deep depth (>220 mbsf) in an area with relatively low fluid flow whereas specimens from Site 996 were collected at shallow depth (<50 mbsf) in a region of active fluid venting on the seafloor (Paull, Matsumoto, Wallace, et al., 1996).

There is no precedent for naming gas samples collected from dissociated gas hydrate specimens recovered from ODP holes. For the remainder of this paper, we give our samples the standard ODP nomenclature for the hole, core, and section from which the hydrate was recovered, followed by a designator for the sample number (i.e., the first two columns in Table 2). Thus, gas released from the second hydrate specimen recovered from Hole 996C, Core 1H, and Section 1 is simply called "Sample 996C-1H-1(2)" (Tables 2, 3), even though it

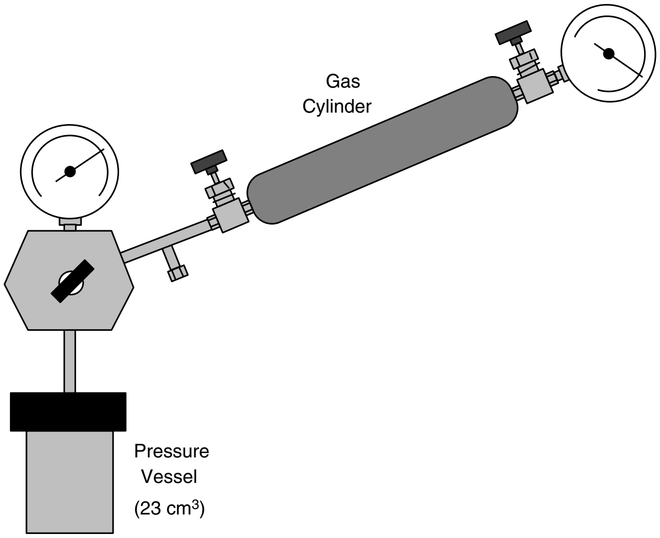

Figure 2. Chamber used to dissociate gas hydrate specimens and collect gas for noble gas analyses.

Table 2. Description of gas samples after hydrate dissociation.

Gas sample number*	Hole, core, section	Hydrate specimen number†	Sample depth (mbsf)‡	Gas volume** (cm^3)	CH_4†† (%)	Water volume (cm^3)	Water Cl^-	Gas/water ratio	Storage (months)
1	994C-31X-7	1	260	617	98.8	4	57	154	7
2	996B-1H-1	1	0	347	99.3	6.5	169	53	1.5
3	996B-1H-1	2	0	183	99.4	9.1	248	20	7
4	996C-1H-1	1	0	195	99.5	3.3	294	65	1.5
5	996C-1H-1	2	0	369	NA	4.8	245	98	7
6	996E-7H-CC	1	61	908	99.7	6.4	21	143	1.5
7	997A-42X-3	1A	331	1250	98.4	9.0	187	139	1.5
8	997A-42X-3	1B	331	(1250)	(98.4)	(9.0)	(187)	(139)	7

Notes: * = numbering scheme used in Tables 2 and 3 and Figures 3–5. † = numbering taken from tables in Paull, Matsumoto, Wallace, et al. (1996) where A and B designate successive gas samples of the same hydrate specimen. ‡ = approximate depth in the sediment column (placed at the top of the core in which the specimen was collected). ** = total volume of gas released from the hydrate specimen inside of the experimental chamber (Fig. 2). †† = methane quantity determined on ship prior to shipping and storage of gas bottles. NA= not analyzed. From Paull, Matsumoto, Wallace, et al. (1996). Parentheses for gas sample 8 indicate that reported values are the same as for gas sample 7.

Table 3. Noble gas composition of dissociated gas hydrate specimens from Leg 164 and appropriate standards.

Sample number*	Gas sample	^{36}Ar (ppmv)	$F(^4He)$	±	$F(^{22}Ne)$	±	$F(^{84}Kr)$	±	$F(^{132}Xe)$	±	R/R_a	±
1	994C-31X-7(1)	0.444	23	1.4	0.91	0.02	1.21	0.02	2.0	0.1	0.18	0.01
2	996B-1H-1(1)	0.300	1.9	0.13	0.97	0.03	1.13	0.03	4.4	0.2	0.74	0.06
3	996B-1H-1(2)	1.038	2.0	0.13	0.84	0.02	1.33	0.03	4.1	0.2	0.42	0.08
4	996C-1H-1(1)	0.225	170	10	0.83	0.02	1.49	0.03	3.9	0.2	0.11	0.01
5	996C-1H-1(2)	1.195	315	19	0.93	0.02	0.99	0.20	1.3	0.1	0.15	0.01
6	996E-7H-CC(1)	0.218	350	21	0.48	0.02	2.58	0.05	7.4	0.4	0.75	0.01
7	997A-42X-3(1A)	0.452	1.5	0.11	0.73	0.02	1.90	0.04	17.8	1.0	1.01	0.14
8	997A-42X-3(1B)	0.893	3.7	0.23	0.94	0.24	1.02	0.02	3.4	0.2	0.30	0.03
	Air	3.148	1.0		1.00		1.00		1.00		1.00	
	AS seawater 0°C		0.19		0.24		1.95		4.04		1.00	
	AS seawater 25°C		0.29		0.33		1.73		3.09		1.00	

Notes: * = numbering scheme used in Tables 2 and 3, and Figures 3–5. Concentration and fractionation values for air and air-saturated (AS) seawater are from Ozima and Podosek (1983).

is not a sample of sediment or gas that would commonly receive this ODP designation.

ANALYTICAL PROCEDURES

Noble gas analyses were performed in the Roving Automated Rare Gas Analysis (RARGA) laboratory at Lawrence Berkeley National Laboratory, University of California (Kennedy et al., 1985; Hiyagon and Kennedy, 1992). Detailed sample preparation and analytical procedures are discussed for fluid samples and can be found in Kennedy et al. (1985) and Hiyagon and Kennedy (1992).

Approximately 10 to 30 cm^3-atm of each gas sample was transferred to a pre-evacuated Cu tube that was subsequently sealed with a refrigeration clamp. Samples in the Cu tubes were then attached to the sample extraction and purification line of the RARGA laboratory that consists of an all-metal gas purification line designed specifically for routine reactive gas cleanup of dirty fluid samples. The extraction system and purification line are connected directly to an all-metal noble gas mass spectrometer laboratory. Each gas sample was analyzed for absolute and relative abundance of isotopes of He, Ne, Ar, Kr, and Xe. Before each sample analysis, a blank was analyzed. In all cases the blanks were <0.1% of the measured Ar composition of the atmosphere. The data has been corrected for mass interference due to HCl and doubly charged ^{40}Ar and $^{44}CO_2$ and instrumental mass fractionation corrections. Uncertainties related to these corrections were propagated quadratically.

Gas samples were analyzed in two batches of four samples each. The first batch (Samples 996B-1H-1[1], 996C-1H-1[1], 996E-7H-CC[1], and 997A-42X-3[1A]) was analyzed approximately one and a half month after gas collection, whereas the second batch (Samples 994C-31X-7[1], 996B-1H-1[2], 996C-1H-1[2], and 997A-42X-3[1B]) was analyzed approximately seven months after gas collection (Table 2).

RESULTS

Shipboard results of gas dissociation experiments are presented in Table 2 and by Paull, Matsumoto, Wallace, et al. (1996). Gas volumes released from dissociation of hydrate specimens ranged between 183 and 1250 cm^3 and were significantly larger than the volume of the chamber (23 cm^3). All gas splits analyzed on ship contained in excess of 98.4% CH_4 with the remainder consisting largely of CO_2. Water volumes released from dissociation of hydrate specimens ranged between 3.3 and 9.1 cm^3, and had Cl^- concentrations between 21 and 294 mM. Volumetric gas/water ratios for samples after hydrate dissociation vary between 20 and 154. In general, volumetric gas/water ratios are proportional to gas volumes and inversely proportional to Cl^- concentrations (Table 2).

Noble gas data is typically presented in terms of F(i) values. An F(i) value is the fractionation factor relative to atmospheric composition, and is defined as

$$F(i) = \frac{(i/^{36}Ar)_{sample}}{(i/^{36}Ar)_{air}},$$

where (i) is the concentration of an isotope of a noble gas. Concentrations of ^{36}Ar and F(i) values (with uncertainties) for the most abundant stable isotope of He, Ne, Kr, and Xe are listed in Table 3 for the gas samples obtained on Leg 164. Relative to air, all samples are enriched in ^{4}He and ^{132}Xe ($F[i] > 1$), and depleted in ^{22}Ne ($F[i] < 1$); most samples are enriched in ^{84}Kr.

Helium isotope data is typically presented in terms of R/R_a values where R is the measured $^3He/^4He$ value in a sample, and R_a is the

$^3He/^4He$ value in air. R/R_a values (with uncertainties) for the gas samples obtained on Leg 164 range between 0.11 and 1.01 (Table 3). The isotopic compositions of Ne, Ar, and Xe were isotopes were indistinguishable from air.

BASIC INTERPRETATIONS

Two related questions provided the impetus for this investigation: (1) is natural CH_4 hydrate significantly enriched in Xe relative to the other noble gases, and (2) can Xe in oceanic CH_4 hydrate account for Xe "missing" from the atmosphere? However, our most intriguing result concerns potential use of noble gases to assess multiple gas sources and processes of gas hydrate formation. We discuss this latter issue first. Then, with this background, we return to our original questions.

Multiple Gas Sources

The most basic result of this study is that our gas samples contain at least three distinct sources of noble gases. This conclusion is best shown by plotting one F(*i*) value against another for all eight gas samples (Figs. 3, 4). Mixing of two gases with different noble gas compositions will result in gas samples that plot as a line on an F(*i*) vs. F(*i*) diagram. Mixing of two end-member gases cannot explain the array of F(*i*) values for our samples (Figs. 3, 4). A plot of F(^4He) vs. R/R_a for all eight samples also indicates multiple gas sources (Fig. 5).

The simplest explanation for the observed noble gas compositions is that there are three gases, and samples are mixtures of two of these gases (Figs. 3–5). Gas A is similar to air but depleted in ^3He; it has a low R/R_a (<0.2), low F(^4He) (<25), and fractionation factors for ^4Ne, ^{86}Kr, and ^{132}Xe that are approximately 1. Relative to air, Gas B is depleted in Ne but enriched in Kr and Xe; it has an R/R_a and F(^4He) of approximately 1, a moderately low F(^{22}Ne) (≤0.7), a moderately high F(^{86}Kr) (>1.9), and a very high F(^{132}Xe) (>17). Relative to air, Gas C is very depleted in Ne but enriched in He, Kr, and Xe; it has an R/R_a <1.0, a relatively high F(^4He) (>300), a low F(^{22}Ne) (~0.4), a high F(^{86}Kr) (>2.5), and a moderately high F(^{132}Xe) (>7).

Hypothesized Gas A comprises a significant component of six and probably all of the samples (Figs. 3–5) and likely reflects air contamination. Three pieces of information lead to this conclusion. First, samples that were most susceptible to slow gas exchange with air appear to have the most air. The volume of gas released from a hydrate specimen (Table 2) is proportional to the initial pressure inside the stainless steel bottle (except for the B split of Section 164-997A-42X-3, which had a low pressure). Samples with low gas volumes (low pressures) or long storage times (seven months) have compositions most similar to Gas A. Second, combining the ^{36}Ar concentrations measured in the gas phase (Table 3) with the gas/water ratios for the samples (Table 2) results in ^{36}Ar concentrations per cubic centimeter water that are ~8–73 times more than that expected for air-saturated seawater. Third, concentrations of N_2 and O_2 (i.e., air) in our gas samples as determined on ship and before shipping were below detection limits, suggesting that air was probably introduced to the stainless steel bottles during storage and shipping. Assuming that Gas A is air and an end-member component of our samples, the depletion of ^3He in Gas A relative to air (Fig. 5) is consistent with mixing the ^4He-enriched sample gas with air, as depicted by the dashed mixing line in Figure 5.

Hypothesized Gas B comprises a significant component of Sample 997A-42X-3(1B) and, perhaps, Samples 996B-1H-1(1), 996B-1H-1(2), 997A-42X-3(1A), and 994C-31X-7(1) (Figs. 3–5). If we make two assumptions, relative ratios of Ar, Kr, and Xe in Gas B are similar to those expected in the clathrate lattice after formation of hydrate from water, CH_4, and air near 0°C. The two assumptions are: (1) noble gas fractionation is similar for all gas-water-hydrate systems (e.g., CH_3Cl and CH_4) where the solid product is a Structure I clathrate (Table 1), and (2) noble gas fractionation at three-phase free gas–dissolved gas hydrate equilibrium conditions (Table 1) is similar to combined fractionation between free gas and dissolved gas and between dissolved gas and hydrate. The second assumption arises because natural gas hydrate probably forms from water in the absence of free gas, but experimental work concerning noble gas incorporation into hydrates was conducted under conditions where hydrate was in equilibrium with free gas. We speculate that noble gases of Gas B enter the clathrate lattice during formation of CH_4 hydrate from CH_4

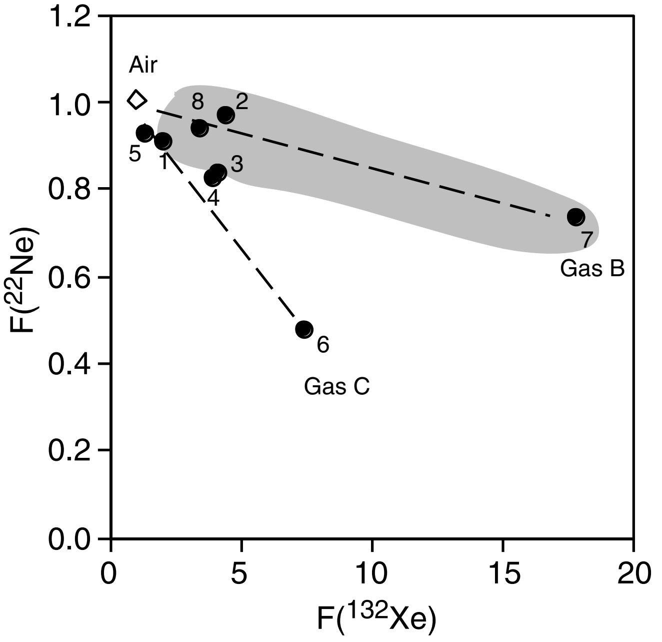

Figure 3. Relative abundance correlation plot (F[*i*] values) for ^{132}Xe and ^{22}Ne of Blake Ridge gas hydrate specimens and air. Sample numbers are those listed in Tables 2 and 3. Samples with a component of hypothesized Gas B are shaded. Dashed lines represent mixing lines between air and hypothesized Gas B, and air and hypothesized Gas C.

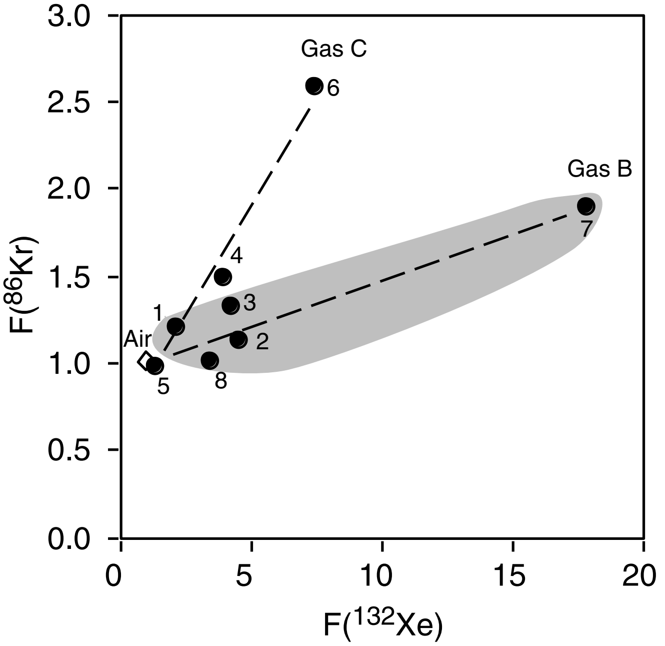

Figure 4. Relative abundance correlation plot (F[*i*] values) for ^{132}Xe and ^{86}Kr of Blake Ridge gas hydrate specimens and air. Sample numbers are those listed in Tables 2 and 3. Samples with a component of hypothesized Gas B are shaded. Dashed lines represent mixing lines between air and hypothesized Gas B, and air and hypothesized Gas C.

and air-saturated seawater when CH_4 quantities surpass the partial saturation curve for CH_4 hydrate (Zatsepina and Buffett, 1997).

Hypothesized Gas C comprises a significant component of Sample 996E-7H-CC(1) and, to a lesser degree, Samples 996C-1H-1(1) and 996C-1H-1(2) (Figs. 3–5). The noble gas composition of Gas C is not air, and it is unlike the expected composition of gas in the hydrate lattice after hydrate formation from water, CH_4, and air.

We cannot constrain the source of Gas B and Gas C without additional and less contaminated samples. However, although we cannot conclude that there are only two sources (other than air contamination) of noble gases in gas hydrate on the Blake Ridge, there must be at least two, and each might be associated with a different flow regime. Gas B is defined by Sample 997A-42X-3(1B) collected in deep sediment in an area of limited fluid flow, whereas Gas C is defined by Sample 996E-7H-CC(1) collected in shallow sediment in a region of active fluid venting. Unfortunately, the extent the two flow regimes interact is not discernible from the present data set. The noble gases suggest that there may be at least two different pathways for the formation of CH_4 hydrate on the Blake Ridge, a conclusion realized by others (Paull, Matsumoto, Wallace, et al., 1996; Egeberg and Dickens, 1999) and compatible with the observation of at least two distinct fluid flow regimes.

Gas Hydrate Detection in Gas Fields

Verkhovsky et al. (1988) presented noble gas analyses for two gas samples collected from wells of the Messoyakha gas field in a permafrost region of Siberia. These analyses are intriguing because the samples have $F(^{132}Xe) < F(^{86}Kr) < 1$ (Fig. 6), a result unlike samples recovered from other gas fields where $F(^{132}Xe) > F(^{86}Kr) > 1$ (e.g., Verkhovsky et al., 1988; Hiyagon and Kennedy, 1992).

The Messoyakha field is known to contain abundant natural gas hydrate predominantly composed of CH_4 (Makogon, 1981). This hydrate component distinguishes the Messoyakha field from other exploited gas fields around the world. Verkhovsky et al. (1988) therefore suggested that depletion of Kr and Xe in their samples is caused by fractionation during hydrate formation such that residual gas collected at wells is depleted in heavier noble gases. These authors then suggested that noble gases could be used to detect the presence (or absence) of gas hydrate in a gas field.

Implicit in the proposals of Verkhovsky et al. (1988) is that natural gas hydrate in a gas field would have $F(^{132}Xe) > F(^{86}Kr) >$ the water from which the hydrate forms, and therefore greater than ~2–4 (e.g., Table 3). Although we do not know the detailed pathways of noble gas incorporation into hydrate on the Blake Ridge, samples that are the least air contaminated have $F(^{132}Xe) > F(^{86}Kr) >$ air-saturated seawater. Our analyses provide support (albeit limited) for the ideas of Verkhovsky et al. (1988). Obviously, the next step for this particular avenue of research would be to determine the noble gas composition of residual gas and gas hydrate in the same gas field. If low F(Xe) values presented by Verkhovsky et al. (1988) are from a residual pore fluid in a hydrated zone, then the hydrate-pore fluid system must be closed, as suggested by Claypool and Kaplan (1974), or at least partly closed, as argued by Egeberg and Dickens (1999).

Global Xenon Inventory

The current estimate for the mass of natural gas hydrate in sediment along continental margins is 7.5 to 15 × 10^{18} g of carbon as CH_4 (Kvenvolden, 1993; Gornitz and Fung, 1994). Our gas sample that is most enriched in Xe (Sample 997A-42X-3[1B]) consists of 98.4% CH_4 with an $F(^{132}Xe)$ value of 17.8 (Tables 2, 3), or a total Xe concentration of 0.22 ppmv (using noble gas concentrations and isotope abundances from Ozima and Podosek, 1983). Thus, the mass ratio of Xe to CH_4 in this particular sample is ~2 × 10^{-7}. Even if this Xe-enriched gas sample was representative of most natural CH_4 hydrate along continental margins, the total inventory of Xe in oceanic CH_4 hydrate would only be 1 to 3 × 10^{13} g. This quantity of Xe is ~100 times less than the amount of Xe in the atmosphere (2.02 × 10^{15} g; Ozima and Podosek, 1983). Oceanic gas hydrate is preferentially enriched in Xe but by an amount that is insufficient to account for any of our Earth's "missing xenon."

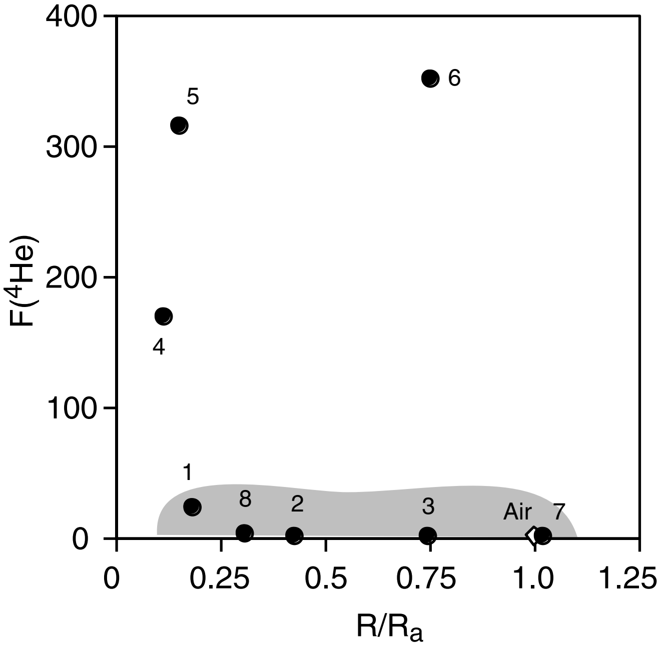

Figure 5. Correlation plot of the relative abundance of He ($F[^4He]$) and He isotopes (R/R_a) of Blake Ridge gas hydrate specimens and air. Samples numbers are those listed in Tables 2 and 3. Samples with a component of hypothesized Gas B are shaded.

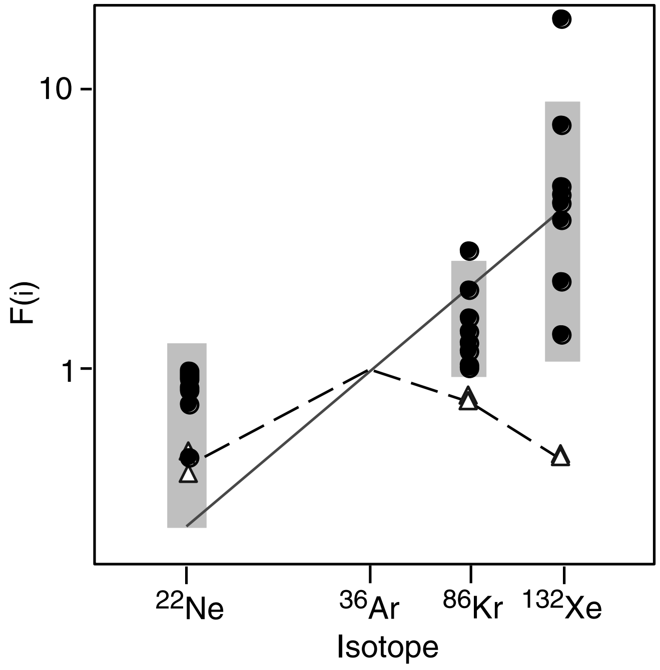

Figure 6. Relative abundance of certain noble gas isotopes in gas hydrate samples from the Blake Ridge (solid circles) compared to gases in the Messoyakha gas field (open triangles; Verkhovsky et al., 1988), gases in other gas fields (shaded boxes; Verkhovsky et al., 1988 and Hiyagon and Kennedy, 1992), and air-saturated seawater at 10°C (solid line; from Ozima and Podosek, 1983).

CONCLUSIONS AND FUTURE WORK

There are at least three sources of noble gases to our eight gas samples collected from dissociation of gas hydrate specimens recovered from the Blake Ridge. One of these sources is air, which is a significant component of six samples. A second source is possibly air-saturated seawater where noble gases have been fractionated during hydrate formation. The other source(s) is largely unconstrained with available data but suggests that there are multiple pathways for gas hydrate formation on the Blake Ridge. Relative to air (and air-saturated seawater), other sources of noble gases are significantly enriched in Xe. Xenon depletion in residual gas of certain gas fields may be related to sequestering of Xe during hydrate formation. However, if our samples are at all representative of oceanic gas hydrate, there is insufficient Xe in hydrates to account for "missing Xe" in the atmosphere.

Major problems with our pilot study were twofold: (1) there was significant introduction of noble gases from air to six of our samples during shipping and storage, and (2) we could not collect samples of residual gas (i.e., free gas or dissolved gas associated with gas hydrate; see Dickens et al., 1997) appropriate for noble gas analyses.

With hindsight, these problems could have been minimized. Samples released during gas dissociation experiments could be collected directly into pre-evacuated Cu tubes with only minor changes to the dissociation chamber. Samples of residual gas also could be collected from the pressure core sampler (PCS; Dickens et al., 1997). Unfortunately, PCS operations on Leg 164 precluded collecting in situ gas at greater than 1 atm, because gas was collected in a simple bubble chamber (Dickens et al., 1997). The bubble chamber should be modified so that gas volumes can be compressed to increase pressure and samples can be collected directly into pre-evacuated Cu tubes.

After dissociation of solid CH_4 hydrate with an initial composition of $CH_4 \cdot 6H_2O$ (Handa, 1986), the volumetric ratio of gas to water should be ~225 at STP. All gas dissociation experiments gave gas to water ratios significantly less than 225 (Table 2). This suggests that partial release of gas from the clathrate structure occurred prior to gas dissociation experiments. In addition to gas sampling, therefore, future investigations may wish to consider how storage of hydrate in a container with liquid nitrogen and rapid pressure drops during core recovery affect noble gas compositions of CH_4 hydrate.

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