



Mass fractionation of noble gases in synthetic methane hydrate: Implications for naturally occurring gas hydrate dissociation



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ABSTRACT

As a consequence of contemporary or longer term (since 15 ka) climate warming, gas hydrates in some settings may presently be dissociating and releasing methane and other gases to the ocean–atmosphere system. A key challenge in assessing the impact of dissociating gas hydrates on global atmospheric methane is the lack of a technique able to distinguish between methane recently released from gas hydrates and methane emitted from leaky thermogenic reservoirs, shallow sediments (some newly thawed), coal beds, and other sources. Carbon and deuterium stable isotopic fractionation during methane formation provides a first-order constraint on the processes (microbial or thermogenic) of methane generation. However, because gas hydrate formation and dissociation do not cause significant isotopic fractionation, a stable isotope-based hydrate-source determination is not possible. Here, we investigate patterns of mass-dependent noble gas fractionation within the gas hydrate lattice to fingerprint methane released from gas hydrates. Starting with synthetic gas hydrate formed under 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.

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1. Introduction

As summarized by Ruppel (2011), recent studies indicate that methane hydrate may be dissociating due to contemporary warming of intermediate ocean waters that are impinging on continental slopes (e.g., Spitsbergen Margin; Westbrook et al., 2009) and in response to long term (since 15 ka) marine inundation and warming of permafrost on Arctic Ocean continental shelves (e.g., East Siberian Shelf; Shakhova and Semiletov, 2007 and Shakhova et al., 2010). For the Arctic shelf in particular, constraining the component of methane emissions directly attributable to gas hydrate dissociation is critical since this methane is more likely to reach the atmosphere without being dissolved in seawater (McGinnis et al., 2006) or oxidized (e.g., Ruppel, 2011) in the shallow water column. In such settings, total methane emissions can include components from deep-seated conventional-hydrocarbon reservoirs, submerged coal beds, shallow marine sediments where microbial methane production is ramping up, newly thawed sediments containing older organic carbon now available to fuel microbial

methane production, and dissociating methane hydrates within and beneath the subsea permafrost. Methane release from each source is subject to different geologic, climatic and biogeochemical controls.

The sheer volume of methane sequestered in the climate-susceptible component of the global gas hydrate reservoir renders identification of the component of methane emissions attributable to dissociating gas hydrate of particular importance (Ruppel, 2011). The IPCC (2007) estimates that dissociating gas hydrate is the source of ~2% of contemporary atmospheric methane, but proof is lacking because a technique for sourcing methane to gas hydrate dissociation has not been systematically developed. Methane hydrate can form from any microbial or thermogenic methane that is within the gas hydrate stability field and able to combine with free water. Widely applied stable isotope analyses that are routinely used to distinguish microbial and thermogenic methane sources are not suitable for determining whether methane emissions originate in recently dissociated gas hydrate. This is because methane enters and leaves the gas hydrate lattice without being isotopically altered (Hachikubo et al., 2007; Luzi et al., 2011). Thus, the best hope for distinguishing methane derived from recently dissociated gas hydrate from other populations of methane is development of a technique that can exploit unique characteristics of the methane recently released from gas hydrates. Noble gases preferentially partition by molecular

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weight (Barrer and Ruzicka, 1962; Barrer and Edge, 1967) in the gas hydrate lattice, but do not have such a predictable relationship in other gas populations. Noble gas analyses might therefore be used to “fingerprint” methane emissions.

This paper addresses the knowledge gap associated with identifying gas derived from dissociating methane hydrate by outlining the first steps in exploiting noble gas signatures to fingerprint these gas mixtures. Here, we use synthetic methane hydrate samples that are formed, stored, and degassed under controlled conditions and freshly-sampled natural gas hydrates from a deepwater marine setting to elucidate noble gas signatures associated with gas hydrate dissociation.

2. Background

Selective enclathration of noble gases in synthetic gas hydrates has been recognized since the work of Barrer and Ruzicka (1962) and Barrer and Edge (1967). Their studies demonstrated that xenon (Xe) and krypton (Kr) were enriched relative to argon (Ar) in hydrate-derived gases and indicated that helium (He) and neon (Ne) could be removed relative to Ar at low temperature (Barrer and Edge, 1967). In a study of naturally occurring methane hydrate, Chersky and Tsarev (1999) noted that He was absent in the gas-hydrate crystal structure and enriched in the residual gas associated with the hydrate formation. Ginsburg et al. (1990, 1992, 1993) noted low He concentrations from hydrate-derived gases from the Okhotsk, Caspian, and Black seas.

Two 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 (2000) analyzed samples obtained from Blake Ridge (ODP Leg 164), while Winckler et al. (2002) present data from near-seafloor samples recovered on Hydrate Ridge located on the U.S. Cascadian Margin. These studies are the only ones to focus on naturally occurring gas hydrate.

Noble gas data are expressed as F values, where F_i equals the isotope ratio of component i (^4He , ^{20}Ne , ^{40}Ar , ^{84}Kr or ^{132}Xe) to argon-36 (^{36}Ar) of the sample normalized to the atmospheric ratio of component i to ^{36}Ar . The ratios of $F^{20}\text{Ne}$ and $F^{84}\text{Kr}$ are plotted against $F^{132}\text{Xe}$ from the

methane hydrate samples reported by Dickens and Kennedy (2000) and Winckler et al. (2002), as shown in Fig. 1.

The figure includes four isotopic components of noble gas isotopes (^{20}Ne , ^{36}Ar , ^{84}Kr and ^{132}Xe) to examine degrees of mass fractionation relative to ^{36}Ar . The data from Winckler et al. (2002), which were originally reported as total elemental composition, have been recalculated to assume an air-like isotopic composition of the noble gas isotopic components in order to compare their results to other data sets presented in this study.

The Dickens and Kennedy (2000) data show a relatively small shift of $F^{20}\text{Ne}$ and $F^{84}\text{Kr}$ values from an atmospheric composition end member with increasing $F^{132}\text{Xe}$. The $F^{20}\text{Ne}$ data falls between atmospheric and solubility constraints, with two samples showing sizable amounts of excess ^{132}Xe (greater than could be explained by solubility fractionation). One sample plotted greater than solubility values for $F^{84}\text{Kr}$, the other at near solubility values for $F^{84}\text{Kr}$. Winckler et al. (2002) report higher $F^{132}\text{Xe}$ and $F^{84}\text{Kr}$ with much lower $F^{20}\text{Ne}$ values (~ 0.06 to 0.02) that suggest extensive loss of light isotopes relative to atmospheric and air saturated sea water (ASSW). This trend is evidence for selective loss of ^{20}Ne during enclathration, as suggested by Barrer and Edge (1967). Mass dependent fractionation is further demonstrated in the $F^4\text{He}$ values reported by Winckler et al. (2002) (e.g., $F^4\text{He}$ from 0.006 to 0.097) as compared to Dickens and Kennedy (2000), who report appreciable amounts of ^4He ($F^4\text{He}$ from 1.5 to 350). Winckler and co-workers speculate that the data from Dickens and Kennedy (2000) reflect contamination by air during sampling and storage in liquid nitrogen (LN_2) prior to analysis. The shipboard techniques used by Winckler et al. (2002) were designed to avoid this issue. However, this explanation does not account for the extreme He enrichments and the two samples with higher $F^{84}\text{Kr}$ and $F^{132}\text{Xe}$ values displayed by some of the data from Dickens and Kennedy (2000) (Fig. 1).

The purpose of our study is to investigate the systematic fractionation of noble gas compositions during the formation and dissociation of methane hydrate in controlled laboratory conditions, and, furthermore, to evaluate whether handling and storage procedures affect the measured compositions. Our goal is to relate the laboratory fractionation data to those from natural methane seeps and to determine if

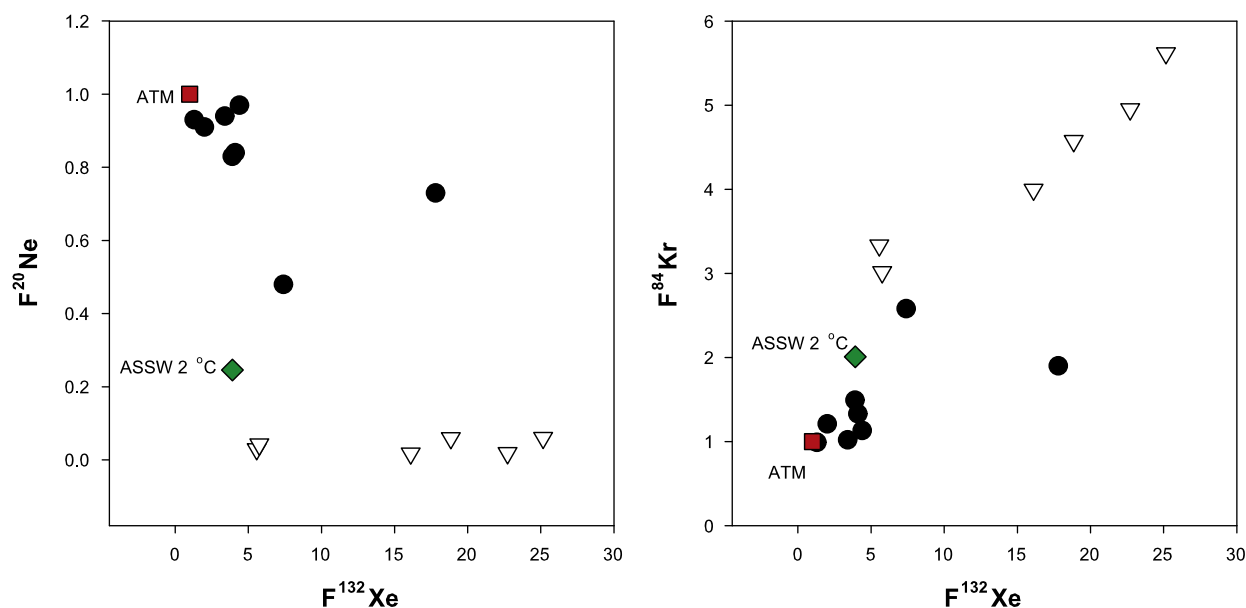


Fig. 1. Plots of $F^{20}\text{Ne}$ and $F^{84}\text{Kr}$ vs. $F^{132}\text{Xe}$. Black circles are from Dickens and Kennedy (2000) for the Blake Ridge. White inverted triangles are from Winckler et al. (2002) for Hydrate Ridge. Red square denotes an atmosphere sample, and the green diamond is air saturated sea water (ASSW) at 2 °C.

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