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Gas origin and migration in the Ulleung Basin, East Sea: Results from the Second Ulleung Basin Gas Hydrate Drilling Expedition (UBGH2)

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ABSTRACT

We have investigated the gas chemistry of marine sediments (up to 250 m below seafloor, m bsf) recovered during the Second Ulleung Basin Gas Hydrate Drilling Expedition (UBGH2) to identify and compare the gas origin and its migration at seismically non-chimney, truncated chimney and chimney sites in this basin. The molecular and isotopic data (C_1/C_{2+} ratios > 300, $\delta^{13}C_{CH_4} < -65‰$, and $\delta D_{CH_4} < -181‰$) of the gases indicate that methane predominantly originates via microbial carbon dioxide reduction. The carbon isotopic fractionation (ε_c) between methane and carbon dioxide below 30 m bsf has a relatively constant value ($\varepsilon_c = 66–68$) at all sites, consistent with the microbial pathway. In contrary, samples shallower than 30 m bsf display significant differences with the seismic characteristics of each site. ε_c ranges from 65 to 81 in non-chimney sites but shows values as low as 45 in chimney sites, which is agreement with previously reported piston core data (Kim et al., 2012), and thought to reflect two-phase methane transport processes. In chimney sites, deep-sourced methane migrates independently of the carbon dioxide, which remains dissolved in the aqueous phase leading to the extremely low ε_c values observed in the upper 30 m bsf. Upward methane diffusion at non-chimney sites may also add a transport-induced fractionation as evidenced in mixing diagrams, but this process does not significantly affect the ε_c values.

$\delta^{13}C_{CO_2}$ shows usually minimum values at the Sulfate–Methane Transition Zone (SMTZ) at all sites. However, in chimney sites, these values have a much more depleted signature, indicating faster rates of methane consumption by Anaerobic Oxidation of Methane (AOM) supported by the higher methane flux. Moreover, here the massive hydrate that forms in shallow sediments incorporates gases with a lower C_1/C_2 ratio (=higher C_2/C_1) than the surrounding sediment, as documented in hydrate-bound gas (BG) and void gas (VG) samples. Gas hydrate dissociation during the core recovery is released enriched ethane (C_2H_6) trapped in gas cage, which leads to have high C_2H_6 in VG samples.

1. Introduction

The presence of gas hydrate in the Ulleung Basin (the East Sea) has been inferred from observations of bottom-simulating reflectors (BSRs) on multi-channel seismic reflection data since the late 1990s (Gardner et al., 1998; Lee et al., 2005; Horozal et al., 2009). Gas hydrates were first recovered on piston cores, which were used to frame the First Ulleung Basin Gas Hydrate Drilling Expedition (UBGH1) in 2007. Drilling results provide additional evidence for the presence of gas hydrates and their mode of distribution, which was based on organic/inorganic geochemistry (e.g., Kim et al., 2007, 2011b, 2012), sedimentology (e.g., Bahk et al., 2011; Riedel et al., 2012; Scholz et al., 2012), and physical property studies (e.g., Kim et al., 2011a). The Second Ulleung Basin Gas Hydrate Drilling Expedition (UBGH2) was conducted in 2010 to expand our understanding of the basin-wide distribution pattern of gas hydrate-bearing sedimentary structures (Ryu et al., 2012).

Formation of natural gas hydrates in marine sediments depends on gas concentration, temperature, and pressure (Kvenvolden,

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1998), and these deposits are known to occur in two principal modes: “pore-filling gas hydrate” and “massive gas hydrate” (Tréhu et al., 2006; Tomaru et al., 2007; Bahk et al., 2013). Recently, massive gas hydrate usually occurs near the seafloor at regions characterized by the presence of “acoustic seismic chimneys”, which are considered to be a conduit for upward gas migration from deep sediments below the BSR which sustain gas hydrate formation at very fast rates (Riedel, 2001; Riedel et al., 2002; Torres et al., 2004, 2011).

The Ulleung Basin sediments are characterized by the presence of numerous seismic chimneys, which originate below the BSR and terminate at different stratigraphic levels. In some cases these structures, which reach ~2 km in width, extend all the way to the seafloor (Horozal et al., 2009; Kim et al., 2011b, 2012, 2013). Based on seismic data and gas chemistry from the piston core samples (<8 m), Kim et al. (2012) documented an upward migration of deep-seated biogenic gas through the chimneys, and development of massive gas hydrate in the shallow sediments of this basin. However, there have been few studies to identify the molecular and isotopic signatures of deep gas samples (~250 m bsf) that would allow for comparison of deep geochemical signals among acoustic chimneys, truncated chimney and non-chimneys areas in this basin. During the UBGH2, samples were collected from 10 sites drilled in these environments up to 300 m bsf (Ryu et al., 2012), which provide us with a rare opportunity to investigate the properties of the deep-seated gases.

In this paper, we report on the molecular and stable isotopic compositions ($\delta^{13}C_{CH_4}$, δD_{CH_4} and $\delta^{13}C_{CO_2}$) of gases collected from headspace analyses of sediment samples (HS), gases sampled directly from voids in the core (VG), and gases released from gas hydrate samples (BG). We targeted two chimney sites (UBGH2-7 and UBGH2-11), a truncated chimney site (UBGH2-2_1) and two non-chimney sites (UBGH2-5 and UBGH2-9). These data augment our understanding of the origin and migration pathway of the gases from deep-seated sediment sources in the Ulleung Basin.

2. Geologic settings

The East Sea is located on the western margin of the mid-latitude North Pacific. There are three deep basins in the East Sea: the Japan, Yamato, and Ulleung basin (Fig. 1). The Ulleung Basin is located in the southwestern part of the East Sea. The northern and western margins of the basin are steep (>10°) and are characterized by numerous slump and slope failure deposits, whereas the southern and eastern margins are bordered by rather gentle slopes (1°–2°) and a broad continental shelf (about 50–150 km wide). The basin floor lies at water depths of 2000–2300 m and gradually deepens northeastward.

The Ulleung Basin was formed during the Late Oligocene to Early Miocene by crustal extension associated with the southward drift of the Japanese Islands Arc away from the Asian mainland (Tamaki et al., 1992; Jolivet et al., 1995). At the end of the Middle Miocene (11–12 Ma), the tectonic regime changed from tensional to compressional, which led to thrust faulting and folding in the southern and western margin of the basin and to the sediment compression (Chough and Barg, 1987; Horozal et al., 2009; Kim et al., 2011a). Since the Pleistocene, mass flows or debris flows rapidly retreated landward, forming debris aprons along the base-of-slope region, while turbidite and hemipelagic sedimentation has prevailed in the central basin (Lee and Suk, 1998).

Many seismic chimney structures have been identified from multi-channel seismic records in the Ulleung Basin (Bahk et al., 2009; Haacke et al., 2009; Horozal et al., 2009), which are typically seismic blank zone and interpreted to be fluid flow and gas vents (Fig. 2). Massive gas hydrates were found near seafloor at these structures in the Ulleung Basin. Actually there are two types of chimney; one is the chimney that reaches to seafloor (Fig. 2C) and the other is the truncated chimney that has not completely penetrated to the seafloor (Fig. 2B).

3. Method

3.1. Sampling

In this study we used core samples collected by drilling during UBGH2 at acoustic chimney, truncated chimney and non-chimney sites (Fig. 1 and Table 1). Sampling depths are presented in Table 2.

Voids within the core liner, which formed from gas expansion during core retrieval were sampled immediately upon recovery using a syringe attached to a hollow stainless-steel tool that punctures the core liner. The gas samples, denoted as VG, were then transferred to 50 mL glass vials that had been pre-filled with saturated NaCl solution.

Bulk sediments (3 mL) were sampled from the open core for analysis of dissolved gas (hereafter defined as headspace gas, HS) using the headspace-technique with a 5 mL cut-off plastic syringe. The sediments were extruded into 20 mL headspace glass vials filled with 2 mL of saturated NaCl solution, and then the vials were immediately capped with rubber septa and sealed with aluminum crimp caps. In order to degas the sediments, the vials were heated at 70 °C for 30 min, and the headspace gas (HS) was sampled. For analyses of hydrate-bound gas (BG), small (~5 mL) pieces of solid gas hydrate were carefully scraped to minimize any contamination from the surrounding sediment and placed into 60 mL syringes, where they were allowed to dissociate. The BG was preserved followed the aforementioned protocols for VG samples.

3.2. Gas analyses

The gas composition in HS, VG, and BG samples was measured with an Agilent 3000A micro gas chromatograph (GC) fitted with thermal conductivity detector (TCD) and two independent columns (8 m × 0.32 mm HP PLOT-U for C_1–C_4 hydrocarbons and 10 m × 0.32 mm Supelco MolSieve 5A Plot for O_2, N_2, CO_2 and CO). The injector temperature of the GC was 90 °C and the column temperatures were set at 90 °C for the Plot-U column and at 105 °C for the MolSieve 5A Plot column. Helium was used as the carrier gas with a column flow rate of 2.2 mL/min. The reproducibility of the analytical system for methane, ethane and carbon dioxide contents from repeated analysis of the mixtures standard gas (hydrocarbons: methane, ethane, ethylene, propane, butane with helium balance; non-hydrocarbons; carbon dioxide, carbon monoxide oxygen, nitrogen with helium balance) was better than 4%, 6% and 6%, respectively.

The stable carbon ($\delta^{13}C$) and hydrogen (δD) isotopic ratios of methane and $\delta^{13}C$ of carbon dioxide in the gas samples were analyzed by using compound-specific isotope ratio-monitoring gas chromatograph/mass spectrometer (GC-C-IRMS) at Isotech Laboratories Inc, Champaign, IL, USA. The stable carbon and hydrogen isotopes are reported in the conventional δ notation in permil (‰) relative to V-PDB and V-SMOW, respectively. The reproducibility of the analyses was ±0.1‰ on carbon and ±2‰ on hydrogen.

4. Results

The concentration of methane, ethane and resulting C_1/C_2 ratios are listed in Table 2, and plotted down core in Figure 2. In the HS samples methane was the dominant hydrocarbon, but no C_{2+} was detected in any of HS samples, and therefore, C_1/C_{2+} ratios cannot