Continental Shelf Research 29 (2009) 1588–1596

Contents lists available at ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

Methane-derived authigenic carbonates from the Ulleung basin sediments, East Sea of Korea

Dhongil Lim [a,*], Jinyong Choi [b], Zhaokai Xu [b,c], Moonkoo Kim [a], Donglim Choi [a], Hoisoo Jung [d], Panmook Lee [e]

[a] *South Sea Institute, Korea Ocean Research and Development Institute, 391 Jangmok-ri Jangmok-myun Geoje 656-830, Republic of Korea*
[b] *Department of Oceanography, Kunsan National University, Kunsan 573-701, Republic of Korea*
[c] *Key Laboratory of Marine Geology and Environment, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China*
[d] *Marine Geoenvironment and Resources Research Division, Korea Ocean Research and Development Institute, Ansan, P.O. Box 29, Seoul 425-600, Republic of Korea*
[e] *Marine and Ocean Engineering Research Institute, Korea Ocean Research and Development Institute, 171 Jang-dong Yuseong, Daejeon 305-343, Republic of Korea*

ARTICLE INFO

Article history:
Received 3 November 2008
Received in revised form
22 April 2009
Accepted 30 April 2009
Available online 18 May 2009

Keywords:
Authigenic carbonates
Methane seep environments
Gas hydrate
East Sea (Japan Sea)

ABSTRACT

Authigenic carbonates were sampled in methane-enriched piston core sediments collected from gas venting sites on the western continental slope of the Ulleung Basin, East Sea of Korea. Multidisciplinary investigations on these carbonates, including the scanning electronic microscope (SEM) observations and mineralogical-geochemical compositions, were carried out to identify the carbon and oxygen sources and the forming mechanism of these carbonates. The authigenic carbonates from the study area correspond to semi-consolidated, compact concretions or nodules ranging from 2 to 9 cm in size. X-ray diffraction and electron microprobe analyses showed that most of the sampled carbonate concretions were composed of almost purely authigenic high-Mg calcite (10.7–14.3 mol% $MgCO_3$). Characteristically, microbial structures such as filaments and rods, which were probably associated with the authigenic minerals, were abundantly observed within the carbonate matrix. The carbonates were strongly depleted in $\delta^{13}C$ (−33.85‰ to −39.53‰ Peedee Belemnite (PDB)) and were enriched in $\delta^{18}O$ (5.16–5.60‰ PDB), indicating that the primary source of carbon is mainly derived from the anaerobic oxidation of methane. Such methane probably originated from the destabilization of the underlying gas hydrates as strongly supporting from the enriched ^{18}O levels. Furthermore, the strongly depleted $\delta^{13}C$ values (−60.7‰ to −61.6‰ PDB) of the sediment void gases demonstrate that the majority of the gas venting at the Ulleung Basin is microbial methane by CO_2 reduction. This study provides another example for the formation mechanism of methane-derived authigenic carbonates associated with gas-hydrate decomposition in gas-seeping pockmark environments.

1. Introduction

The East Sea is a mid-latitude, semi-enclosed deep marginal sea (average water depth of 1350 m) surrounded by Korea, Japan, and Russia (Fig. 1). Structurally, it comprises three basins (the Ulleung Basin, the Japan Basin, and the Yamato Basin), which are separated by the Korea Plateau, Oki Bank, and Yamato and Kita-Yamato Ridges. The East Sea, especially Ulleung Basin is a region where well-developed gas seepage-related structures are widely distributed in deep-water environments (Gardner et al., 1998; Horozal et al., 2009). Acoustic backscatter imagery data obtained in this basin showed well-developed seepage-related structures, which are interpreted to be pockmarks, or mounds likely created by seepage of methane (CH_4)-rich fluids (Gardner et al., 1998). Recently, multi-channel seismic investigation in the Ulleung Basin, East Sea, showed various seismic indicators of the presence of gas hydrate and associated gas, including the bottom-simulating reflector (BSR), and seismic chimneys (Horozal et al., 2009). The presence of both BSR and pockmarks suggested that the East Sea must be an active gas-seeping region, comparable to the Black Sea, which is the world's largest anoxic marine basin (Mazzini et al., 2004). In addition, occurrence of carbonate ($CaCO_3$) nodules from the piston core sediments from the Ulleung Basin of the East Sea was reported (Dr. D. Yoo, personal communication).

At the active fluid seepage areas, precipitation of authigenic carbonate is a common phenomenon, which is related to the activity of archaea and bacteria oxidizing methane near the seafloor (Ritger et al., 1987; Boetius et al., 2000). Accordingly, authigenic carbonate precipitation in cold seep environments is one of the most important indicators for the presence of gas-rich fluids, which may indicate, in some cases, presence of shallow gas hydrates (e.g., Ritger et al., 1987; Bohrmann et al., 1998; Aloisi

---

[*] Corresponding author. Fax: +82 55 639 8589.
E-mail address: oceanlim@kordi.re.kr (D. Lim).

0278-4343/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.csr.2009.04.013

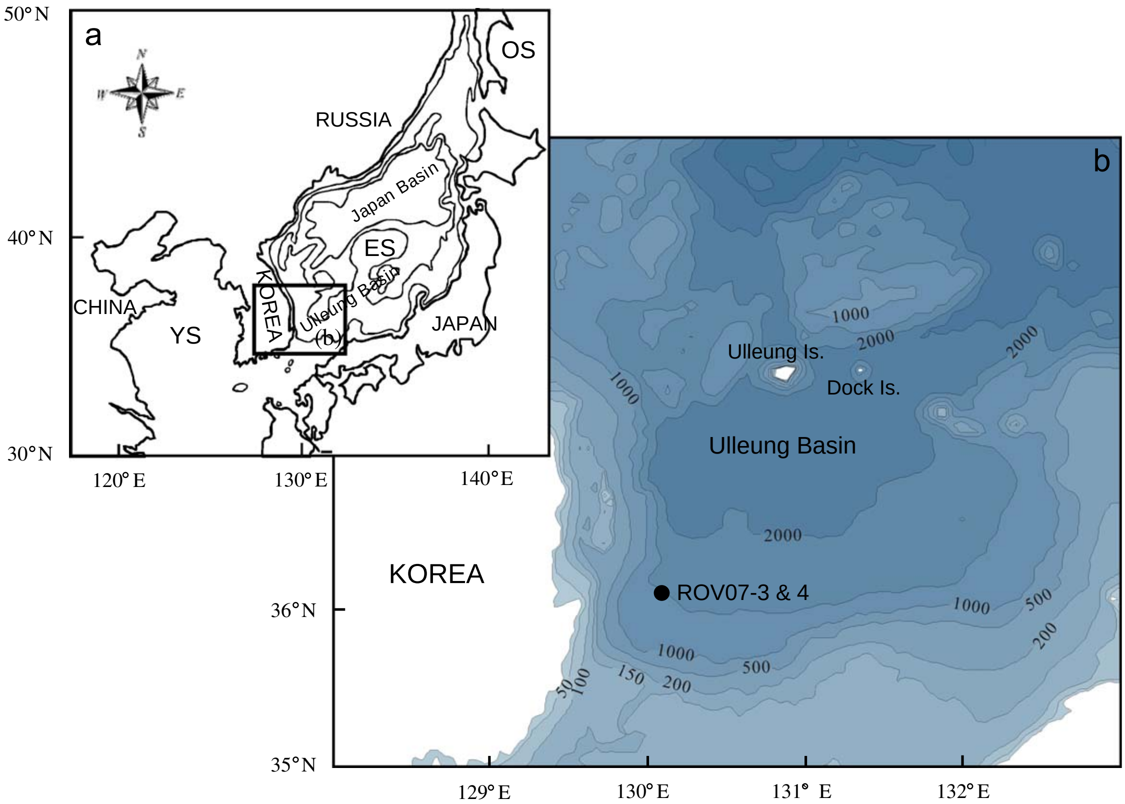

Fig. 1. Map showing (a) study area and (b) core location in the study area with bathymetry (m). ES: East Sea, YS: Yellow Sea, and OS: Okhotsk Sea.

et al., 2000; Greinert et al., 2001; Luff and Wallmann, 2003; Lu et al., 2005; Chen et al., 2006; Bayon et al., 2007). The typical seep carbonate mineral species are mainly composed of microcrystalline calcite, aragonite, and dolomite (Peckmann et al., 2001; Lu et al., 2005; Chen et al., 2006), although the chemo-physical factors controlling the mineralogy of seep carbonates are still incompletely understood. Recent studies have shown that authigenic carbonate can occur as discrete phases throughout the sediment column at cold seeps, with a wide variety of lithologies and carbonate compositions, in relation to the presence of gas hydrate (Rodriguez et al., 2000; Bayon et al., 2007). The identification of such carbonate phases in marine sediments can therefore provide a unique window into the distribution and magnitude of ancient seep settings.

Here, we present internal micro-texture, and geochemical and mineralogical data for authigenic carbonates recovered from gas hydrate-bearing sediments in the Ulleung Basin of the East Sea and further focus on the relationship between these carbonates and the gas hydrate, especially the origin of the fluids and the possible evidence of gas hydrate dissociation.

2. Materials and methods

Two piston cores (ROV07-3 and 4) were taken from the western slope region (approximately 1500 m water depth) of the Ulleung Basin, East Sea, where gas-seeping structures were observed. The cores, with lengths of 1.8 and 3.2 m, were split lengthwise, photographed, and logged in detail by visual examination. Grain-size analysis was carried out by a standard dry-sieving technique for the sand fraction ($>4\varphi$) and by a pipette method for the mud fraction ($<4\varphi$). Total carbon (TC) and organic carbon (OC) contents of the sediments (dry wt%) were determined using a Carlo Erba Elemental Analyzer 1108 (CE Instruments, Milan, Italy), the carbonate content being calculated using the equation $\mathrm{CaCO3}\ (\%) = (\mathrm{TC}-\mathrm{OC}) \times 8.333$ (Stein et al., 1994).

Sediment samples for pore water CH_4 analysis were collected using a tipless syringe from pre-drilled holes on plastic liner of cores and then transferred into 50 mL gas-tight serum vials containing 20 mL NaOH solution (Ferdelman et al., 1997). Methane concentrations of the samples were determined by injecting an aliquot of headspace into a gas chromatograph coupled with indium oxide (InO_2) semiconductor detector (GC/SCD, Sensortec GS-23, Japan). The separation of gases was accomplished by the column (stainless steel, $2\,\mathrm{m} \times 3\,\mathrm{mm}$ i.d.) packed with molecular sieve (13X-S, 60/80 mesh, GL Science Co., Japan). Details on the methane analysis using GC/SCD are given in Ohta et al. (1999).

The stable carbon isotope ratios of methane in sediment void gas and gas hydrates were measured in the geochemistry laboratory at the Hokkaido University (Japan) by the method of Tsunogai et al. (2002). Briefly, an aliquot of hydrate-bound and/or void gases was injected into a gas chromatograph and methane was separated from gas mixture by a 25 m long, 32 μm i.d., PoraPLOT-Q capillary column. Separated methane was then quantitatively combusted to CO_2 and the isotopic composition of CO_2 gas was measured using a mass spectrometer (Finnigan MAT 252). Stable carbon isotope ratios are reported in the standard δ-notation in per mil (‰) relative to Peedee Belemnite (PDB) standard and the precision of the analysis was estimated to be 0.3‰.

For this study, carbonate concretions were collected at various depths (4–6, 9–11, 20–21.5, 28, 31–32.5, 41–42.5, and 237 cm) along the ROV07-4 core. Bulk mineralogy was determined on compressed powder pellets using a high quality XG X-ray diffractometer (XRD) with Cuk$_\alpha$ radiation. XRD patterns were obtained from 3° to 47° 2θ at a scanning speed of 0.04° 2θ/s at conditions of 40 kV and 40 mA. The microstructure on fresh surfaces and thin sections of selected carbonate concretion