Marine and Petroleum Geology 58 (2014) 206–222

Contents lists available at ScienceDirect

Marine and Petroleum Geology

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

Research paper

Grain-scale imaging and compositional characterization of cryo-preserved India NGHP 01 gas-hydrate-bearing cores

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ARTICLE INFO

Article history:
Received 26 March 2014
Received in revised form
23 July 2014
Accepted 26 July 2014
Available online 13 August 2014

Keywords:
Gas hydrate
Scanning electron microscopy
Gas chromatography
Grain morphology
Gas geochemistry
NGHP-01
Indian ocean

ABSTRACT

We report on grain-scale characteristics and gas analyses of gas-hydrate-bearing samples retrieved by NGHP Expedition 01 as part of a large-scale effort to study gas hydrate occurrences off the eastern-Indian Peninsula and along the Andaman convergent margin. Using cryogenic scanning electron microscopy, X-ray spectroscopy, and gas chromatography, we investigated gas hydrate grain morphology and distribution within sediments, gas hydrate composition, and methane isotopic composition of samples from Krishna–Godavari (KG) basin and Andaman back-arc basin borehole sites from depths ranging 26 to 525 mbsf. Gas hydrate in KG-basin samples commonly occurs as nodules or coarse veins with typical hydrate grain size of 30–80 μm, as small pods or thin veins 50 to several hundred microns in width, or disseminated in sediment. Nodules contain abundant and commonly isolated macropores, in some places suggesting the original presence of a free gas phase. Gas hydrate also occurs as faceted crystals lining the interiors of cavities. While these vug-like structures constitute a relatively minor mode of gas hydrate occurrence, they were observed in near-seafloor KG-basin samples as well as in those of deeper origin (>100 mbsf) and may be original formation features. Other samples exhibit gas hydrate grains rimmed by NaCl-bearing material, presumably produced by salt exclusion during original hydrate formation. Well-preserved microfossil and other biogenic detritus are also found within several samples, most abundantly in Andaman core material where gas hydrate fills microfossil crevices. The range of gas hydrate modes of occurrence observed in the full suite of samples suggests a range of formation processes were involved, as influenced by local *in situ* conditions. The hydrate-forming gas is predominantly methane with trace quantities of higher molecular weight hydrocarbons of primarily microbial origin. The composition indicates the gas hydrate is Structure I.

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1. Introduction and background

Gas hydrates are nonstoichiometric crystalline solids consisting of a network of water molecules that are hydrogen-bonded in a manner similar to ice and that interstitially encage gases of small molecular diameter, such as methane, ethane, propane, CO_2, etc. (Sloan and Koh, 2007). Depending on gas composition, gas hydrate will usually form as one of two crystallographic cubic (also called isometric) arrangements, termed structure I (the most common) and structure II, or more rarely as hexagonal structure H (Sloan and Koh, 2007). The formation of gas hydrate typically requires moderately low temperatures, high pressure, and sufficient quantities of water and free- or dissolved-phase hydrate-forming gas. Such conditions occur globally – and often extensively – in permafrost regions and shallow marine environments such as in seafloor sediments along continental margins (Kvenvolden and Lorenson, 2001; Lorenson and Kvenvolden, 2007). Consequently, gas hydrates are fairly ubiquitous in these regions and harbor a significant hydrocarbon source that is of keen interest for economic as well as geohazard considerations (e.g., Collett, 2002; Max et al., 2006; Ruppel, 2007; Maslin et al., 2010). Although estimates of their total global inventory vary by several orders of magnitude, even the more conservative estimates predict extremely large total amounts of carbon bound by gas hydrates that are greater than the total amount in the atmosphere and in conventional natural gas reserves (e.g. Milkov, 2004, and references therein). Estimates continue to be improved by advances in global modeling and geophysical mapping of gas hydrate inventories (e.g., Boswell and Collett, 2011; Dickens, 2011; Wallmann et al., 2012).

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http://dx.doi.org/10.1016/j.marpetgeo.2014.07.027
0264-8172/Published by Elsevier Ltd.

Evaluating the amount, concentration, and distribution of gas hydrates in nature continues to pose challenges due to variations in local saturation levels as well as the complex arrangements in which they may be distributed in the subsurface. For example, estimating gas hydrate saturation in the Krishna–Godavari basin at site NGHP-01-10 is complicated by the anisotropic nature of the gas hydrate reservoir due to its accumulation within high-angle fractures (Lee and Collett, 2009). On a finer scale, evaluation of gas hydrate grain characteristics (grain size, morphology, etc), composition, and the nature of the hydrate grain contacts with sediments is important for understanding growth and formation processes as well as for reliable interpretation of physical property measurements. Also critical to assess is the presence and distribution of a secondary ice phase, such as a dissociated ice product or frozen pore water, which can greatly influence the material characteristics of recovered samples in cold storage. Ice formed by alteration of naturally occurring gas hydrates during their transit to the surface can also mask, if not obliterate, clues about the *in situ* state of the hydrate.

Here we use cryogenic scanning electron microscopy (cryo-SEM), gas chromatography, and other analytical methods to assess grain-scale morphology and gas compositions of cryo-preserved gas-hydrate-bearing cores provided to us by NGHP Expedition 01 (hereafter referred to as NGHP-01). The overarching goal of this expedition was to study gas hydrate occurrences off the Indian Peninsula and along the Andaman convergent margin, with special emphasis placed on understanding the geologic and geochemical controls on the occurrence of gas hydrate in these settings (Collett et al., 2008a, 2008b, 2014). Dedicated gas hydrate coring, drilling, and downhole logging operations were conducted from April 2006 through August 2006, and the scope of the Expedition is summarized in Collett et al. (2014).

Previously we reported cryo-SEM imaging results from synthetic gas hydrates formed and tested under closely controlled conditions in the laboratory (Stern et al., 2004), as well as of natural gas hydrates recovered from marine settings including the Gulf of Mexico (Stern and Kirby, 2005) and Cascadia margin (Stern and Kirby, 2008), and from sub-permafrost environments including the Mallik test site in NW Canada and the Mount Elbert site in Alaska (Stern et al., 2008, 2011). We also provided a “first look” at NGHP-01 samples by cryo-SEM (Stern and Kirby, 2008.) Here, we build on this earlier body of work to further investigate the physical state, gas hydrate distribution, grain morphology, and other grain characteristics within NGHP-01 samples from Krishna–Godavari (KG) Basin and Andaman Site cores, and compare the results to our previous studies. Gas composition as well as methane and carbon dioxide isotopic analyses were also conducted on dissociated gas from the bulk samples examined here, in order to determine the specific composition of the gas hydrate phase, to note any contrast with the composition of the gas in the sediment containing the hydrate, and to assess the hydrate crystalline structure.

Table 1
NGHP-01 gas hydrate samples.

Sample No	Site	Depth (mbsf)	Area[a]	Type[b]
HYD 29	10B	110	KG	M
HYD 92	12A	143	KG	M
HYD 115	17A	525	And	DA
HYD 7	10B	26	KG	M
HYD 19	10B	75	KG	M
HYD 96	14A	105	KG	DS
HYD 82	10D	131	KG	M
HYD 71	10D	102	KG	M
HYD 41	10D	35	KG	M
HYD 55	10D	65	KG	M

[a] **Area:** KG: Krishna–Godavari Basin; And: Andaman Island site.
[b] **Type:** M: Massive nodule or vein filled; DS: Disseminated in sand/silt; DA: Disseminated in volcanic ash.

2. Experimental methods

2.1. Sample retrieval and transit

Samples were recovered by standard IODP coring systems and distributed to a number of institutions for a variety of uses. We received 10 cryo-preserved samples, mostly 8.9-cm-diameter whole-round core sections, in a liquid nitrogen (LN_2) dual-use liquid/vapor shipper (model MVE Doble-47). Samples are listed in Table 1 by sample number, corresponding borehole/site number, depth (mbsf), locality, and sediment type. Nine originated from the KG Basin (7 samples from Site 10, plus 1 each from Sites 12 and 14) and one sample from Andaman Site 17. Each sample or plastic-lined core was individually bagged or wrapped in Al foil. A small but sufficient amount of free LN_2 remained in the base of the shipper upon arrival, ensuring that samples remained thermally stable during the shipping process. However, due to the length of time required for initial core recovery, transit through warm water, and processing on the catwalk, all hydrate-bearing samples underwent at least minor and in many cases significant dissociation prior to being bagged, stored, cryo-preserved, and shipped. Water ice from gas hydrate dissociation mixed with pore water and seawater could therefore be present in each sample.

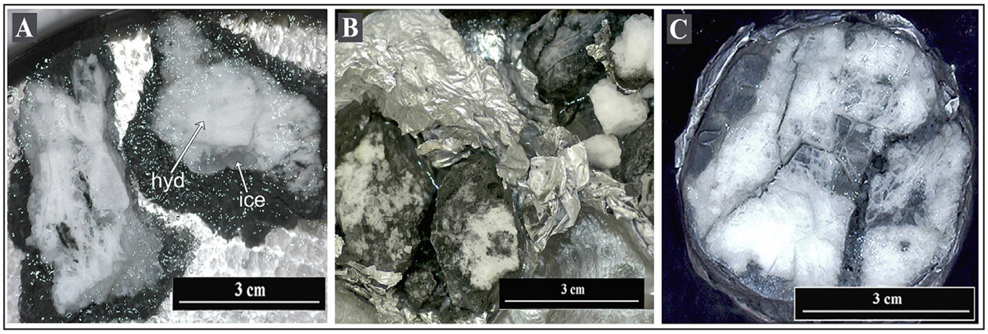

Figure 1. NGHP-01 nodules HYD 55 (**A**) and HYD 82 (**B**) from KG Basin Site 10D, 65 and 131 mbsf respectively. **C** shows IODP Leg 311 Cascadia margin sample 1328B from a cold vent site near the seafloor surface for comparison. Methane hydrate appears bright white within the nodules whereas ice appears translucent gray, as labeled in A. Dark gray to black marine silts and clays surround the hydrate + ice phases in all three images.