Grain-scale imaging and compositional characterization of select India NGHP Expedition-01 gas-hydrate-bearing cores, and comparison to other natural gas hydrates

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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 is 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.

Key words: gas hydrate; scanning electron microscopy; gas chromatography; grain morphology; gas geochemistry; NGHP-01; Indian Ocean

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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, CO₂, 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 hydrates 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, 2004a, 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 et al., 2011; *Wallman et al.*, 2012).

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; also this volume). 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. (this volume).

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, 2005a) 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., 2005b, 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 (see also Lorenson et al., this volume).

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 (LN₂) 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 LN₂ 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.

2.2. Cryo-SEM sample imaging procedures

Cryogenic scanning electron microscopy (cryo-SEM) serves as an excellent method for obtaining grain-scale and textural information of gas-hydrate-bearing material due to its versatility in detection capabilities, its resolution, and its relatively large depth of focus. That said, certain technical issues must be addressed to maintain samples at stable conditions and to minimize vacuum or electron-beam damage of the imaging area. Distinguishing handling-induced and imaging-induced surface artifacts from the intrinsic sample surface morphology can also be difficult, as can be distinguishing hydrate from ice.

NGHP-01 samples were first broken apart at LN₂ temperature to expose the inner region of core presumed to contain the best preserved gas hydrate with least disturbed textural arrangement, contamination, or alteration. Small sections of samples (~0.5 cm x 0.5 cm x 0.75 cm) were cleaved from the bulk material and transferred to a sample stage within an evacuated and pre-chilled (<100 K) cryo-preparation station (Gatan Alto Model 2100) that in turn attached to a LEO 982 field emission SEM. In the preparation chamber, samples were again cleaved by

cold knife to produce fresh fracture surfaces uncontaminated by surface-water condensation. While still under vacuum, samples were inserted directly through the back of the preparation chamber and onto an auxiliary cryo-imaging stage in the SEM column. Temperature was monitored by a thermocouple embedded in the stage just below the sample, and imaging was conducted at temperatures below 102 K and vacuum below 10^{-6} kPa (10^{-5} mbar). Low accelerating voltage (1.7 to 2kV) was typically used to minimize sample alteration or beam damage to the sample surface, increasing to 10 kV only for energy dispersive X-ray spectroscopy (EDS) elemental analysis as described below. Using low voltage also allowed us to image the samples without coating them, thus minimizing their time in the preparation chamber. Further details of imaging procedures are given elsewhere (Stern et al., 2004).

Before being sectioned for cryo-SEM work, whole-round core sections were first imaged by cryogenic x-ray computed tomography (CT) at Lawrence Berkeley Laboratory in order to non-invasively determine the location of gas hydrate nodules or veins within them (see Kneafsey and Moridis, this volume). One sample (HYD 29) was imaged by cryo-SEM both before and after CT imaging. No apparent differences between the before and after samples were noted, indicating that the cores were not altered by CT scanning processes.

In the SEM column, gas hydrate could be distinguished from ice using the instrument's EDS capability to identify distinct carbon peaks when focused on flat, dense, undissociated gas hydrate surfaces. EDS was also used to identify Na and Cl peaks in salt observed in some samples, as described in Results section 3.1.2.

2.3. Gas chromatography and isotopic analyses

For analyses of the hydrate-forming gas, small sections of each sample were first removed from LN₂ and briefly warmed in a dry environment before inserting them into a syringe. Samples typically released a small amount of additional N₂ gas that was pushed from the syringe before the onset of the main dissociation event. After the section had completely dissociated, the syringe gas was admitted to pre-evacuated receptacles that were then shipped to Isotech Laboratories, Champaign, Illinois, for full gas compositional analyses and isotopic analyses of methane.

Gas compositional analyses were measured on a custom-configured Shimadzu 2040 gas chromatography (GC) system. The system operates isothermally, utilizing valve-switching and multiple columns to separate the various components found in natural gas samples. The major fixed gases and high concentration methane were quantified using a thermal conductivity detector (TCD), while low concentration methane and other hydrocarbons (from 100 ppm down to 1 ppm) were measured using a flame ionization detector (FID). Peak integration and quantification was accomplished utilizing EZChrom software.

A gas chromatography–combustion–isotope ratio mass spectrometer (GC–C–IRMS) system consisting of an Agilent 6890 CG combustion unit and Finnigan GCCIII interfaced with a mass spectrometer (Delta V Plus or Delta Plus Advantage) was used to analyze the carbon isotopic value of methane. Samples were injected into the HP6890 split/splitless injector either manually or using an auto-sampler. The resultant CO₂ was introduced directly into the mass spectrometer, and Thermo’s Isodat software was utilized for peak detection and quantification. Hydrogen isotopic values for methane were determined using the same system, but the gas was channeled through a high-temperature pyrolysis furnace instead of through the combustion furnace. The pyrolysis furnace converts methane into H₂ and carbon, and the H₂ gas is introduced directly into the mass spectrometer. Reference gases were analyzed at the start of each analysis sequence, and 10% of the samples were analyzed in duplicate as check samples.

2.4. X-ray diffraction

X-ray powder diffraction (XRD) was used primarily for cursory analysis of sediment composition, and in one case for gas hydrate analysis. For sediment analysis, sections of samples were warmed and vacuum dried overnight to remove the gas hydrate or ice phases. The remaining material was gently ground by mortar and pestle, packed into sample holders, and scanned at room temperature with a Rigaku MultiFlex X-ray diffractometer. One additional sample (HYD 55) was run at 140 K to analyze the gas hydrate + ice portion of a nodule. That sample was ground under LN₂ before being transferred to a custom cryo-stage designed for our diffractometer. Similar methods were used previously to x-ray lab-synthesized methane hydrate as well as Cascadia gas hydrate (Stern and Kirby, 2008) that are used for comparison here.

3. Results and interpretation

3.1 Cryo-SEM results of NGHP-01 samples

3.1.1 Distinguishing gas hydrate from ice

The examined samples often contain a small to significant fraction of ice in addition to gas hydrate, as evidenced in hand specimen (Fig. 1), x-ray diffraction (Fig. 2), and cryo-SEM (Fig. 3). Differentiating gas hydrate from ice and establishing the source of the ice are critical for evaluation of physical property measurements made on the samples and for distinguishing between original features and artifacts of the recovery process. The XRD scan of NGHP-01 sample HYD 55 (Fig. 2B) from Site 10D, for instance, shows a significant fraction of ice in addition to structure I gas hydrate, although difficulties in maintaining a uniformly smooth surface during scanning procedures resulted in high background noise. Nonetheless, the pattern compares favorably with those of the laboratory-synthesized samples made from known amounts of pure methane hydrate mixed with ice (Fig. 2A), as well as methane hydrate + ice from Cascadia Margin sample 1328B recovered by IODP Exp. 311 (Fig. 2C). This result is also in general agreement with the high-pressure x-ray diffraction results reported previously by Schaef and McGrail (2007) on NGHP-01 samples from Site 10.

In most cases it is reasonable to assume the ice is a byproduct of hydrate dissociation during core retrieval and/or subsequent handling given that ice is not stable at the *in situ* sub-seafloor marine conditions relevant to the NGHP-01 study sites. In some cases the presence of ice may also result from pore water being frozen in place during LN₂ treatment. While it can be difficult to distinguish gas hydrate from ice by cryo-SEM upon first inspection, the phases can often be discriminated by their markedly different behavior under high vacuum conditions in the SEM column and particularly when situated directly under the beam. Gas hydrate commonly displays rapid changes along exposed surfaces, such as recession and pitting, whereas ice typically remains stable for far longer periods of time (Fig. 3). However, even surface behavior is not always an accurate indicator, as the apparent rate of surface change of the hydrate phase is to some extent also influenced by its location within the sample holder, as well as its surface-to-volume ratio. When hydrate is positioned relatively

high in the sample holder for example, or is poorly connected between sediment grains, it typically exhibits extremely rapid surface deterioration relative to ice. When the hydrate sits low in the holder or is partially secluded within a cavity, the rate of change may be slower and less dramatic. In any case, the presence of a carbon signature in the EDS spectra (examples are shown in sections 3.1.2 and 3.1.3) can differentiate hydrate from ice as long as the section analyzed is not too small, thin, or uneven, given that the beam spans a couple of microns (typically ~ 2 μm diameter) during EDS spot analysis.

3.1.2 Characteristics of nodular or massive gas hydrate.

The hydrate phase in nodular gas hydrate from NGHP-01 commonly forms a dense substrate bounded by sediments and enclosing bubble-like pores (Figs. 4 and 5). In some cases (e.g., HYD 19 from Site 10B), up to about 20 vol. % marine sediments may be intermixed within the gas hydrate sections (Fig. 4). Where hydrate grain boundaries are visible, grain sizes typically range 30-80 μm in diameter, with some grains measuring smaller at 10-20 μm and others larger at upward of 100 to 200 μm (Figs. 5 and 6; also SI figure 1). However, because this size range is based on SEM imaging of only a limited number of samples, it should not necessarily be viewed as a statistically representative range of gas hydrate grains in the suite of samples as a whole, or in nature. Klapp et al. (2007), using high-energy synchrotron radiation to evaluate grain size distribution, suggest that natural gas hydrate grain sizes may in fact largely cluster in the 300-600 μm range with larger sizes correlating with increasing depth, but we do not have a sufficient inventory of samples to comment on this finding.

All of the nodular gas hydrate samples observed here contain numerous and often isolated “macropores” that account for roughly 5 to 20 vol % of the domains (Figs. 4 and 5). These pores are typically round and range from several microns to several tens of microns in diameter, or sometimes upward of 100 μm , and are termed macropores here to differentiate them from the micro- or nano-porous surface appearance that gas hydrate develops with time in the SEM column. In some cases, obvious dissolution or dissociation features were observed that precluded determination of whether the pores were in fact original features. For example, the macropores shown in Figure 3 are surrounded by thin rims of ice, with the ice rims in turn encompassed by

gas hydrate. While the macropores may well have been produced by dissociation, the extent of dissociation is minor and quite localized. In comparison, the macropores in Figure 7 are entirely enclosed within a larger region of ice that in turn borders a region of gas hydrate with no macropores, suggesting that this sample suffered a greater extent of dissociation to produce prominent regions of gassy ice. However, in other sections of NGHP-01 samples, as well as in samples from other localities, gas hydrate crystal faces are sometimes observed to line macropore interiors or exposed surfaces (Fig. 8A, B). The gas hydrate crystals lining pore interiors are typically fine grained and resemble the finely crystalline gas hydrate formed in the laboratory under high pressure, low temperature, excess-gas conditions (Fig. 8C).

In several samples from NGHP-01 such as HYD 19 and 82 (from Sites 10B and 10D, respectively), gas hydrate grains are occasionally delineated or bounded by a resistant material that forms thin rinds at hydrate grain exteriors and that remains intact as the interior gas hydrate sublimates (Figs. 4–6). These unusual features are exhibited by gas hydrate nodules recovered from other marine environments, including Cascadia (Fig. 5D) and Gulf of Mexico samples, discussed in section 4.1 below. Where the boundary material is present, it is often embedded well within the samples and is not merely a surface artifact, as evidenced by time-lapse imaging during which the hydrate phase sublimates and retreats to increasingly expose the resistant rims. We do not know if the boundary material is the same composition among the various samples in which it is observed. However, the material was positively identified in sample HYD 82 by EDS to contain Na and Cl, with no other peaks appearing in the spectra except for carbon and oxygen from the background hydrate (Fig. 6). Hence at least in some regions, the material is identified as sodium chloride salt.

3.1.3 Characteristics of mixed gas hydrate + sediment sections.

Many of the NGHP-01 samples appear uniformly dark grey to black in hand specimen, with only small lenses, thin layers, or thin veins of gas hydrate visible. HYD 96, representative of Site 14A (Fig. 9), contains primarily disseminated gas hydrate with only sporadically distributed lenses of hydrate within it. Other samples such as HYD 19 and 92 (from Sites 10B and 12A; Fig. 10 and SI Fig. 2), contain numerous lenses or thin veins of hydrate typically 50 to several hundred microns in thickness. Veins or layers of hydrate typically appear in two

general orientations; parallel or sub-parallel to depositional layering and interlaminated with fine sand and silt, or sub-parallel to the vertical length of the core and presumably fracture filling. The resolution and spatial capabilities of SEM imaging are not well suited for rigorous investigation of the distribution and orientation of coarse veins or other large-scale features, and these characteristics are instead best assessed by non-invasive, 3-dimensional imaging techniques such as computed tomography (CT) imaging. CT scans of NGHP-01 cores can be found in Rees et al. (2011), and scans of the specific cores discussed here are included in Kneafsey and Moridis (this volume, supplementary material). On a more localized level, sublimation of the hydrate phase in the SEM column can be utilized to reveal the fine-scale 3-dimensional framework of hydrate + sediment sections as well as for qualitative estimates of the thickness and general distribution of thin veins of hydrate (*e.g.* SI Fig. 2).

Several of the NGHP-01 samples (*e.g.* certain sections from HYD 29, 92, 96, and 7, from Sites 10B, 12A, and 14A) exhibited some of the most interesting and intact gas hydrate crystals that we have observed to date, from any locality worldwide. These NGHP samples show finely crystalline gas hydrate that extensively lines cavity walls within the sediment sections (Figs. 11, 12, also SI Fig. 3). The gas hydrate is closely intergrown with the sediments below, but grows unimpeded into sometimes astonishingly euhedral forms that in some cases displays markedly unusual crystal habits (Figs. 11 and 12). The crystals can be identified as gas hydrate by EDS (Fig. 12A, inset) and in some cases by their fully-developed isometric crystalline forms (Fig. 12B and 12C for example), and otherwise by their rapid sublimation compared to ice and the mottled or damaged surface they developed upon exposure in the SEM column or when positioned directly under the beam (Figs. 11D and 11E). Loose, hexagonal platelets of ice are observed in some of these sections, but the gas hydrate crystals here are also found to sometimes exhibit pseudo-hexagonal forms that not only sublime or alter rapidly under the beam, but that also exhibit the signature carbon peak that distinguish them from ice (Fig. 11D.) We note that this finely crystalline habit is not the dominant manner in which gas hydrate occurs in these samples. Instead, these samples most commonly contain hydrate in small veins, layers, pods, or disseminated in sediment (Fig. 10, see also SI Figs. 3A and 4). Veins of hydrate, presumably fracture-filling, are often oriented sub-parallel with respect to the length of the core (SI Fig. 4). Certain regions were also found to be dominated by ice rather than hydrate (SI Fig. 3B). Water available for ice formation within these sediment sections may have at least 3 sources; from gas

hydrate dissociation, pore water, and incidental seawater contamination on the outside of the core, or some combination of these. Identifying the source of the water is difficult by SEM imaging alone, with the exception of water ice produced by dissociation as described in 3.1.2 above.

The sediment phase of KG Basin samples was examined by X-ray diffraction and found to be dominated by quartz with minor clay, likely illite. Six samples were scanned, all but one yielding virtually identical patterns. The one sample with markedly different sediment composition was HYD 115, from Andaman Site 17, discussed below in section 3.1.4. For a more in-depth review of the composition and geotechnical properties of NGHP-01 sediments we refer the reader to Winters et al. (this volume), and, specifically for Site 17 sediments, to Rose et al. (this volume).

Imaging of NGHP-01 cores also revealed gas-hydrate-bearing sections that contain minor to significant fractions of microfossil or other biogenic material. Although most pronounced in Andaman sample HYD 115 (described below), other samples such as HYD 19 (KG Basin Site 10B) also exhibit minor amounts of fossil material intermixed with silt and clay fragments (Fig. 10A).

Framboids, *i.e.* spheroidal accumulations of discrete, euhedral, pyrite micro-crystallites, were also observed in several samples, most notably in HYD 19 from Site 10B (Fig. 13; see also SI Fig. 5). In HYD 19, framboids were observed either clustered in microfossils (Fig. 14) or dispersed within the sediments (SI Fig. 5).

3.1.4 Cryo-SEM imaging of Andaman Site 17 gas-hydrate-bearing sediment

The examined core section from Andaman Site 17A (HYD 115, from 525 mbsf) differs markedly in macroscopic appearance from all other samples we received due to its texture and uniformly green color (Fig. 14). X-ray diffraction identified the sediments as primarily calcite with minor amounts of quartz, mica, clays and feldspar. The sediment is also volcanic ash-bearing (Collett et al., 2008b; Rose et al. this volume) in addition to containing a significant amount of intact micro- or nano-fossils. The biogenic content consists of various fractions of rapidly deposited calcareous (including foraminifera) and siliceous (including diatoms and

spicules) material (see Winters et al, this volume; also Collett et al. 2008a). Although the core contains a significant amount of gas hydrate, little was apparent by macroscopic observation.

SEM imaging of HYD 115 revealed both gas-hydrate-bearing and ice-bearing sections of sample that were easily distinguished by their behavior in the SEM (Fig. 15). Where gas hydrate was present, it typically occupied cavities and crevices within or between the microfossils and other sediment fragments (Fig. 15A,B). The gas hydrate within these sections then sublimated rapidly in the SEM to reveal the remarkably well-preserved nature of the biogenic material below, often intermixed with clay platelets and/or silt particles (Figs. 15A1, 15B1, and 16). Some sections contained clusters of framboidal pyrite as well, although fewer framboids were observed in HYD 115 compared with KG basin samples. Several sections of HYD 115 also exhibited localized regions of finely faceted gas hydrate crystals, typically 10-20 μm in size (Fig. 17).

3.2 Gas Chromatography and isotopic analyses results

Gas from dissociated NGHP-01 hydrate-bearing samples is composed mainly of methane, with trace concentrations of higher molecular weight hydrocarbon gases as large as propane (Table 2a). Carbon dioxide is also present in widely variable amounts, sometimes exceeding the concentration of methane (Table 2a). We consider the high- CO_2 cases to be an artifact of sample preservation and handling inherent with sampling gas hydrates outside of their *in-situ* pressure-temperature stability conditions, and not a true reflection of the hydrate-sequestered gas. Hydrate gas compositions are given in units of ppm of total evolved gas, then normalized to the sum of methane and carbon dioxide to better reflect the *in-situ* gas compositions expected in an air-free environment (Table 2b). We consider the best representation of *in-situ* gas hydrate composition to be those samples with normalized methane concentrations (mathematically removing the primary atmospheric gases that should be absent from a pristine subsea hydrate sample; N_2 , O_2 and Ar) exceeding 900,000 ppm, of which there are only three examples (Table 2b). The overall composition of the gas hydrate gas restricts the crystal structure to Structure I (Sloan and Koh, 2007).

The gas hydrate gas samples have methane isotopic compositions that reflect a microbial genesis by carbonate reduction with $\delta^{13}\text{C}_1$ values that range from -71.2 to -61.4 ‰, and δDC_1 from -196 to -183‰. Complementary carbon isotopic compositions for carbon dioxide range from -18.4 to +3.1‰, which mainly reflect the exsolution of carbon dioxide from HCO_3^- in sediment pore water during core recovery. Two samples enriched in ^{13}C with $\delta^{13}\text{CO}_2$ values of -4.1 and +3.1‰ may represent some process where a portion of the sample's original carbon dioxide (or dissolved inorganic carbon) was lost or metabolized resulting in a ^{12}C depleted pool. One ethane carbon isotope composition, measured from one sample with high enough concentration of ethane to be cryogenically enriched, yielded a value of -51.9‰ reflecting an isotopic composition expected from a microbial source. These values as a whole fall within the general range of those measured from gases collected near the same depth from pressure coring systems and void gases (Lorenson et al., this volume) demonstrating that there is no fractionation between the sediment gas isotopic composition and that incorporated into gas hydrate.

We note that the differing scales of measurement do not allow us to directly compare individual SEM images (small scale) with the full-sample bulk gas composition. Here, the gas composition of the hydrate is assumed to be homogenous, and gas measurements are assumed to represent both sample-wide and localized occurrences of hydrate. Water released from the dissociated hydrate was collected but not analyzed, due to the unknown extent of contamination by surrounding sediment grains during and after the melting process, as well as the difficulty in differentiating dissociated water from frozen pore water. Hence, we cannot comment on the concentration of dissolved phases such as CO_2 or NaCl in the residual fluids.

4. Discussion

4.1 Comparing sample characteristics to natural gas hydrate from other localities or from the lab

Despite the diverse settings from which gas hydrate samples have been recovered worldwide, a surprising number of similarities are apparent, particularly when comparing gas hydrate that occurs as nodules, thick veins, or in similarly massive or relatively pure form. Figures 1 and 2 compare nodular gas hydrate collected

from the Cascadia margin (Fig. 1C) to gas hydrate examined in the current study, both in hand specimen and XRD analysis. Minor differences in macroscopic appearance are apparent, but the compositions are quite similar (Fig. 2). Moreover, cryo-SEM shows that the hydrate phase in samples from both the KG Basin and Cascadia margin forms as a dense material encapsulating widely distributed but mostly isolated macropores (compare Fig. 5A with Fig. 5B-D).

The textural similarities extend to gas hydrates retrieved from other localities as well, including samples from the Mississippi Canyon in the Gulf of Mexico, from the Mallik test site in NW Canada, and from laboratory-made methane hydrate that was formed under closely controlled, excess-gas conditions and subsequently transferred to a natural seafloor environment (*e.g.* Fig. 4 in Stern and Kirby, 2008 and Fig. 12 in Stern et al. 2004). Strikingly similar is the grain size exhibited by the recovered gas hydrate samples in all comparisons – typically 20-80 μm and less commonly ranging up to 100-200 μm – as well as the general distribution, sizes, and shapes of the bubble-like pores that can comprise upward of 20 vol. % of the material. This holds true even for the lab-made samples that exhibited markedly different grain and pore structures prior to their ocean-floor exposure (Stern and Kirby, 2008). In all cases, the sample textures tended to converge to a surprisingly uniform appearance. These consistencies are encouraging as they not only lend increased confidence to the extrapolation of measurements made on lab-synthesized material, but also to the interpretation of what morphological features in recovered natural samples are original versus an artifact of recovery.

Textural similarities also emerge when comparing the mixed hydrate + sediment sections from different localities. In Cascadia samples 1328B and E, for instance, sediment sections commonly include small pods, lenses, or thin layers of gas hydrate that are surrounded by silt and clay platelets $\pm$ other material (Fig. 18). The small lenses or pods of hydrate range in size up to several hundred microns around which the platelets are oriented in sub-parallel fashion (Fig. 18 A, B, B1). Other sections sometimes exhibit rims of what may be NaCl intermixed with fine sediment and forming a matrix around gas hydrate pods, giving an overall honeycomb-like appearance (Fig. 18C, D) similar to that exhibited in Figure 4B. We did not analyze the rims displayed in the Cascadia samples by EDS, but note that some contain small crystallites that resemble salt and do not appear to be comprised entirely of sediments. Furthermore, the resistant boundary material that is occasionally found to

rim gas hydrate grains in both Cascadia and Gulf of Mexico samples is sometimes exhibited in sediment-free portions of samples as well (Fig. 5D for example, see also Fig. 6 in Stern and Kirby, 2008). We suspect that these boundary rims are in fact salt-bearing and form by NaCl exclusion during original hydrate grain growth, similar to those exhibited in Figure 6 from HYD 82. The gas hydrate within these pods is dense (see Fig. 18A inset, also Fig. 18D) and shows no obvious signs of prior decomposition or other evidence to suggest alteration from its original texture.

4.2 Implications for gas hydrate formation processes

We have discussed that nodules or massive gas hydrate observed here – as well as from other localities worldwide – may contain up to about 20% intercalated sediment and were found to contain abundant but isolated macropores that can occupy up to 20% of the domain. In many sections of samples it is apparent that the pores are likely associated with partial to significant dissociation of sample material during the recovery and subsequent handling processes, as the pores are often rimmed or completely encased by ice rather than gas hydrate. However, some samples show evidence that the bubble-shaped macropores could be original features, based on their being lined and/or surrounded by gas hydrate (Fig. 8), which in turn suggests the likely presence of free-phase gas during original formation. The implications for hydrate formation are of interest and relevance to NGHP-01 (and other) sites given on-going debate regarding mechanisms of gas hydrate formation in subsea sediments. Current views favor gas hydrate formation in subsea sediments from primarily dissolved-phase gas (e.g. Waite et al., 2009), but textural considerations suggest that the massive gas hydrate examined in the current study formed from a free gas phase.

The close juxtaposition of salt and gas hydrate may also speak to the formation mechanism of gas hydrate from free-phase gas, given that even small increases in salinity (resulting from hydrate formation) of local pore water should effectively limit further formation of gas hydrate by reducing methane solubility and decreasing the stability of the gas hydrate (see for example Tohidi et al., 1997, Milkov et al, 2004b). We noted that at least one NGHP-01 sample exhibited gas hydrate with grains unequivocally bordered by NaCl-bearing material forming thin rinds along hydrate grain exteriors, presumably produced by salt exclusion during original hydrate

formation. To the best of our knowledge, this is the first reporting of salt being imaged and verified as creating rims surrounding gas hydrate grains. Indeed, there are several higher-than-normal chlorinity values reported from shipboard measured porewaters in association with gas hydrate in the KG basin (Collett et al., 2008a). We have identified similar features in samples from other localities worldwide as discussed in section 4.1. Tohidi et al. (1997) postulate, through thermodynamic modeling validated against experimental data, that hydrate formation from dissolved-phase gas in seawater should result in only very small increases in salt concentration, whereas under conditions of formation from free gas, a significant increase in the salt concentration of the pore water should result. More recently, Milkov et al. (2004b) provided evidence for the natural coexistence of gas hydrate, free gas, and hypersaline pore water at Hydrate Ridge, and suggest that such coexistence may also occur in shallow marine sediments elsewhere in regions of high upward methane flux.

5. Summary and conclusions

SEM serves as a powerful tool enabling close examination of the morphology and grain contacts in samples from nature as well as for making relevant comparisons to other natural gas hydrates or to those made and tested in the laboratory. In some cases, SEM can also offer insight into original formation processes. Where gas hydrate formed in sediments in the NGHP-01 samples, it most commonly formed as small pods or lenses distributed throughout the sediments, as thin veins or layers ranging from several tens to several hundred microns in thickness, or disseminated throughout the sediment, similar to hydrate + sediment samples from other localities. Less commonly, the NGHP-01 samples exhibited certain morphological features that are perhaps best considered as oddities or curiosities, yet are exhibited by numerous samples from different cores and different depths. Most noteworthy are the highly faceted gas hydrate crystals found extensively lining the interiors of cavities, intermixed with the sediment and clays surrounding the cavities, and growing unconstrained into remarkably euhedral crystalline forms with a wide range of crystal habits within the isometric crystal system. These features, resembling geological vugs, were observed in near-seafloor samples as well as in those of deeper origin (> 100 mbsf), and their crystalline nature again suggests growth from free-phase gas. While we cannot say with certainty that this mode of occurrence formed *in situ*, we have no evidence to suggest that it is a recovery artifact, nor have we observed this type of gas hydrate formation in samples recovered by similar coring methods

from other localities worldwide. Also noteworthy from the NGHP-01 suite of samples is the remarkably well preserved fine structure of microfossil and other biogenic detritus in the Andaman Site core that is revealed only after sublimation of the gas hydrate that fills the may recesses and crevices within and between the fragments.

The gas geochemistry shows that in general the NGHP-01 samples suffered partial to significant dissociation prior to immersion in LN₂ and that the only possible hydrate structure that can be formed by the observed gas composition is structure I, the most common structure of hydrate found in nature (Sloan and Koh, 2007). The implication of the latter is an important consideration in predicting the gas hydrate stability zone in both regions, as well as predicting other physical properties of the sediment containing gas hydrate. The genesis of the hydrocarbon gases is from microbial processes and the gases are very similar to the surrounding sediment gas, an observation that predicts that the hydrates formed in place and are not from gas that migrated from non-local distances and sources.

Despite the many thousands of cryo-SEM images of natural gas hydrates archived to date, it's likely that the full range of textures, fabrics, and crystal habits displayed by natural gas-hydrate-bearing systems have yet to be observed. So far, both the similarities and oddities exhibited by gas hydrates from different localities have been quite surprising. With respect to the NGHP-01 drilling sites, the wide range of gas hydrate modes of occurrence exhibited by the relatively small number of samples examined in this study suggest that there is no single mode that can be ascribed as dominant or even representative of the region as a whole. Instead, the range of textures suggests that a variety of gas hydrate formation processes were active, likely influenced by localized *in situ* conditions dependent on gas availability and amount relative to saturation level, sediment type and porosity, and small- or large-scale fracture patterns.

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TABLE AND FIGURE CAPTIONS:

Table 1. NGHP-01 gas hydrate samples.

Table 2a. Hydrate gas (dissociated gas from NGHP-01).

Table 2b. Hydrate gas (dissociated gas from NGHP-01) normalized to methane.

Figure captions:

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 grey, as labeled in **A**. Dark grey to black marine silts and clays surround the hydrate + ice phases in all three images.

Figure 2. X-ray diffraction patterns of (**A**) lab-made sI methane hydrate + ice (67:33 vol. %, respectively), (**B**) NGHP-01 sample HYD 55, and (**C**) IODP Leg 311 Cascadia sample 1328B. Macroscopic views of **B** and **C** are in Fig. 1. Similar proportions of ice and sI gas hydrate appear in all scans, although HYD 55 exhibits slightly higher ice content.

Figure 3. A section of NGHP-01 HYD 82 (Site 10D) showing several pores surrounded by thin walls of ice, which in turn are surrounded by gas hydrate. The outlined box in **A** is enlarged in **B-D** and the images were taken sequentially about 10-12 minutes apart. During the interim, the beam was repositioned elsewhere within the sample, returning to the initial spot only to re-focus and capture the image. (The central dark rectangular regions in **B-D** indicate beam focus.) Although both gas hydrate and ice exhibit a smooth surface appearance upon initial inspection (**A**), the hydrate phase quickly begins to exhibit surface deterioration and sublimation

(**B**), resulting in an increasingly spongy or nanoporous surface appearance (**C**, **D**). In comparison, ice remains relatively stable under the beam and exhibits very little change (see labels in **D**).

Figure 4. Image **A** shows a section of a gas hydrate nodule intermixed with sediment from HYD 19 (Site 10B, 75 mbsf). Here, the hydrate phase appears as the smooth material containing isolated bubble-like macropores. The sediment phase is the fine-grained and often brighter material standing high in relief relative to the hydrate. **B** shows a detail of smaller regions of gas hydrate that have partially sublimated and retreated from the sediments and/or any other boundary material surrounding them. With time, the surface of the hydrate develops the characteristic surface pitting and nanoporous topology (**C**) as it degrades within the SEM.

Figure 5. Panel **A** shows a section of a nodule from HYD 82 (Site 10D, 131 mbsf) exhibiting a dense gas hydrate substrate enveloping many isolated macropores. Grains within the substrate are typically 20-80 μm , or occasionally larger (SI Fig. 1), and in some instances are rimmed by salt (lower right quadrant; see Fig. 6). Similar substrate, grain, and pore structures are exhibited by Cascadia 1328B shown in panels **B-D** (and Fig. 1C) as well as nodular samples from other localities (see text).

Figure 6. A section of HYD 82 showing an expanded view from the lower right quadrant of Fig. 5, detailing the boundary material that rims many hydrate grains in this sample. EDS shows the rims contain salt, based on the Na and Cl peaks in the spectra (panels 1 and 2 at right), and identifies the host phase as gas hydrate, not ice, based on the presence of a carbon peak (panel 3). Only a portion of the EDS scans are shown here; no additional peaks appeared in the full scans. The tall, unlabeled peak in each scan is oxygen.

Figure 7. The transition from gas hydrate (labeled “hyd” at left) to ice (at right) in a section of HYD 55 that likely formed by partial dissociation during sample retrieval. Here, gas hydrate appears nanoporous due to extended time and sublimation in the SEM column (see also Fig. 3). In comparison, the smooth material surrounding all the macropores at right is ice, not gas hydrate, confirmed by EDS.

Figure 8. Small, dense, well-developed gas hydrate crystals sometimes line the macropores or other exposed surfaces within massive or nodular gas hydrate. **A** shows crystalline gas hydrate lining an exposed surface of NGHP-01 sample HYD 55, and **B** shows crystalline gas hydrate lining a pore in Cascadia sample 1328B. (Large-scale views of both samples are in Fig. 1.) **C** shows lab-made pure methane hydrate grown in the presence of excess free gas by methods discussed in *Stern et al.* (2004), displaying similar grain size, habit, and dense substrate.

Figure 9. Macroscopic (**A**) and cryo-SEM (**B**) images of HYD 96 (Site 14A, 105 mbsf) indicate that the gas hydrate primarily occurs as disseminated in the sediments, although small pods of gas hydrate are found here as well (central section of **B**).

Figure 10. Thin and often wavy layers of gas hydrate in HYD 19 (Site 10B) at different magnifications. Microfossil fragments are sporadically incorporated within the sediments as shown in **A**. The gas hydrate phase is partially dissociated here, resulting in it sitting low in relief relative to the sediment layers as shown in **B** and **C**. The layering in **B** is sub-horizontal relative to the core diameter, appearing diagonal here due to the sample stage positioning. The central outlined box in **B** is expanded in **C**.

Figure 11. Several NGHP-01 cores exhibit a network of cavities lined with crystalline gas hydrate attached to the sediment below and growing unimpeded into euhedral forms and exhibiting a wide variety of crystal habits, including some pseudo-hexagonal platelets that resemble ice. **A** shows crystalline gas hydrate in HYD 29 (Site 10B, 110 mbsf), with close-up views from this and neighboring regions in **B-E**. The surface deterioration and pitting of the crystals with time in the SEM and the signature carbon peak in EDS spectra confirm it is gas hydrate, not ice (**D**).

Figure 12. **A** shows gas hydrate crystals lining a cavity wall in HYD 92 (Site 12A). A variety of crystalline habits is exhibited including some that resemble ice (see also Fig. 11D), but carbon in the EDS spectra identifies the crystals as gas hydrate (**A**, **inset**). Top and bottom outlined boxes in **A** are enlarged in **B** and **C** respectively, both showing examples of well-developed isometric crystal forms.

Figure 13. In several NGHP-01 samples such as HYD 19 (Site 10B) shown here, framboidal pyrite formed in the sediment portion or within chambers of microfossil fragments, as seen in **A**. Detailed views are in **B-D**. Pyrite framboids are also found in some NGHP-01 samples more closely intermixed with the sediment phase (shown in SI Fig. 5).

Figure 14. Macroscopic appearance of one end of HYD 115 (Andaman Site 17A, 525 mbsf), 8.9 cm in diameter, showing its distinctive green, homogenous color and friable texture. The light-colored discolorations at the top and lower-right of the sample are artifacts of liquid nitrogen immersion and resulting condensation. Small sections of sample were removed from the center of the core for SEM imaging.

Figure 15: Gas hydrate sublimation effects exhibited by HYD 115 from Andaman Site 17A. Panels **A** vs. **A1**, and **B** vs. **B1**, show 2 different regions after a 30-minute time lapse. Nearly all the crevices and recessed regions within the microfossils that are filled with hydrate in **A** and **B** (some are labeled “hyd” here for ease of identification) have greatly receded in **A1** and **B1**. After the hydrate sublimates, the detail and fine structure of the microfossil fragments that comprise much of this core are revealed. In comparison, panels **C** and **C1** show a section where the frozen phase is ice rather than hydrate, and exhibits essentially no change even after the 3-hour time lapse shown here. Ice is labeled in some sections of **C** and phase identification was verified by the absence of a carbon peak when analyzed by EDS.

Figure 16. Images from Andaman sample HYD 115 showing the wide variety of microfossil fragments that are revealed after gas hydrate has fully sublimated from recessed areas. Outlined box in **A** is enlarged in **B**.

Figure 17. Where gas hydrate had not fully sublimated in HYD 115 and was not disseminated in sediment or ash, it occasionally formed as faceted crystals (**A**) and was easily identified by its rapid deterioration under the SEM beam (**B, C**) and/or a carbon peak in EDS scans (not shown).

Figure 18. Images showing predominantly sI methane hydrate that formed as clustered pods in Cascadia margin sample 1328E from IODP Leg 311. **A** shows a section immediately after entry to the SEM column. The

dense hydrate substrate is shown in inset **A1**. **B** shows the same section 40 minutes later after the gas hydrate sublimated, revealing a 3-dimensional view of the lens-like regions originally occupied by gas hydrate. Clay platelets commonly orient sub-parallel around the lenses, shown in inset **B1**. **C** and **D** show different magnifications of a section of 1328E exhibiting a framework of gas hydrate rimmed by silt and clay platelets plus possibly other material (see text), similar in appearance to Figs. 4B and 5D.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Figure 18

Sample No.	Site	Depth (mbsf)	Area*	Type**
HYD 29	10 B	110	KG	M
HYD 92	12 A	143	KG	M
HYD 115	17 A	525	And	DA
HYD 7	10 B	26	KG	M
HYD 19	10 B	75	KG	M
HYD 96	14 A	105	KG	DS
HYD 82	10 D	131	KG	M
HYD 71	10 D	102	KG	M
HYD 41	10 D	35	KG	M
HYD 55	10 D	65	KG	M
<p>*Area: KG: Krishna-Godavari Basin And: Andaman Island site</p> <p>**Type: M: Massive nodule or vein filled DS: Disseminated in sand/ silt DA: Disseminated in volcanic ash</p>				

Table 1: NGHP-01 gas hydrate samples

Table 2a. Hydrate gas (dissociated gas from NGHP-01)

Name	Basin	Hole-Core-Interval Lab No.	Depth mbsf	O ₂ + Ar ppm	CO ₂ ppm	N ₂ ppm	CO ppm	C ₁ ppm	C ₂ ppm	C ₂ H ₄ ppm	C ₃ ppm	C ₃ H ₆ ppm	iC ₄ ppm	nC ₄ ppm	iC ₅ ppm	nC ₅ ppm	C ₆ + ppm	δ ¹³ C ₁ ‰	δ ¹³ C ₂ ‰	δDC ₁ ‰	δ ¹³ CO ₂ ‰	C ₁ /C ₂
HYD 7	KG	10B 4X3 62-72	25.62	155300	15500	828400	0	768	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	-71.2			-17.3	
HYD 41	KG	10D 5X3 0-23	34.85	95900	6700	885800	0	11600	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	-68.8		-183	3.1	3867
HYD 55	KG	10D 8X2 64-84	52.64	30300	3200	148400	0	818000	74.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-69.1		-185	-11.7	11054
HYD 71	KG	10D 16X3 109-129	102.09	38500	3700	911600	0	46200	5.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	-69.2		-194	-4.3	9240
HYD 96	KG	14A 16X2 120-135	104.70	161100	21000	815600	0	2280	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	-68.1		-184	-15.3	
HYD 29	KG	10B 17X1 130-140	110.10	84300	11800	903100	0	810	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-66.3			-18.4	
HYD 82	KG	10D 20X4 74-80	131.27	95700	2300	462400	0	439500	56.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	-69.1	-51.9	-196	-11.9	7848
HYD 92	KG	12A 13X2 120-135	143.08	186700	15900	796000	0	1430	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-61.4			-17.1	
HYD 115	AD	17A 63X4 72-82	524.95	159400	43600	786500	0	10500	11.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	-62.3		-188	-12.1	955

Table 2b. Hydrate gas (dissociated gas from NGHP-01) normalized to methane

Name	Basin	Hole-Core-Interval Lab No.	Depth mbsf	CO ₂ ppm	C ₁ ppm	C ₂ ppm	C ₂ H ₄ ppm	C ₃ ppm	C ₃ H ₆ ppm	iC ₄ ppm	nC ₄ ppm	iC ₅ ppm	nC ₅ ppm	C ₆ + ppm	δ ¹³ C ₁ ‰	δ ¹³ C ₂ ‰	δDC ₁ ‰	δ ¹³ CO ₂ ‰	C ₁ /C ₂
HYD 7	KG	10B 4X3 62-72	25.62	952791	47209	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	61.5	-71.2			-17.3	
HYD 41	KG	10D 5X3 0-23	34.85	366060	633776	163.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	54.6	-68.8		-183	3.1	3867
HYD 55	KG	10D 8X2 64-84	52.64	3896	996014	90.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-69.1		-185	-11.7	11054
HYD 71	KG	10D 16X3 109-129	102.09	74141	925759	100.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	60.1	-69.2		-194	-4.3	9240
HYD 96	KG	14A 16X2 120-135	104.70	902062	97938	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	43.0	-68.1		-184	-15.3	
HYD 29	KG	10B 17X1 130-140	110.10	935765	64235	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-66.3			-18.4	
HYD 82	KG	10D 20X4 74-80	131.27	5205	994666	126.7	0.0	2.3	0.0	0.0	0.0	0.0	0.0	0.0	-69.1	-51.9	-196	-11.9	7848
HYD 92	KG	12A 13X2 120-135	143.08	917484	82516	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-61.4			-17.1	
HYD 115	AD	17A 63X4 72-82	524.95	805751	194046	203.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	37.0	-62.3		-188	-12.1	955