Gas hydrate distribution and carbon sequestration through coupled microbial methanogenesis and silicate weathering in the Krishna-Godavari basin, offshore India

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Abstract

The National Gas Hydrate Program Expedition 01 cored ten sites in the Krishna-Godavari basin, located on the southeastern margin of India. A comprehensive suite of pore water solute concentrations and isotope ratios were analyzed to investigate the distribution and concentration of gas hydrate along the margin, *in situ* diagenetic and metabolic reactions, and fluid migration and flow pathways. Gas hydrate was present at all of the sites cored, and *in situ* microbial methanogenesis leads to estimates of depth-integrated average gas hydrate saturations that are typically <5%. Deep-sourced fluid and gas migration produces gas hydrate saturations up to 68% along an isolated coarser-grained stratigraphic horizon at Site 15 and up to 41% within a fractured clay-dominated system at Site 10. Our results show that the CO₂ produced through net microbial methanogenesis is effectively neutralized by silicate weathering throughout the sediment column drilled at each site (~100-300 m), buffering the pore water pH and generating excess alkalinity via the same reaction sequence as continental silicate weathering. Most of the excess alkalinity produced by silicate weathering in the Krishna-Godavari basin is sequestered in Ca- and Fe-carbonates as a result of ubiquitous calcium release from weathering detrital silicates and dissolved Fe production within the methanogenic sediments. Formation of secondary hydrous silicates (e.g. smectite) related to incongruent primary silicate dissolution acts as a significant sink for pore water Mg, K, Li, Rb, and B. The consumption of methane through anaerobic oxidation of methane, sequestration of methane in gas hydrate, and sequestration of dissolved inorganic carbon in authigenic carbonates keeps methanogenesis as a thermodynamically feasible catabolic pathway. Our results combined with previous indications of silicate weathering in anoxic sediments in the Sea of Okhotsk, suggest that silicate weathering coupled to microbial methanogenesis should be occurring in continental margins worldwide, providing a net sink of atmospheric CO₂.

Keywords: gas hydrate, silicate weathering, methanogenesis, carbon sequestration

1. Introduction

Elevated primary production, the export of terrestrial organic matter from land to the ocean, and high sedimentation rates at continental margins contribute to an increased burial flux of metabolizable organic matter at the seafloor (e.g. Hedges and Keil, 1995; Gélina et al., 2001). As a result, subseafloor microbial metabolism causes rapid pore water anoxia and drives high rates of sulfate reduction, providing biogeochemical conditions that promote microbial methanogenesis at shallow depths in the sediment column (e.g. Claypool and Kaplan, 1974; Froelich et al., 1979). Microbial methanogenesis is ubiquitous along continental margins worldwide, and within the gas hydrate stability zone (typically water depths >500 m; >300 m in the Arctic), gas hydrates form when the concentration of methane dissolved in the pore water exceeds gas hydrate solubility.

Estimates of global rates of microbial methanogenesis in marine sediments range from ~2 to 20 Tmol CH₄/yr (Hinrichs and Boetius, 2002; Reeburgh et al., 1993; Wallmann et al., 2012). Most of the methane that is produced in continental margin sediments is either sequestered in gas hydrate or is oxidized through anaerobic oxidation of methane (AOM) at the sulfate-methane transition zone (SMTZ). An unconstrained fraction of the methane produced bypasses these filters and is emitted to the ocean. The cycling of methane in marine sediments has been actively studied over the past several decades, but far less attention has been paid to the cycling of CO₂ in methanogenic sediments.

During net microbial methanogenesis, CO₂ is also produced such that for every mole of CH₄ released to the pore water, approximately a mole of CO₂ is released. Recent studies based on piston cores (<25 m in length) in the Sea of Okhotsk and Black Sea (Aloisi et al., 2004; Wallmann et al., 2008) suggest that much of the CO₂ produced in shallow sediments through microbial methanogenesis is neutralized through weathering of detrital silicate minerals leading to the production of alkalinity. It is not known whether this is ubiquitous within gas hydrate-bearing sediments worldwide, but it may be an important sink of CO₂ and source of alkalinity to the ocean (Wallmann et al., 2008). Additionally, the removal of dissolved CO₂ may influence the thermodynamics and rate of methane production.

Recent estimates of the global gas hydrate inventory, based on multiple approaches, suggest that ~400 to 3000 Gt of methane-bound carbon is stored in gas hydrate in marine sediments (e.g. Archer et al., 2009; Buffet and Archer, 2004; Milikov et al., 2004; Piñero et al.,

2013). Considering the large mass of methane carbon stored in the global gas hydrate reservoir, it may be a potential energy resource (e.g. Boswell and Collett, 2011). Since the gas hydrate reservoir is sensitive to pressure and temperature perturbations, it also has the potential to affect climate (e.g. Dickens et al., 1995; Kvenvolden, 1993). Gas hydrates, however, are typically not uniformly distributed in the sediment within the gas hydrate stability zone (e.g. Malinverno, 2011; Torres et al., 2008). This complicates assessing their global inventory and resource potential as well as predicting the vulnerability and environmental consequences of gas hydrate dissociation driven by environmental change. The Indian National Gas Hydrate Program (NGHP) Expedition 01 was designed to study the occurrence of gas hydrate off the Indian Peninsula and along the Andaman convergent margin (Fig. 1) with emphasis on understanding the geologic and geochemical controls on methane dynamics and the distribution of gas hydrate in the two settings (Collett et al., 2008).

Here we report on geochemical analyses of pore water samples collected at high-resolution from ten sites cored in the Krishna-Godavari (K-G) basin during NHGP Expedition 01 (Supp. Table 1) and focus our discussion on six of these sites (Table 1; Fig. 1). A comprehensive suite of major, minor, and trace element concentrations, as well as isotope ratios, were analyzed to investigate the spatial distribution of gas hydrates across the margin, *in situ* diagenetic and metabolic reactions, fluid migration and flow pathways, and fluid and gas sources. Here we focus on both CH₄ and CO₂ dynamics in the sediment column to better understand the processes and sinks controlling CO₂ produced through methanogenesis. The pore water geochemical data set presented herein is one of the most extensive collected to date from a gas hydrate system, and provides new insights into co-occurring microbial and inorganic reactions that control carbon and elemental fluxes. These results highlight the importance of silicate weathering driven by microbial methanogenesis in generating excess alkalinity that leads to the long-term storage of carbon through pervasive authigenic carbonate precipitation in continental margin sediments.

2. Geologic Setting

The eastern continental margin of India evolved as a consequence of rifting between India and Australia/Antarctica in the Late Jurassic and Early Cretaceous. The Krishna-Godavari basin (K-G basin), located along the central east coast of India, occupies an onshore area of ~28,000 km² and extends beyond the mid-slope, encompassing an offshore area of 24,000-

49,000 km² (Radhakrishna et al., 2012). The tectonic activity along the eastern continental margin of India resulted in the formation of several NE-SW trending horst and graben-like structures (Rao, 2001), and the grabens are filled with a thick pile of sediments with a maximum sediment thickness of >7 km (Bastia and Nayak, 2006). The Godavari and Krishna rivers supply the bulk of the detrital sediments to the K-G basin.

The collision between the Indian and Eurasian plates resulted in the building of the Himalayas. Subsequent monsoon activity promoted rejuvenation of major rivers (Ganges, Brahmaputra, Mahanadi, Krishna, Godavari, and Cauvery) and minor tributaries, which collectively transport large amounts of sediments into the Bay of Bengal (Curry and Moore, 1971). This sediment discharge is manifested in the forms of deltas and delta fronts on the inner shelf, extending beyond the shelf break (Ramana et al., 2009). The shelf is incised by headward eroding point-source canyons that are now abandoned and filled with clay and reworked sediments. Several V-shaped canyons flanked by steep faults characterize the upper to mid-slope regions, while turbidity channels and levee wedges transverse the shelf and slope (Ramana et al., 2009; Riedel et al., 2011). Widespread mass transport deposits have been observed over the modern upper continental slope and have also contributed to the total sediment accumulation/dynamics (Ramprasad et al., 2011; Shanmugam et al., 2009; Hong et al., this issue). The high sedimentation rates on the K-G basin slope and POC concentrations of 1.5-2.5 wt.% create favorable conditions for methane generation. Indeed, the K-G basin is one of the most important petroliferous basins of India, and large conventional gas and gas hydrate deposits have been discovered over the past decade (e.g. Bastia, 2006; Collett et al., 2008).

The high sedimentation rates on the slope-intraslope basin has led to the development of listric extensional faults (Bastia and Nayak, 2006). The deeper part (>800 m water depth) of the K-G deltaic system, which is the focus of this study (Fig. 1), is significantly deformed by normal faults and toe-thrusts (Bastia and Nyak, 2006; Ramana et al., 2009; Riedel et al., 2011). The regional geothermal gradient increases with water depth (Table 1), however local deviation from this general trend may occur due to fluid advection along fault systems (e.g. Dewangan et al., 2011; Mazmudar et al., 2012). There are numerous features indicative of fluid expulsion along the basin such as bathymetric mounds and deep-seated mud diapirs (Ramana et al., 2007; Mazmudar et al., 2012). The bathymetric mounds are commonly associated with fault/fracture systems that facilitate fluid and gas migration from depth (Dewangan et al., 2010).

3. Methods

3.1. Sample Collection

Whole-round samples for pore water chemical analyses were collected at a resolution of 2-18 samples per 9 m of core. Whole-round sampling of conventional cores was guided by catwalk infrared (IR) scans so that both gas hydrate-bearing sections (those with cold IR anomalies) and background sections (those without IR anomalies) were sampled (Collett et al., 2008; Riedel et al., 2006; Trehu et al., 2004; Torres et al., 2008). Background whole-rounds were immediately transferred to the shipboard geochemical laboratory and stored in an anoxic glove bag at the same temperature as *in situ* bottom water ($\sim 6^{\circ}\text{C}$) until further processing (typically < 1 hr). Sediment samples with IR anomalies were immediately extruded from the core liner in the geochemistry laboratory and imaged with a hand-held IR camera to identify the locations where gas hydrate had dissociated during core recovery (Supp. Fig. 1). The sample was then carefully split in half lengthwise and further imaged with the IR camera and a visible spectrum camera. If the sediment and/or anomaly were heterogeneous, the lithologies were separated (e.g. clay, silt, sand) and squeezed separately for pore water. Pressure cores were also sub-sampled for pore water chemical analyses based on x-ray images of the cores before and after depressurization, which places constraints on the spatial distribution of the gas hydrate (Collett et al., 2008). Typically, one gas hydrate-bearing and one background sample were collected per pressure core.

3.2. Sample Processing and Analytical Methods

Before squeezing, the whole-round samples were carefully cleaned by removing the outside layers of sediment that were potentially contaminated by drilling fluid. The cleaned sediment samples were placed in Ti squeezers, modified after the stainless steel squeezer of Manheim and Sayles (1974), and gauge forces up to 30,000 pounds ($P < 20$ MPa) were applied using laboratory hydraulic presses to extract the pore water. The pore water was passed through a pre-washed $11\text{ }\mu\text{m}$ filter above a Ti screen and a secondary $0.45\text{ }\mu\text{m}$ syringe filter, and subsequently extruded into acid-cleaned plastic syringes attached to the bottom of the squeezer assembly. Salinity was measured immediately after pore water recovery using an optical hand-held refractometer. High-precision Cl concentrations were determined within 48 hours after recovery by Mohr titration with silver nitrate (Gieskes et al., 1991). Quantification was based on

comparison with International Association of the Physical Sciences of the Ocean (IAPSO) standard seawater, and reported sample concentrations are based on duplicate analyses (Supp. Table 1). The precision of the Cl data based on repeated analysis of the IAPSO standard over the expedition was $\leq 0.2\%$.

Immediately after pore water collection, $\text{Cd}(\text{NO}_3)_2$ was added to sub-samples for shipboard determinations of sulfate concentrations to precipitate any sulfide in solution that could be oxidized to sulfate prior to analysis. Sulfate and bromide concentrations were determined by manual injection into a Metrohm 761 ion chromatograph. Based on repeated analysis of IAPSO standards, the precision of the SO_4 analyses was $< 0.3\%$ and the precision of the Br analyses was $\leq 1.5\%$ (Collett et al., 2008). Sample pH was determined with an ion selective electrode, and alkalinity was determined soon after sample collection (< 1 hr) by Gran titration with a Metrohm autotitrator (Gieskes et al., 1991). Accuracy and precision were monitored by repeated analysis of IAPSO standard seawater as well as 10, 20, and 40 mM sodium bicarbonate and sodium carbonate standards. The average precision and accuracy of the alkalinity analyses was $\sim 1\%$ and $< 2\%$, respectively.

Sub-samples for shore-based chemical analyses were immediately stored in containers and treated with preservatives appropriate for the specific analysis. Dissolved inorganic carbon (DIC) concentrations were determined on a Marianda AIRICA DIC analyzer that uses a high precision pump to deliver 1 ml of sample into a stripper. The DIC is liberated after acidification with HCl and transferred to a LICOR Model 7000 non-dispersive IR analyzer. The primary laboratory standard for the DIC analyses was Batch 94 certified reference material obtained from the laboratory of Andrew Dickson at Scripps Institution of Oceanography ($\text{DIC} = 2015.92 \pm 0.85$ mmol/kg). The standard was analyzed at least three times at the start of a batch of analyses and after every fifth sample during the batch. The analytical precision based on repeated analysis of the certified standard was $\leq 1\%$.

Ammonium was determined spectrophotometrically based on the method by Solórzano (1969) on a Shimadzu UV mini 1240 spectrophotometer with an analytical precision $< 2\%$. Dissolved silica concentrations were determined on a Thermoscientific Genesys 10s Vis spectrophotometer using the colorimetric method described in Gieskes et al. (1991). The precision and accuracy of the dissolved silica determinations based on repeated analysis of in-house standards was $< 1\%$ and $< 1.5\%$, respectively.

Concentrations of major and minor elements (Na, K, Ca, Mg, Sr, B, Mn, and Fe) were determined on a Perkin Elmer Optima 3000 DVP ICP-OES. Standard curves for the major element analyses were prepared from IAPSO standard seawater, and standard curves for the minor element analyses were prepared from Spex CertiPrep certified reference standards. Analytical precision based on repeated analysis of drift and check standards were: Na <2%, K <1.5%, Ca <0.5%, Mg <0.5%, Sr <1%, B <0.8%, Mn <0.8%, and Fe <1.5%. Average accuracy of the major and minor element determinations by ICP-OES was monitored by replicate analysis of a series of check standards and was: Na <2%, K <1.5%, Ca <1%, Mg <1.5%, Sr <2%, B <1%, Mn <1%, and Fe <2%. Lithium and rubidium concentrations were determined on a Thermoquest Finnigan Element 2 ICP-MS. Standard curves for each element were prepared from Spex CertiPrep certified reference standards, and analytical precision and accuracy were monitored by repeated analysis of check and drift standards. Analytical precision of the Li and Rb analyses were <0.5% and <0.8%, respectively. Analytical accuracy of the Li and Rb analyses were <0.7% and <1%, respectively.

Measurements of pore water $\delta^{18}\text{O}$ and δD were made in the Light Stable Isotope Mass Spectrometry Laboratory at the University of Florida. All values are reported in per mil (‰) relative to the Vienna Standard Mean Ocean Water (VSMOW) standard. The average 2σ error of the $\delta^{18}\text{O}$ and δD analyses are $\pm 0.03\text{‰}$ and $\pm 0.3\text{‰}$, respectively. Unfortunately, due to problems with sample storage, $\delta^{13}\text{C}$ -DIC was only analyzed for select samples at Sites 3 and 10. The $\delta^{13}\text{C}$ -DIC analyses of these samples were made on a Thermofinnigan DeltaPlus stable isotope mass spectrometer at SIO with an average percent precision of $\sim 1.5\%$. All values are reported in per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB) standard. Sr isotope ratios were measured by thermal ionization mass spectrometry (TIMS) at SIO and by multi-collector ICP-mass spectrometry (MC-ICP-MS) at Oregon State University. The 2σ errors in the Sr isotope ratios measured by TIMS at SIO were ± 0.000020 , and the average 2σ errors of the Sr isotope determinations made by MC-ICP-MS at OSU were ± 0.000051 .

3.3. Contamination Correction

Below the sulfate-methane transition zone (SMTZ), we assume sulfate is depleted in the pore fluids and any sulfate present in a sample is a result of contamination with surface seawater that is pumped down the hole during coring. Surface seawater is not circulated during APC

coring, hence APC cores are typically not contaminated, however seawater circulation during XCB coring has the potential to infiltrate cores. Though the XCB whole-rounds were thoroughly shaved in the shipboard geochemistry laboratory prior to squeezing, some samples collected at each site were slightly contaminated with surface seawater. Based on the sulfate concentration of each IW sample, we used the chemical composition of surface seawater to correct each analyte for contamination following the method described in Harris et al. (2013). All the data presented in Supplementary Table 1 have been corrected for seawater contamination during drilling.

3.4. Calculation of Gas Hydrate Saturations, S_h

When gas hydrates dissociate during core recovery, freshwater is released and pore water Cl concentrations are lowered in gas hydrate-bearing horizons in comparison to *in situ* background pore water. Since Cl behaves conservatively at the temperatures at the study sites (i.e. it is an ideal monitor of the addition or uptake of H_2O), the decrease in Cl concentrations relative to the background value is proportional to the amount of gas hydrate that was present. Thus, in order to use the negative chloride anomalies as a quantitative tracer of *in situ* gas hydrate concentrations, the baseline *in situ* Cl concentration profile needs to be known (e.g. Ussler and Paul, 2001; Torres et al., 2004; Malinverno et al., 2008). This estimation technique assumes that any local deviation from the background Cl concentration profile driven by H_2O production or consumption (e.g. gas hydrate formation and dissociation, authigenic clay formation) will be smoothed-out by diffusion and will be undetectable within a few tens of thousands of years (e.g. Ussler and Paull, 2001). At some sites, however, gas hydrate and potentially authigenic clays may form faster than diffusion can smooth the Cl profile leading to local zones with background Cl values that are greater than the general background profile. In these horizons, the background profile was modified to envelope the maximum Cl values, which only allows for a minimum estimate of gas hydrate saturation as it is not possible to determine if gas hydrate was present in these zones from the Cl profiles. Furthermore, the track-line IR scans were used to guide the samples that were used to construct the baseline Cl profile (Supp. Fig. 1).

Gas hydrate concentrations were calculated assuming that the gas hydrates are Structure I hydrates. The discrete negative Cl anomalies were then used to estimate a gas hydrate saturation value, S_h :

$$S_h = [\alpha(C_b - C)]/[C + \alpha(C_b - C)] \quad (1)$$

where C_b is the *in situ* background pore water Cl concentration adjacent to the Cl anomaly, C is the Cl concentration measured in the core sample after gas hydrate dissociation, and α is a dimensionless constant that quantifies the density change from gas hydrate to water due to dissociation and equals 1.257. Malinverno et al. (2008) showed that by propagating uncertainties associated with these parameters, the typical uncertainty in estimating S_h from the Cl concentrations is $\pm 1.5\%$.

4. Results

4.1. Tracers of Gas Hydrate Distribution and Concentration – Cl, $\delta^{18}O$, and δD

Based on the dissolved Cl concentration, $\delta^{18}O$ and δD profiles, and catwalk infrared images, gas hydrate was present at all 10 sites cored in the Krishna-Godavari basin (Figures 2-7). The depth distribution, mode of occurrence, and concentration of gas hydrate, however, varies from site to site. The gas hydrate distribution in the K-G basin can be split into three general groups: 1) disseminated gas hydrate with discrete intervals of elevated concentrations (Sites 3, 7, 14, and 16), 2) sites with thick intervals of disseminated gas hydrate at moderate concentrations (Sites 5 and 20), and 3) sites that contain high concentrations of gas hydrate associated with high-angle fractures in clay-dominated sediments (Site 10, Supp. Fig. 2) or along coarser-grained sediment horizons (Site 15, Supp. Fig. 1).

In general, $\delta^{18}O$ decreases with depth while δD increases at all sites except for Site 10. Positive excursions in $\delta^{18}O$ and δD from the background downhole trends are correlated with depletions in pore water Cl concentrations at Site 10, and corroborate gas hydrate dissociation during core recovery within these depth intervals (Fig. 5).

Background Cl concentrations are significantly elevated above modern seawater value (Cl = 559 mM) over a vertical distance of ~50-100 m at Sites 5, 7, 10, and 16. At Site 5, Cl concentrations increase from 559 mM at 27 mbsf to 576 mM at 40 mbsf (~3% greater than seawater value; Fig. 8). Cl concentrations remain elevated above modern seawater value to a depth of ~80 mbsf. At Site 7, Cl concentrations increase from a value of 558 mM at 29 mbsf to 564 mM at 72 mbsf (Fig. 4). Cl concentrations remain elevated above modern seawater value to ~150 mbsf (Fig. 8). At Site 10, background Cl concentrations increase above modern seawater

value at ~18 mbsf and remain elevated to ~130 mbsf with a concentration maximum of 663 mM at 80 mbsf (19% greater than seawater value, Fig. 5).

Minor increases in sedimentary pore water Cl concentration of ~2.5% have been observed in diffusive settings and attributed to increases in global ocean salinity during the last glacial maximum (e.g. McDuff, 1985; Adkins and Schrag, 2001). The extremely elevated Cl at Site 10 over a depth range of ~115 m precludes trapped glacial seawater as the source of the elevated salinity below the sulfate-methane transition zone (SMTZ). The broad zones of elevated Cl concentrations below the SMTZ at Sites 5, 7, and 16 that extend up to 80 m are also inconsistent with trapped glacial seawater as the source. In order for these enrichments above seawater concentration to be maintained over time requires continuous uptake of H₂O in mineral phases. These zones are likely the result of active or recent formation of gas hydrate (e.g. Haeckel et al., 2004; Torres et al., 2004; Torres et al., 2011) and/or formation of authigenic clay minerals.

4.2. Tracers of Carbon and Sulfur Cycling – SO₄, Alkalinity, DIC, Ca, Mg, $\delta^{13}\text{C}$ -DIC

Dissolved sulfate is one of the most abundant electron acceptors available for microbially-mediated oxidation of organic matter in continental margin sediments. Sulfate is supplied from the burial of or diffusion from overlying seawater or from the re-oxidation of sulfide. Electrons for the reduction of sulfate are ultimately supplied by oxidation of sedimentary organic matter (particulate organic carbon-sulfate reduction, POCSR), methane (anaerobic oxidation of methane, AOM), or other petroleum hydrocarbons. The principle sequence of net reactions within and above the SMTZ generally is:

Dissolved inorganic carbon (DIC) and alkalinity are roughly equivalent above the SMTZ as a result of consumption of HS⁻ in Fe-sulfide minerals. Although alkalinity production through POCSR and AOM drives authigenic carbonate formation within the sulfate reduction zone,

authigenic carbonate precipitation can occur throughout the sediment column (as discussed later).

Below the SMTZ, methane is produced through coupled microbial fermentation and methanogenesis following the net reaction:

Thus, one mole of CO₂ is produced for every mole of CH₄ in marine methanogenic sediments assuming that carbohydrates are metabolized (the molar ratio of CO₂/CH₄ will vary slightly if proteins and lipids are metabolized). This is observed as an increase in DIC concentrations. Total alkalinity below the SMTZ, however, is only produced through carbonate mineral dissolution, Fe reduction, and silicate weathering.

Sulfate concentration-depth profiles at Sites 5, 7, 10, 14, and 15 are S-shaped, characterized by a rapid decrease in SO₄ concentrations in the upper ~5 m of the sediment column followed by relatively constant concentrations or a shallow gradient to ~15-30 mbsf (Fig. 3-7). Below this depth, SO₄ decreases sharply reaching depletion at depths that range from 18 to 36 mbsf. The S-shaped sulfate profile at Site 15 is the most distinct where concentrations decrease from 8.3 mM just below the seafloor to near depletion at 8.9 mbsf, then increase to 13.3 mM at 20.5 mbsf and decrease to depletion at 31.5 mbsf (Fig. 7). These profiles clearly indicate that sedimentation at most of the sites cored in the K-G basin is not at steady-state, and the S-shaped profiles are likely the effect of recent mass transport deposits (MTDs). Additionally, this sediment deposition must be recent enough that molecular diffusion has not smoothed the dissolved sulfate distribution between the two sulfate reduction zones (Hong et al., this issue).

Furthermore, there are also large variations in the SMTZ depth at a single site. The SMTZ depth in Hole 5C was 24 mbsf, whereas the SMTZ depth at nearby Hole 5D was 11.5 mbsf (Fig. 3). This large change in SMTZ depth over a very short distance highlights the dynamic nature of sedimentation on the continental slope of the K-G basin. As a result of the recent MTDs, extending from Site 5 to Site 7 (over 90 km distance, Fig. 1) and subsequent non-steady state sulfate reduction profiles, the SMTZ depths are deeper than other continental margin sites harboring gas hydrate deposits (e.g. Hong et al., 2013; Riedel et al., 2006; Trehu et al., 2003).

Alkalinity is biologically produced through POCSR (Eq. 2), AOM (Eq. 3), and Fe-reduction in the upper sediment column. In general, the alkalinity profiles from the seafloor to the SMTZ are a mirror image of the sulfate profiles (Fig. 2-7). At the sites influenced by mass transport deposits, alkalinity exhibits a maximum within the first sulfate reduction zone and a second, higher concentration maximum at the SMTZ. As a result of authigenic carbonate precipitation driven by alkalinity production within the sulfate reduction zone, Ca and Mg concentrations decrease from seawater values at the seafloor to local minimum concentrations near the SMTZ (Eq. 4), which also drives down the concentration of alkalinity observed within this interval. Below the SMTZ, Ca and Mg concentration profiles vary from site to site.

Site 3 is the only site without an S-shaped sulfate profile (Fig. 2). At Site 3, SO_4 decreases linearly from 21 mM near the seafloor to depletion at 9.9 mbsf. Despite the shallow SMTZ depth, the $\delta^{13}\text{C}$ -DIC at the SMTZ is -17.61‰. In contrast, the $\delta^{13}\text{C}$ -DIC at the SMTZ at Site 10 is -45.7‰, clearly highlighting the importance of AOM in sulfate reduction at this site. At Sites 3, 5, 7, and 10, alkalinity decreases below the SMTZ reaching values less than 10 mM at depths between 90 and 130 mbsf (Fig. 2-5). Pore water $\delta^{13}\text{C}$ -DIC at Site 3 increases with depth below the SMTZ reaching 8.89‰ at 175 mbsf. Pore water $\delta^{13}\text{C}$ -DIC increases much more sharply at Site 10 reaching 11.69‰ at 37 mbsf below which it remains relatively constant. The increase in $\delta^{13}\text{C}$ -DIC below the SMTZ at these sites is consistent with microbial methane production through CO_2 -reduction (e.g. Torres and Kastner, 2009; Hong et al., 2013).

The downhole concentrations of alkalinity and DIC are virtually equivalent at each site, such that all samples plot along a 1:1 line on a cross-plot of DIC versus alkalinity (Fig. 2-7). Below the minima in alkalinity at Sites 3, 5, and 7, alkalinity increases sharply reaching values up to 50 mM below ~120 mbsf. These large alkalinity increases suggest a deeper zone of intense alkalinity production at these sites with no concomitant increases in Ca concentrations (Fig. 2-4), but rather net Ca consumption reflecting authigenic carbonate precipitation that sequesters some of the alkalinity within these zones.

The observation of equivalent DIC and alkalinity concentrations within the zone of active methanogenesis strongly suggests that metabolic CO_2 is effectively neutralized in the sediment column through silicate weathering. Furthermore, methane concentrations in pressure core samples are near Structure I gas hydrate saturation at all sites or exceed solubility with CH_4 concentrations at Sites 5 and 10 reaching several hundred millimolar (Fig. 8) while CO_2

concentrations are orders of magnitude lower (Collett et al., 2008). Considering DIC is produced through POCSR and AOM in the upper 30 m of the sediment column, DIC concentrations within the GHSZ should be greater than CH_4 concentrations, as the inventory includes the HCO_3^- produced in the SRZ and the DIC produced through methanogenesis (Equation 5). In contrast to this expectation, DIC concentrations are well below CH_4 concentrations as well as Structure I gas hydrate solubility at all the sites cored. Furthermore, dissolved Ca concentrations remain below seawater value and are variable with depth at each site. Thus, there is a substantial DIC-deficit driven by coupled silicate weathering and authigenic carbonate precipitation occurs within the GHSZ at all the sites cored (see Section 5.4).

4.3. Non-Carbon Tracers of Organic Matter Degradation – NH_4 and Br

Dissolved NH_4 is released to the pore water during organic matter degradation. During the early diagenesis of organic matter, dissolved Br is also released to the pore water through organohalogen respiration, fermentation, or spontaneous dehalogenation (Dolfing, 2003; Martin et al., 1993; Mohn and Tiedje, 1992; von Breymann et al., 1990). At all the sites cored except Site 3, NH_4 concentrations increase abruptly from seawater value near the sediment-water interface to an interval where the concentration gradients are minimal (typically extending from ~5-10 mbsf to the SMTZ), followed by a pronounced increase at the base of the SMTZ (Fig. 3-7). Site 3 is the only site that does not appear to be affected by recent, abrupt sedimentation associated with MTDs (Hong et al., this issue). At this site, NH_4 concentrations are more typical of profiles in continental margin sediments, and increase almost linearly from near the sediment-water interface through the SMTZ to ~30 mbsf. Below this depth, the NH_4 concentrations increase more gradually to a maximum of 6.9 mM at 81.8 mbsf. The NH_4 profiles at all sites have an inflection point between ~40-90 mbsf.

At Sites 3, 10, and 14, NH_4 concentrations are relatively constant below the inflection point, whereas they decrease slightly with depth below the inflection point at Site 15 (Fig. 7). At Sites 5 and 7 there is a deeper zone of NH_4 production below the inflection point (Fig. 3-4). The deeper zone of NH_4 production at Site 5 begins at ~125 mbsf and extends to the base of the hole with concentrations reaching 12 mM. At Site 7, the deeper NH_4 production begins at ~130 mbsf and ammonium concentrations increase to 12.8 mM at the last depth ammonium was measured

at this site (200 mbsf). These deeper intervals of NH_4 production are directly correlated with the zones of alkalinity production discussed previously, and suggests enhanced organic matter degradation that is related to the intense alkalinity production below ~120 mbsf at these sites (further discussed in Section 5.4).

Br concentration profiles are similar to the NH_4 profiles and can be separated into three distinct zones in the upper sediment column. Within the sulfate reduction zone, Br concentrations increase slowly with depth relative to the underlying methanogenic zone, where Br concentrations increase relatively quickly until an inflection point in the profiles also at ~40-90 mbsf as in the NH_4 profiles. Below the inflection point, Br concentrations are either constant (Sites 5 and 7) or increase slowly with depth (Sites 3, 10, 14, and 15). The primary control on the Br and NH_4 profiles in the first zone appears to be recent sedimentation associated with MTDs, which also exert a first-order control on the dissolved sulfate profiles.

4.4. Tracers of Fluid-Rock Reactions – K, Rb, Li, Si, B, Ca, Mg, Sr, $^{87}\text{Sr}/^{86}\text{Sr}$

Dissolved K, Rb, and B concentrations are at or above seawater value in the upper 10 m of the sediment column except at Site 15. The K, Rb, and B profiles are all concave-down with a relatively slow decline in concentrations in the upper 20-40 mbsf followed by a sharp decrease in concentrations then relatively constant values below ~50-90 mbsf. K, Rb, and B concentrations at Site 15 are low near the sediment-water interface with a slight decrease to 8.9 mbsf, then increase to near seawater values (greater than seawater for B) at 25 mbsf followed by a sharp decrease in concentrations similar to the other sites. Li concentrations are low at 4-20 μM (~15 to 77% of seawater value) in the upper 5-10 mbsf at Sites 5, 7, 10, and 15. Li then increases to a concentration maximum of near seawater value or greater between 5-20 mbsf, then decrease sharply and remain relatively constant at values less than 10 μM below 40-60 mbsf.

Dissolved Si concentrations are variable with depth and range from ~50-600 μM . In general, dissolved Sr profiles are similar to the pore water Ca and Mg profiles at each site. Pore water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary from site to site and are presented in Figures 2-7. Pore water $^{87}\text{Sr}/^{86}\text{Sr}$ is an important tracer of fluid source and fluid-rock interaction, and is discussed in more detail in Section 5.

5. Discussion

5.1. Gas Hydrate Distribution and Saturations

The pore water geochemical results, together with the core IR images and methane volumes recovered from pressure cores (Collett et al., 2008), are consistent with gas hydrate being present at each of the sites cored in the K-G basin. However, the gas hydrate depth distribution, mode of occurrence, and concentration vary across the basin (Fig. 8). The region within the gas hydrate stability zone where gas hydrates are actually observed is often referred to as the gas hydrate occurrence zone (GHOZ). Typically, the GHOZ is tens of meters deeper than the SMTZ. Over time, the dissolved methane in the pore water increases and sedimentation at the seafloor continues, effectively burying pore water, sediment, and organic matter deeper in the gas hydrate stability zone. Where the amount of methane exceeds methane hydrate solubility, gas hydrate precipitates (Fig. 9) – the first occurrence of gas hydrate is at the depth where pore water methane concentration at least equals methane hydrate solubility. Models of methanogenesis in marine sediments typically assume the highest rates of methane production occur just below the SMTZ and rates decrease quasi-exponentially with depth parameterized with an age-dependent rate constant for organic matter degradation (e.g. Middleburg et al., 1989; Wallmann et al., 2006). These models predict the highest concentrations of gas hydrate to occur near the base of the gas hydrate stability zone with the depth of the first occurrence of gas hydrate dependent on the rate of methanogenesis, the concentration of metabolizable organic matter, sedimentation rate, and compaction (e.g. Davie and Buffett, 2001; Egeberg and Dickens, 1999; Malinverno, 2011; Wallmann et al., 2006). Though Site 5 follows this general trend (Fig. 8), the other sites in the K-G basin have a wide distribution of gas hydrate with concentration maxima occurring well within the gas hydrate stability zone (Sites 3, 7, 14, 15, and 16) or throughout the gas hydrate stability zone (Site 10).

The range in gas hydrate saturation based on the dissolved Cl profiles, as well as the depth-integrated average S_h at each site are presented in Table 2. The depth of the first occurrence of gas hydrate ranges from ~23 mbsf at Site 10 to 72 mbsf at Site 7, and gas hydrate saturation across the sites cored in the K-G basin ranges from 0.8% to 68%. Sites 10 and 15 have the highest average S_h , with values of 16% and 8.9%, respectively. At the other sites in the K-G basin, average S_h is less than 5%. In general, our estimates of the GHOZ and trends in S_h are similar to those based on downhole electrical resistivity logs that show gas hydrate saturations are typically less than 5% (Shankar and Riedel, 2011). The two methods, however, do not totally

agree, with intervals containing CI anomalies dictating gas hydrate is present where gas hydrate is not apparent in the resistivity data, and vice versa. There are several reasons for the discrepancies between the two datasets: 1) the spatial coverage of pore water sampling is scattered compared to the continuous downhole resistivity measurements; 2) some of the pore water samples specifically targeted IR anomalies where gas hydrate was present which tends to skew the average S_h towards higher values; 3) heterogeneous gas hydrate distribution between the hole drilled during logging and that drilled during coring (typically the holes are separated by several meters to 10s of meters); and 4) differences associated with the anisotropic nature of the reservoir, particularly fractured reservoirs like at Sites 5 and 10 affect resistivity-based estimates (e.g. Cook and Goldberg, 2008; Lee and Collett, 2009).

Methane $\delta^{13}\text{C}$ values suggest a predominantly microbial source at all of the sites cored with values ranging from -61 to -71‰ with C_{3+} hydrocarbons below detection limit (Lorenson et al., this issue). Reliable methane concentration measurements are difficult since most of the dissolved methane is lost from the pore water during core recovery due to the formation of gas voids during depressurization. Fortunately, several pressure cores were collected at each site during NGHP Expedition 01 (Collett et al., 2008), which provide relatively reliable estimates of *in situ* methane concentrations at discrete (1 m) depth intervals within the sediment column (Fig. 8). Pressure core methane concentrations are similar at Sites 3, 7, 14, 15, and 16. At these sites, methane is generally at Structure I gas hydrate saturation or slightly above or below solubility. The low methane concentrations and S_h values at these sites suggest the gas hydrate is likely microbially produced *in situ* within the gas hydrate stability zone.

Methane concentrations measured from pressure core samples at Site 5, however, are elevated in comparison to these sites with values up to 678 mM in an isolated interval between ~75-85 mbsf (Fig. 8). Note that the pressure core methane concentrations in Figure 8 are after depressurization and include methane stored in gas hydrate. Thus, concentrations above methane hydrate solubility reflect the methane that is sequestered in gas hydrate *in situ*. Saturations up to 40% were observed within this interval in the resistivity logs (Shankar and Riedel, 2011). This interval coincides with an isolated zone of gas hydrate-filled fractures that extend from ~60-91 mbsf (Cook and Goldberg, 2008). These fractures occur within three holes drilled at Site 5, and detailed statistical analyses show that the fracture planes in these holes are not correlated, but rather are produced locally and only extend a few meters from the respective borehole (Cook and

Goldberg, 2008). The pressure core and logging results suggest enhanced rates of microbial methanogenesis has supplied enough gas *in situ* to generate the hydrate-filled fractures within this isolated interval. This hypothesis is corroborated by the pore water geochemical data as there is no indication of lateral or vertical fluid migration within this depth interval or below.

Methane concentrations from pressure cores at Site 10 are extremely high compared to the other sites ranging from 221 to 1951 mM within the GHSZ. These concentrations are an order of magnitude greater than at the other sites and, combined with the elevated gas hydrate saturations throughout the hole and the occurrence of gas hydrate in high-angle fractures (Supp. Fig. 2), clearly indicate that this is an advective system with methane being supplied from a deeper microbial source. Based on 3-D seismic data, Riedel et al. (2010) confirmed the association of gas hydrate with fractures and conclude that the distribution and occurrence of gas hydrate at Site 10 is the result of a combination of tectonic fault/fracture orientations and the abundance of free gas, which migrated from a deeper source.

Typically, the rate of *in situ* gas hydrate formation is slower than rates of diffusion for the excluded ions. Thus, over time, the chloride of the adjacent pore water does not greatly exceed the chloride above and below the zone of hydrate formation. If, however, the rate of gas hydrate formation exceeds the rate of diffusion (or mixing with other fluids), elevated pore water Cl concentrations will be observed (e.g. Torres et al., 2011). At Site 10, Cl concentrations measured in samples without IR anomalies (assumed to represent background concentrations) increase above modern seawater value immediately below the SMTZ at ~20 mbsf and remain elevated to ~130 mbsf with background concentrations ranging from 566-663 mM (Fig. 5). Pore water Cl concentrations of ~800 mM were sampled in shallow sediments (1.2 mbsf) at southern Hydrate Ridge and were attributed to elevated rates of gas hydrate formation driven by high fluid flow rates (45-300 cm/yr) and transport of methane as a free gas (Haeckel et al., 2004; Torres et al., 2004). Similar to Hydrate Ridge, in order to sustain active gas hydrate formation at Site 10 over time requires a considerable and relatively constant supply of CH₄ within the interval immediately below the SMTZ, a methane supply that is much greater than can be produced *in situ*. The slightly elevated Cl concentrations at Sites 5, 7, and 16 are likely not the result of active gas hydrate formation, as these intervals are either above the GHOSZ or are in intervals with very low gas hydrate saturations, necessitating another mechanism for H₂O uptake to increase pore water Cl concentrations (Fig. 8). As will be discussed in Section 5.4, the elevated Cl at these

sites likely reflects intervals of active formation of authigenic clay minerals related to silicate weathering.

Based on 3-D seismic reflection data, the fractured system around Site 10 extends over a triangular-shaped area of $\sim 2.5 \text{ km}^2$ (Riedel et al., 2010). This area is bound by two normal faults that act as migration conduits. Deformed sediment associated with these faults likely provides a migration pathway for free gas sourced at greater depths in the sediment column to enter the gas hydrate stability field. Both NGHP coring and previous piston coring programs documented the presence of a buried paleo-chemosynthetic community at ~ 16 mbsf, including clam shell-debris and large tube- and chimney-shaped carbonate concretions (Collett et al., 2008; Mazmudar et al., 2009; Teichert et al., this issue). The $\delta^{13}\text{C}$ of carbonate material ranges from -41 to -52‰, indicating the carbonate was derived from oxidized biogenic methane and precipitation was driven by alkalinity produced by AOM (Mazmudar et al., 2009). Thus, this was a paleo-cold seep site with active methane venting at the seafloor. The age of the paleo-chemosynthetic community is between 40 and 58 ka based on sediment ^{14}C ages and U-Th ages of the recovered carbonate material (Mazmudar et al., 2009; Teichert et al., this issue), and suggest that methane venting to the seafloor was likely ongoing to at least 40 ka. The entire area around Site 10 is dominated by a succession of MTDs or debris flows. The depth of the topmost MTD was identified in a high-resolution, single-channel seismic line at ~ 16 mbsf (Riedel et al., 2010), coincident with the depth of the paleo-chemosynthetic community. These results suggest that the fault/fracture system provided a conduit for free gas migration that enabled gas venting at the seafloor and led to massive gas hydrate formation along high-angle fractures. The rapid increase in pore water Cl and the presence of gas hydrates just ~ 4 m below the paleo-chemosynthetic community suggests that massive gas hydrate deposits occurred very close to the seafloor prior to burial by MTDs. After this recent rapid sediment deposition, methane seepage at the seafloor ceased.

The background Cl concentrations at Site 10 are lower than at other regions where active gas hydrate formation sustained by advection of free gas within the GHSZ has been inferred. These locations include Hydrate Ridge (Site 1249, Cl ~ 900 mM; Trehu et al., 2004), Site U1328 offshore Vancouver Island (Cl > 750 mM; Riedel et al., 2006), and Site UBGH 2-3 in the Ulleung Basin (Cl > 1400 mM; Kim et al., 2003). Without detailed pore water modeling, it is not possible to determine whether the lower Cl concentrations at Site 10 in comparison to these other

locations are the result of slower rates of gas hydrate formation or whether gas hydrate formation has ceased at this site as a result of the fault/fracture system being sealed or “clogged” by hydrate and the Cl anomaly has decreased due to diffusion. It is possible that gas transport through the fault/fracture system continues at present forming gas hydrate at modest rates, this gas is currently trapped below the MTDs, and venting at the seafloor has yet to be re-established.

Throughout Site 15, S_h within the GHOS is less than 5%, except for an isolated interval between ~70-90 mbsf where gas hydrate saturations exceed 67%. The gas hydrate within this interval occurs within layers of fine sand separated by clay (Supp Fig. 1). Numerous other silt/sand layers and laminae were encountered at this site, however, massive gas hydrates were only observed within this interval. In fact, silt and sand horizons occur at the majority of the sites cored in the K-G basin, yet relatively little gas hydrate was observed within these layers. Within the gas hydrate-bearing zone at Site 15, ammonium concentrations abruptly increase from 2.9 mM to 10.6 mM, and the pore water $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases from seawater value (~0.7092) to a radiogenic value of 0.709471 (Fig. 7). This is the highest $^{87}\text{Sr}/^{86}\text{Sr}$ measured across all the sites cored in the K-G basin, and the sharpness of the peak strongly suggests lateral flow of an “exotic” fluid within the gas hydrate-bearing interval that likely originated from a deeper source. This interbedded sand/clay interval is linked to a prominent seismic reflection observed in the 3-D seismic data (Riedel et al., 2011) that was mapped over an area of about 1 km² south of Site 15, and is bound by a fault at its northern limit. This fault is likely the migration conduit for the methane-rich, deeper-sourced fluid with more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$. It is likely that fluids migrate along the fault conduit then flow laterally along the sand horizon and charge the sand-rich interval within the gas hydrate stability zone, leading to the elevated S_h in this horizon.

5.2. Mass Transport Deposits and Non-Steady State Pore Water Profiles

The buried paleo-cold seep chemosynthetic community and deep SMTZ, especially for an area containing high concentrations of shallow gas hydrate, at Site 10 illustrates the impact MTDs can have on the gas hydrate system and shallow pore water solute profiles. High-resolution seismic records and bathymetry show widespread evidence of slumping and sliding on the upper to mid-slope sediments directly upslope of Site 3 (Ramprasad et al., 2011). These MTDs exhibit widths of 3-9.5 km and extend 10-13 km offshore with an average thickness of ~45 m (Ramprasad et al., 2011). Surprisingly, Site 3 is the only site cored in the K-G basin that

does not exhibit non-steady state solute profiles in the upper sediment column (Fig. 2). All other sites with high-resolution geochemical profiles (5, 7, 10, 14, and 15) are not in steady state. They are characterized by an S-shaped sulfate profile in the upper ~35 m of the sediment column, and concomitant Z-shaped alkalinity profiles.

At all the sites cored, except Site 3, NH_4 concentrations increase abruptly from seawater value near the sediment-water interface to an interval where the concentrations remain relatively constant (typically extending from ~5-10 mbsf to the SMTZ), followed by a pronounced increase at the base of the SMTZ. Dissolved Br concentrations are either constant at seawater value (0.86 mM) or increase slightly within the sulfate reduction zone, then increase sharply below the SMTZ. Both NH_4 and Br are released during POCSR but not during AOM, thus the rate of ammonium and bromide production are typically the highest where POCSR dominates, decreases where AOM is occurring, then increase within the underlying methanogenic zone. The shapes of the NH_4 and Br profiles are consistent with rapid deposition by an MTD where there is modest production in the upper sulfate reduction zone, and relatively constant concentrations until the SMTZ. The profiles suggest that burial was too fast and recent for diffusional gradients to be established from the zone of metabolite accumulation (below the SMTZ) to the sediment-water interface causing the kink in the profiles at the SMTZ.

Numerical simulations of the non-steady state pore water SO_4 and NH_4 profiles confirm that MTDs are responsible for their shapes and show that the most recent MTDs at these sites range from 8-25 m in thickness and are 300-1600 years old (Hong et al., this issue). This highlights the importance of considering non-steady state sedimentation when interpreting pore water profiles at the K-G basin sites, especially for those solutes that are the most sensitive to the early diagenesis of organic matter (e.g. SO_4 , NH_4 , Br, alkalinity, DIC, Ca, and Mg).

5.3. Organic Matter Degradation and Methanogenesis

Nitrogen is released as NH_4 during diagenesis of organic matter in anoxic marine sediments, resulting in an increase with depth. Below the SMTZ, NH_4 is released by fermentation reactions associated with methanogenesis (Equation 5). Above the SMTZ, NH_4 concentrations are anomalously low due to recent deposition of MTDs at all sites except Site 3. Below the SMTZ, NH_4 concentrations increase sharply to an inflection point in the profiles at depths ranging from ~50-70 mbsf. The interval between the SMTZ and the inflection point

coincides with the region where kinetic models predict the highest rates of microbial methanogenesis (e.g. Davie and Buffett, 2001; 2003; Malinverno, 2011; Wallmann et al., 2006). Indeed, $\delta^{13}\text{C}$ -DIC increases abruptly below the SMTZ reaching relatively constant positive values between ~40-80 mbsf at Sites 3 and 10 (Fig. 2, 5), suggesting methane production through CO_2 reduction within this interval.

Numerical reaction-transport modeling of the S-shaped sulfate profiles at each site suggests apparent sedimentation rates of 8-56 m/kyr in the upper ~8-25 m of the sediment column (Hong et al., this issue). Likewise, radiocarbon dating of sediments retrieved from Calypso piston cores near Site 10 show multiple MTDs in the upper 30 m of the sediment column, with estimated sedimentation rates up to 7.48 m/kyr (Mazmudar et al., 2012). Based on the sediment radiocarbon ages, average sedimentation rates in the upper 30 m of the sediment column range from 0.4 to 6.3 m/kyr (Mazmudar et al., 2012). The sedimentation rates in the upper sediment column at the K-G basin sites are 1-2 orders of magnitude faster than typical continental slope rates of ~0.1 to 0.5 m/kyr. The dynamic nature of sedimentation and high deposition rates in the K-G basin greatly decreases the amount of time POC spends in the sulfate reduction zone and enhances delivery of labile POC to the methanogenic zone likely allowing for high rates of NH_4 and CH_4 production.

Kinetic models of microbial methanogenesis at other margins with lower, steady-state sedimentation rates predict maximum methane hydrate saturations of ~1% or lower (e.g. Davie and Buffett, 2003; Wallmann et al., 2006) and invoke fluid advection or gas transport to explain higher gas hydrate saturations. Alternatively, the elevated saturations of >1% observed in the K-G basin sites with no evidence for fluid advection (Sites 3, 5, 7, and 14) may be the result of higher rates of *in situ* organic matter degradation and methanogenesis related to the high, non-steady state sedimentation rates across the basin.

Below the inflection point, NH_4 concentrations are relatively constant with depth at Sites 3 and 14, and decrease gradually at Site 15. At Sites 5 and 7, however, NH_4 remains relatively constant to ~115-135 mbsf, then increase sharply below this depth to concentrations up to 13 mM. The deeper NH_4 production at Sites 5 and 7 is more pronounced than in the upper methanogenic zone (between the SMTZ and inflection point), indicating rapid organic matter degradation at depths typically assumed to be characterized by low rates of particulate organic carbon turnover and methanogenesis.

Considering the gross instability of the mid to upper continental slope in the K-G basin exemplified by recent MTDs observed at sites across the margin, it is likely that both sedimentation and POC accumulation rates have been variable over time. POC concentration profiles at these sites do not display the conventionally assumed exponential decrease expected for steady-state sedimentation and consumption through POCSR and coupled fermentation/methanogenesis. Rather the POC concentrations are relatively constant with depth with concentrations >1.2% throughout the sediment column with no significant changes in the upper methanogenic zone nor in the deeper zone of intense ammonium production (Johnson et al., this issue). Thus, the system is not carbon-limited below the inflection point, and more importantly periods of high sedimentation rates related to MTDs enhances the delivery of labile POC into methanogenic zone. The pore water data suggests there is enough bioavailable organic matter and substrates to accommodate the enhanced ammonium production below 100 mbsf at Sites 5 and 7. The hydrogen and/or acetate (and other substrates) produced through these fermentation reactions likely fuels methanogenesis and CO₂ production deeper in the sediment column, as indicated by the concomitant increase in DIC within the same depth interval. Furthermore, the highest methane concentrations observed in the pressure cores collected at Site 7 as well as the highest observed gas hydrate saturations occur within this zone (Fig. 9). Likewise, the highest gas hydrate saturations and elevated CH₄ concentrations in pressure cores at Site 5 occur within the zone of intense NH₄ production.

5.4. Silicate Weathering and Pervasive Authigenic Carbonate Precipitation Coupled to Methanogenesis

Metabolic pathways of fermentation and methanogenesis are diverse, however the dominant source of methane documented in continental margin sediments is microbial methane produced through CO₂-reduction (e.g. Claypool et al., 1985; Claypool et al., 2006; Kvenvolden and Kastner, 1990; Pohlman et al., 2009; Whiticar et al., 1995). At steady state, net organic matter fermentation and CO₂-reduction are balanced with equivalent amounts of CO₂ and CH₄ being produced per mole of organic matter degraded (Equation 6).

Carbohydrate Fermentation:

Most reactions between carbonate species in pore water are nearly instantaneous, and chemical equilibria among the species are described by

Methanogenesis produces CH₄ and CO₂ concentrations that reach or exceed methane hydrate saturation at depth (Fig. 8). During CO₂ production at typical initial pore water pH of 7.5 ± 0.5, dissolved CO₃²⁻ is titrated very quickly, pore water pH decreases, and carbonate equilibrium is dominated by Equation 7.

The CO₂ produced through microbial methanogenesis is measured as dissolved inorganic carbon (DIC; Equation 9), and total alkalinity within marine methanogenic sediments can be approximated by Equation 10.

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (9)$$

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [HS^-] + [B(OH)_4^-] - [H^+] \quad (10)$$

Below the SMTZ, HS⁻ is no longer being produced through AOM and concentrations are typically low and controlled by precipitation in Fe-sulfide minerals. Dissolved boron concentrations are also typically low and less than 0.5 mM, and CO₃²⁻ is titrated by continuous CO₂ production. Thus, the two most important species expected to factor into total alkalinity in methanogenic sediments are HCO₃⁻ and H⁺. As a result, charge balance dictates that coupled fermentation and CO₂-reduction has no direct net effect on total alkalinity (Equation 10). Thus, DIC should increase while alkalinity remains constant during balanced fermentation and methanogenesis, and the difference between DIC and alkalinity could be used as a measure of the net CO₂ released during methanogenesis (Fig. 10).

Potential complications arise during core recovery because as ambient pressures decrease and temperature increases, CO₂ can degas when pore water partial pressures are greater than one atmosphere. Based on the core temperatures measured by IR and temperature probe on the catwalk during core sampling (Collett et al., 2008), the *in situ* CO₂ solubility in the pore water, at

one atmosphere, should have ranged from ~33-45 mM (Weiss, 1974). Thus, in intervals where alkalinity is below this concentration range and methanogenesis is occurring, DIC concentrations should be greater than alkalinity reflecting CO₂ production during methanogenesis.

However, in contrast to this expectation, at all depths cored at all sites, the concentrations of DIC and alkalinity are equivalent and indicate neutralization of metabolic CO₂ in the methanogenic zone across the basin. This observation is consistent with CO₂ measurements from pressure cores collected across the basin that show CO₂ concentrations <2 mM at all sites cored (Supp. Table 2). Methane concentrations in paired samples range from 60-1951 mM, thus DIC concentrations should be equally as high or greater, considering DIC is also produced above the SMTZ through POCSR and AOM, further indicating the CO₂ produced through methanogenesis is lost from the system either microbially or inorganically.

The CO₂-deficit could be the result of unbalanced fermentation and CO₂-reduction where the rate of CO₂ produced through fermentation reactions is much less than the rate of CO₂ consumed through CO₂-reduction. Like the DIC concentrations, the $\delta^{13}\text{C}$ of the DIC should also increase as a result of ongoing methanogenesis because of the kinetic isotope effect during CO₂-reduction. The isotope fractionation factor, α , describes the kinetic fractionation between the produced CH₄ and its substrate CO₂ and ranges from ~1.04-1.09 (e.g. Valentine et al., 2004). As a result of POCSR and AOM (Equations 2 and 3), HCO₃⁻ is added to the pore water from the sediment-water interface to the SMTZ, driving up concentrations of both DIC and alkalinity and contributing to $\delta^{13}\text{C}$ -DIC values at the SMTZ that typically range from -21 to -50‰. Below the SMTZ, DIC is produced through fermentation with a $\delta^{13}\text{C}$ of -21 to -25‰. The $\delta^{13}\text{C}$ of this deeper pool of CO₂ progressively increases as a result of continued CO₂-reduction. Indeed, there is a sharp increase in the $\delta^{13}\text{C}$ -DIC below the SMTZ at Sites 3 and 10 as a result of CO₂-reduction (Fig. 2, 5) as is also observed at other continental margin sites (e.g. Torres and Kastner, 2011).

The $\delta^{13}\text{C}$ of the authigenic carbonates recovered from Site 10 are consistent with the $\delta^{13}\text{C}$ -DIC of the pore water and further confirm methanogenesis via CO₂-reduction (Teichert et al., this issue). The $\delta^{13}\text{C}$ of authigenic carbonates range from -50 to -55‰ at the SMTZ and increase to a value of +10‰ from ~40 to 200 mbsf matching the trend observed in the $\delta^{13}\text{C}$ -DIC of the pore water (Fig. 5). The $\delta^{13}\text{C}$ of authigenic carbonates recovered from Site 7 increase from

a value of -40‰ near the SMTZ to ~+15‰ by 200 mbsf (Teichert et al., this issue), also consistent with progressive methane production via CO₂-reduction.

The $\delta^{13}\text{C}$ -DIC values measured along the IODP Exp. 311 transect and at Hydrate Ridge, however, are more enriched than those in the K-G basin pore water and authigenic carbonates ranging from +10 to +32‰ (Torres and Kastner, 2011). Likewise, the $\delta^{13}\text{C}$ of the CO₂ is greater along the Expedition 311 transect ranging from -10 to +25‰ (Pohlman et al., 2009) compared with values ranging from -17 to -7‰ in the K-G basin (Lorenson et al., this issue). Along the IODP Exp. 311 transect both $\delta^{13}\text{C}$ -CH₄ and $\delta^{13}\text{C}$ -CO₂ become more enriched downhole moving upslope from the deformation front (Pohlman et al., 2009). The downhole enrichment of $\delta^{13}\text{C}$ -CH₄ and $\delta^{13}\text{C}$ -CO₂ at the most landward site (Site U1329) is ~40‰, whereas the down hole enrichment in $\delta^{13}\text{C}$ -CH₄ observed in the K-G basin ranges from 5-15‰ (Lorenson et al., this issue). Based on a simple Rayleigh distillation model of the enrichment in $\delta^{13}\text{C}$ -CO₂ and CH₄ with depth at Cascadia, Pohlman et al. (2009) estimate consumption of ~20-52% of the original CO₂ within the methanogenic zone. Quantification of the amount of CO₂ produced through fermentation used for methanogenesis at the K-G basin sites would require non-steady state numerical modeling of both carbon species and their isotopes that take into account alkalinity/DIC production and removal in carbonates, methane production, and diffusion, and is beyond the scope of this paper. However, this simple comparison between the degree of enrichment of the pore water $\delta^{13}\text{C}$ -DIC, $\delta^{13}\text{C}$ -CO₂, and $\delta^{13}\text{C}$ -CH₄ between the K-G basin sites and the Expedition 311 sites indicates that only a fraction of the CO₂ produced through fermentation is consumed through CO₂-reduction.

Thus, the CO₂-deficit in the pore waters at the K-G basin is related to processes other than CO₂-reduction. This process is most clear in the zones of deep methanogenesis at Sites 5 and 7, but is likely operating at all of the sites cored in the K-G basin. As stated above, microbial methanogenesis does not contribute to the total alkalinity, however in the zones of intense NH₄ production at these sites there is also intense alkalinity production coupled to organic matter degradation (Supp. Fig. 3). At Site 5, in the exact same interval as the NH₄ increase, alkalinity abruptly rises from 7.27 mM at 116 mbsf to 51.7 mM at 159 mbsf (Fig. 3). Likewise, at Site 7, alkalinity sharply increases in the same interval as NH₄ from a value of 9.57 mM at 139 mbsf to 45.29 mM at 179 mbsf (Fig. 4). There is also a deep interval of alkalinity production at Site 3 that extends from 150-300 mbsf (Fig. 2), and there is a slow increase in alkalinity with depth at

Site 14 with no change in Ca concentrations (Fig. 6). In the intervals of intense alkalinity production at Sites 3, 5, and 7, Ca concentrations gradually decrease indicating that alkalinity production is not the result of carbonate dissolution. Thus, at these sites, co-occurring authigenic carbonate precipitation related to alkalinity production control dissolved Ca concentrations (Fig. 10c).

It is well known that the incongruent weathering of silicate minerals exposed on the continents consumes atmospheric CO₂ and produces alkalinity, clay minerals, dissolved cations, and dissolved silica, and is the largest sink of CO₂ on geologic timescales (e.g. Berner and Berner, 1996; Wallmann et al., 2001). Aloisi et al. (2004) was the first to propose that CO₂ produced through methanogenesis in anoxic marine sediments results in low pore water pH and can cause silicate minerals to dissolve rapidly. Based on two sediment cores in the Sea of Okhotsk, Wallmann et al. (2008) used a kinetic numerical model to show that alkalinity production below the SMTZ is the result of coupled methanogenesis and silicate weathering. These studies were based on pore water profiles from piston cores that penetrated the shallowest zone of methanogenesis. Our results extend these observations showing that alkalinity production related to ongoing coupled methanogenesis and silicate weathering extends from the SMTZ past the base of the gas hydrate stability zone, up to 200 mbsf at Sites 5 and 7 (Fig. 3-4).

Though clay minerals (smectite, illite, and kaolinite) comprise between ~60-85% of the minerals in the sediments cored in the K-G basin, other silicates, mainly plagioclase and quartz, account for ~5-20% of the mineral assemblage (Phillips et al., this issue), suggesting ample reactive silicates are available for weathering at each site. Considering that Ca concentrations remain elevated throughout the sediment column despite being saturated with respect to authigenic carbonates, weathering of plagioclase feldspars is likely the dominant sink of pore water CO₂ and a source of alkalinity. The coupled reaction can be described as,

where CaAl₂Si₂O₈ is the primary mineral Ca-plagioclase and Al₂Si₂O₅(OH)₄ is the secondary clay kaolinite. The neutralization of 2H⁺ and production of 2HCO₃⁻ leads to equivalent production of alkalinity and DIC.

The formation of kaolinite or other clay minerals through weathering of plagioclase consumes water, which is consistent with the elevated Cl concentrations in the methanogenic zone at Sites 5, 7, and 16 (Fig. 8), the decrease in $\delta^{18}\text{O}$ with depth at Sites 5, 7, 14, and 16, and the increase in δD at these sites. These trends are not the result of gas hydrate dissociation during core recovery, as dissociation releases ^{18}O and deuterium to the pore water and Cl concentrations decrease. Likewise, gas hydrate formation preferentially consumes ^{18}O and causes an increase in dissolved Cl, but also preferentially consumes deuterium leading to a decrease in δD with depth. Authigenic clay formation at low temperatures, however, leads to a decrease in $\delta^{18}\text{O}$ and increase in δD . We acknowledge that other reactive silicates may also be weathered in the sediment column besides plagioclase (e.g. K-feldspar, biotite) that could lead to the formation of different authigenic clay minerals. Equation 11 is just an example of many possible reactions, and other clays such as smectite could be forming, which could act as sinks for the alkali metals and boron. For example, at all of the sites cored there is a marked depletion in pore water concentrations of K, Li, Rb, and B below the SMTZ. Dissolved H_4SiO_4 concentrations remain relatively constant within the methanogenic sediments and are likely controlled by secondary clay formation. The net consumption of these elements at all sites suggests that authigenic hydrous silicate formation in methanogenic sediments can act as an important sink for the alkali metals and boron.

Despite the continuous release of Ca from plagioclase during silicate weathering, Ca concentrations remain below seawater value at all depths. The low Ca concentrations throughout the methanogenic zone indicate that the added alkalinity produced through silicate weathering that does not accumulate in the pore water is removed during CaCO_3 precipitation. Thus, the Ca released during silicate weathering is masked by the coeval precipitation of authigenic carbonates. Similar trends are observed in the Mg and Sr concentrations profiles, consistent with Mg and Sr released during silicate weathering also being controlled by the coeval precipitation of authigenic carbonates. Authigenic carbonate precipitation is likely also acting as a sink for dissolved Fe and Mn, as Fe and Mn-rich carbonates were observed in the methanogenic zone in the sediment column at most sites (Collett et al., 2008). Coupled plagioclase (anorthite-rich) weathering and carbonate precipitation acts as a long-term and important sink for CO_2 released during methanogenesis:

Coupled methanogenesis and silicate weathering is thus a sink of DIC as a result of continuous authigenic carbonate production (Figure 10). The alkalinity not consumed through carbonate precipitation must diffuse upwards providing an additional source of alkalinity to pore waters near the seafloor that needs to be considered in mass balances of carbon cycling near the SMTZ (e.g. Hong et al., 2013; Sun and Turchyn, 2014). Wallmann et al. (2008) suggested that the alkalinity produced through silicate weathering may be an important source to the global ocean, however much of the excess alkalinity is likely sequestered in authigenic carbonates near the seafloor as a result of constant diffusion of Ca and Mg into the sediment column from overlying seawater. The long-term storage of CO₂ derived from buried organic matter through sequestration in authigenic carbonates, however, must be an important sink of carbon not explicitly considered in the current global carbon budget.

The large drop in alkalinity between the SMTZ and ~130 mbsf at Sites 3, 5, and 7 is the opposite of what would be expected if coupled methanogenesis and silicate weathering were the only process affecting alkalinity below the SMTZ. Rather, if silicate weathering were the sole process, an increase in alkalinity with depth would be expected. The steady decrease below the SMTZ at these sites reaching concentrations between ~5-8 mM before increasing again at ~130 mbsf suggests that some co-occurring reaction is competing with silicate weathering within this interval. These steady decreases in alkalinity cannot be totally explained by authigenic CaCO₃ precipitation as Ca concentrations remain constant within this interval or even increase (Site 7). Authigenic carbonates are ubiquitous at all of the sites cored in the K-G basin, and Fe-rich carbonates dominate comprising >50% of the authigenic carbonate phases present at each site (Teichert et al., this issue). The Fe-rich carbonates are evenly distributed throughout the sediment column below the SMTZ at Sites 3, 5, 14, and 15 while they occur in separate horizons below the SMTZ at Sites 7, 10, and 16. All the Fe-rich carbonates are isotopically enriched in δ¹³C relative to the other authigenic carbonate phases, strongly suggesting that FeCO₃ formation is related to neutralization of methanogenic CO₂ and alkalinity production during silicate weathering, with δ¹³C values ranging from -9 to +20‰ (Teichert et al., this issue). While we are not able to unequivocally determine the cause of the marked alkalinity consumption within this interval at some of the sites, the low dissolved Fe and Mn below the SMTZ coupled with the

presence of abundant authigenic Fe-rich carbonates with enriched $\delta^{13}\text{C}$ suggests that Fe and Mn reduction is involved. A coupled reaction that could explain the observed decrease in alkalinity and DIC while Ca concentrations remains constant is co-occurring methanogenesis, silicate weathering, and iron reduction. During the reaction, excess alkalinity produced through silicate weathering and the DIC produced through methanogenesis is precipitated as CaCO_3 and FeCO_3 . It should be noted, however, that when there is enough Ca and some Fe and Mg present, ankerite, $\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$ typically precipitates.

Through this reaction, 2 moles of DIC and alkalinity are consumed whereas Ca and Fe are conserved following the trends observed at Sites 3, 5, and 7. Thus, Fe/Mn reduction within the methanogenic zone could act as an important sink for alkalinity produced through silicate weathering effectively storing the dissolved inorganic carbon released during methanogenesis in authigenic Fe/Mn carbonates or mixed carbonates. Equation 13 represents just one of many potential co-occurring reactions involving reduction of Fe oxides and oxyhydroxides, silicate weathering, and precipitation of authigenic carbonates in the methanogenic zone. This process could act as an important filter limiting the amount of alkalinity produced through silicate weathering that could be returned to the ocean, thus further limiting its impact on the alkalinity balance of the global ocean and efficiently storing the CO_2 released during methanogenesis in authigenic carbonates.

In summary, DIC and alkalinity are produced from the seafloor to the SMTZ through POCSR and AOM. The concentrations of DIC and alkalinity are roughly equivalent within the SRZ as a result of HS^- precipitation within Fe-sulfide minerals. Below the SMTZ, CO_2 is produced through net microbial methanogenesis and observed as an increase in DIC concentrations. Without co-occurring silicate weathering, alkalinity would remain constant below the SMTZ because methanogenic CO_2 dissociates to $\text{HCO}_3^- + \text{H}^+$, thus has no net effect on pore water alkalinity (Fig. 10). Ongoing CO_2 production within methanogenic sediments increases pore water H^+ concentrations and decreases pore water pH. This decrease in pH drives silicate weathering within the methanogenic zone, which, in turn, serves as a critical buffer for pH and leads to alkalinity concentrations that are equivalent to DIC.

Downhole CH₄ concentrations within the GHZO are near Structure I gas hydrate solubility to several hundreds of millimolar. DIC concentrations are well below methane concentrations at all sites. The simultaneous buffering of pore water pH through silicate weathering and intense HCO₃⁻ production through methanogenesis promotes authigenic carbonate precipitation consuming much of the DIC produced through methanogenesis. The continual precipitation of authigenic carbonate phases below the SMTZ drives the large deficit in DIC and alkalinity at all the sites in the K-G basin. Considering that methane concentrations measured in pressure cores range from 60-1951 mM and that DIC concentrations in the absence of silicate weathering should be at least equal to the methane concentrations, this coupled reaction sequence has the potential to sequester up to 1900 mM DIC in authigenic carbonates. Thus, the coupled process of alkalinity production through silicate weathering and authigenic carbonate precipitation effectively consumes most of the carbon that was produced as CO₂ through methanogenesis from the pore water and, along with gas hydrate precipitation, keeps methanogenesis as a thermodynamically feasible catabolic pathway.

6. Summary and Implications

Our results show that the relative rates of microbial methanogenesis fluctuate throughout the sediment column with intense organic matter degradation and methane production occurring below ~130 mbsf at several of the sites in the K-G basin. Most of the CO₂ (acidity) produced through microbial methanogenesis is neutralized producing excess alkalinity through silicate weathering in the methanogenic sediments. We show that silicate weathering coupled to methanogenesis occurs from the SMTZ to a depth of at least 300 mbsf in the K-G basin, extending the depth range where this coupled reaction is observed and acts as a sink of CO₂ and source of alkalinity. Considering coupled methanogenesis and silicate weathering have also been observed in the Sea of Okhotsk (Wallmann et al., 2008), Black Sea (Aloisi et al., 2004), and offshore Chile (Scholz et al., 2013), it is likely that this is a common process in continental margin sediments worldwide and required to buffer pore water pH. Indeed, silicate weathering at continental margins should occur anywhere there are primary silicates and rapid POC burial that supports microbial methanogenesis. Weathering of detrital smectites to kaolinite is also likely to occur in these settings but at a slower rate than weathering of detrital pyroxenes, plagioclases, and feldspars (e.g. Appelo and Postma, 1996). Thus, the regions of methanogenic CO₂-

neutralization during chemical weathering occupies a large volume of continental margin sediments, and this process is capable of playing a significant role in modulating the global carbon cycle over geologic timescales.

Authigenic mineral precipitation related to silicate weathering may act as a significant and important sink not only for the DIC released by microbial methanogenesis but also for seawater K, Li, Rb, Ca, Mg, and B not currently considered in the global geochemical budgets for these elements. For example, the current Li and K budgets predict that the sources of these elements to the ocean are much greater than the sinks, an imbalance that has been an issue since nearly the beginning of modern chemical oceanography (Emerson and Hedges, 2008). Low temperature alteration of volcanic ash and the oceanic crust, as well as illitization (for K) are sinks for these elements, and our results as well those of Aloisi et al. (2004) show that authigenic clay formation related to silicate weathering in marine sediments may also be an important sink not currently included in the mass balance of solutes and isotope ratios in seawater. These results also suggest that smectite rather than kaolinite is likely the important authigenic clay phase forming through silicate weathering in the K-G basin and elsewhere.

It is clear from the comprehensive pore water geochemical dataset from the K-G basin that many co-occurring reactions control the solute profiles, and that quantifying rates of individual reactions is extremely challenging. The pore water profiles of alkalinity, DIC, Mg, or Ca cannot be unambiguously used as a tracer for silicate weathering as Ca, alkalinity, and Mg are simultaneously produced by silicate weathering and consumed from the pore water and sequestered in authigenic hydrous silicates and carbonates. The profiles of these solutes are further controlled by coupled reactions associated with Fe and Mn reduction (Eq. 13). Mg and alkalinity were used as tracers for quantifying rates of silicate weathering in the Sea of Okhotsk (Wallmann et al., 2008). However, as a result of precipitation in authigenic silicates and carbonates, Mg is not a conservative tracer for silicate weathering in the K-G basin. Likewise, the alkalinity produced through silicate weathering is immediately precipitated in authigenic carbonate minerals and cannot be used as a tracer in this setting. Thus, rates of silicate weathering based on Mg and alkalinity profiles in the K-G basin would be minimum estimates.

The balance of river inflow and alkalinity removed from the ocean is not well understood. Currently recognized sinks are CaCO_3 precipitation, hydrothermal alteration, and reverse weathering in marine sediments. During reverse weathering, metal hydroxides and opal

combine to form authigenic clay minerals, and alkalinity is consumed through this reaction while CO_2 is produced (e.g. Mackenzie and Garrels, 1966; Michalopoulos and Aller, 1995; Michalopoulos et al., 2001). Reverse weathering is limited by the supply of Al and Fe hydroxides to the sediment column as well as biogenic silica. Since CO_2 is produced through reverse weathering, it would counteract the CO_2 consumed through silicate weathering and lead to lower net CO_2 consumed in marine sediments. In the Sea of Okhotsk, reverse weathering was only observed in the sulfate reduction zone, and estimated rates were one order of magnitude lower than silicate weathering rates, with net CO_2 consumption occurring within the sediment column associated with higher rates of silicate weathering (Wallmann et al., 2008). Our results show that silicate weathering occurs over a much larger depth range, clearly highlighting the importance of silicate weathering in buffering the pH, generating alkalinity, and promoting authigenic carbonate precipitation in marine methanogenic sediments. As clearly observed at Sites 5 and 7 in the K-G basin, only a fraction of the alkalinity produced in the deeper methanogenic zone is precipitated as authigenic carbonate. However, there is net alkalinity consumption in the middle of the sediment section cored (~50-130 mbsf). Based on the presence of Fe/Mn-rich carbonates and the pore water geochemical data, we propose that coupled silicate weathering and Fe/Mn reduction consumes much of the excess alkalinity in $(\text{Ca}, \text{Mg}, \text{Fe}, \text{Mn})\text{CO}_3$. If this process is common in continental margin sediments, it can act as a long-term sink of carbon released from organic matter during methanogenesis and filters out alkalinity that would be returned to the ocean from silicate weathering, thus minimizing the impact that silicate weathering might have on the ocean alkalinity balance. If authigenic carbonate formation is indeed widespread, it would also indicate that, though not explicitly considered by global carbon models, coupled silicate weathering and carbonate precipitation is implicitly treated in global models by carbon burial within marine sediments.

While we are unable to quantify the rates of silicate weathering and methanogenic CO_2 sequestration in authigenic carbonates in the K-G basin at present, a preliminary maximum estimate of the potential global rate of coupled methanogenesis and silicate weathering in marine sediments has been made (Wallmann et al., 2008). Based on the estimated range in global methane production in marine sediments (5-20 Tmol CH_4 per year; Reeburgh et al., 1993; Hinrichs and Boetius, 2002) and assuming that methanogenic CO_2 is completely neutralized through silicate weathering, Wallmann et al. (2008) estimate that the global rate of marine

silicate weathering could be as high as 5-20 Tmol CO₂ per year. This preliminary estimate suggests that the global rate of CO₂ neutralization through silicate weathering in marine sediments rivals that of continental silicate weathering (Gaillardet et al., 2009), which is considered to be the primary sink for atmospheric CO₂ over geologic timescales (Wallmann et al., 2001). The environmental factors that control marine methanogenesis and silicate weathering are somewhat separate from those that control CO₂ uptake through continental silicate weathering. The rate of silicate weathering on land is dependent on topography, surface temperature, vegetation, and precipitation, while methanogenesis and silicate weathering are predominantly influenced by sedimentation rates, POC concentrations, the reactivity of organic matter, and availability of primary silicate minerals. While some of these factors are not mutually exclusive, seafloor sediment deposition and POC burial may vary over shorter timescales than tectonic process on land for instance. Thus, changes in the rate of silicate weathering in marine sediments may have an impact on the global carbon cycle over shorter timescales than silicate weathering on the continents.

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Figure Captions

Figure 1. Top. Bathymetric map showing the locations of the Krishna-Godavari and Mahanadi basins and Site 17 cored in the Andaman sea during NGHP Expedition 01. **Bottom.** Map of the sites cored in the K-G basin. Adapted from Collett et al. (2008).

Figure 2. Pore water solute profiles at Site 3. Blue profiles are from Hole 3B and red profiles are from Hole C. Arrows denote seawater values for comparison.

Figure 3. Pore water solute profiles at Site 5. Blue profiles are from Hole 5C and red profiles are from Hole 5D. Arrows denote seawater values for comparison.

Figure 4. Pore water solute profiles at Site 7. Blue profiles are from Hole 7B and red profiles are from Hole 7D. Arrows denote seawater values for comparison.

Figure 5. Pore water solute profiles at Site 10. Blue profiles are from Hole 10D and red profiles are from Hole 10C. Arrows denote seawater values for comparison.

Figure 6. Pore water solute profiles at Site 14. Arrows denote seawater values for comparison.

Figure 7. Pore water solute profiles at Site 15. Arrows denote seawater values for comparison.

Figure 8. A) Cl concentration-depth profiles from Site 5, **B)** Cl concentration-depth profile from Site 7, **C)** $\delta^{18}\text{O}$ and δD profiles from Site 5, and **D)** $\delta^{18}\text{O}$ and δD profiles from Site 7. **A** and **B** show broad intervals where Cl concentrations are elevated with respect to modern seawater value ($\text{Cl}_{\text{sw}} = 559 \text{ mM}$; denoted by arrows). The elevated concentrations mainly occur above the zone where gas hydrate saturations are elevated, indicating active gas hydrate formation is likely not the cause of the enrichment. Rather, these occur in the zone of active methanogenesis and likely indicate authigenic hydrous silicate formation as a result of silicate weathering coupled to methanogenesis. These reactions are compatible with the $\delta^{18}\text{O}$ and δD profiles in **C** and **D**. Authigenic clay formation produces a decrease in $\delta^{18}\text{O}$ and an increase in δD , whereas gas

hydrate dissociation produces and increase in these isotope ratios. These reactions are distinguishable from clay dehydration, which produces a decrease in δD but an increase in $\delta^{18}O$.

Figure 9. Gas hydrate saturation estimates from pore water Cl profiles using Equation 1 from Sites 3, 5, 7, 10, 14, and 15. Cl anomalies present below the BSR were not included in the saturation estimates as they are the result of gas hydrate burial and dissolution below the base of the gas hydrate stability zone. Gas hydrate saturations are denoted by black marked lines at all sites except Site 5 where the pore water sample resolution was low and saturations are denoted with black dots. Green dots (green lines at Site 10) denote gas hydrate saturations in different holes at the same site. The solid black line denotes Structure I methane hydrate solubility based on the method outlined in Tishchenko et al. (2005). Blue triangles are methane concentrations from the headspace method immediately below the SMTZ where methane concentrations are below gas solubility at STP (from Collett et al., 2008). Red triangles are not saturations based on pressure cores, but rather are estimated methane concentrations based on pressure core measurements (Collett et al., 2008). These values are computed based on the total amount of methane recovered after depressurization and the pore volume of the sample. Thus, the pressure core pore water methane concentrations include methane that was stored in gas hydrate *in situ*. SMT = sulfate-methane transition, BSR = bottom simulating reflector, HS = headspace concentrations (mM), PC = pressure core concentrations (mM), and Sol = methane hydrate solubility (mM). Note the different S_h scale for Sites 10 and 15, and the different CH_4 concentration scale for Site 10.

Figure 10. Schematic diagram illustrating the expected changes in DIC and alkalinity with depth related to co-occurring microbial and inorganic reactions in the K-G basin. Above the SMTZ, alkalinity and DIC are produced through POCSR. At the SMTZ, AOM produces both alkalinity and DIC (not shown in the figure); if HS^- is sequestered during precipitation of Fe-sulfides, alkalinity and DIC should be approximately equivalent. **A)** Illustrates DIC and alkalinity profiles that would result from methanogenesis without silicate weathering and authigenic carbonate precipitation; in this scenario DIC increases following the increase in microbial methane but alkalinity remains constant. **B)** CO_2 produced through net microbial methanogenesis is effectively neutralized through silicate weathering, consuming acidity and generating excess

alkalinity. C) Illustrates DIC and alkalinity consumption within the entire methanogenic zone by authigenic carbonate precipitation. Pervasive authigenic carbonate precipitation is the result of both alkalinity and dissolved calcium production through silicate weathering.

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Table 1. NGHP Expedition 01 Leg 3 site summary data

	Latitude	Longitude	Water Depth (m)	Bottom Water Temperature (°C)	Geothermal Gradient (°C/m)	BSR Depth (m)
Site 3	15° 53.8881' N	81° 53.9638'E	1074	6.5	0.039	209
Site 5	16° 01.7172'N	82° 02.6733'E	946	7.1	0.044	125
Site 7	16° 31.2747'N	82° 40.8612E	1284	5.3	0.052	188
Site 10/12	15° 51.8647'N	81° 50.0709'E	1039	6.5	0.045	160
Site 14	16° 03.5577'N	82° 05.6218'E	895	7.9	0.038	109
Site 15	16° 05.6983'N	82° 09.7467'E	926	7.7	0.04	126
Site 16	16° 35.5986'N	82° 41.0070'E	1253	5.9	0.052	170

ND = not determined

Table 2. Gas hydrate occurrence zone and saturation based on porewater chlorinity

	SMTZ Depth (mbsf)	BGHSZ (mbsf)	GHOZ (mbsf)	S _h Range (%)	Average S _h (%)
Site 3	9.8 - 19.0	209	22-29, 60-183, 205-206	0.8 - 10.2	2.3
Site 5	11.5 - 24	130	51-52, 70-130	2.3 - 13.4	5.2
Site 7	36.0	198	72-195	1.0 - 16.9	2.4
Site 10/12	18.0	160	23-160	1.5 - 41.3	15.5
Site 14	23.0	150	59-101, 122-123	0.9 - 15.5	3.1
Site 15	31.5	126	61-119	1.4 - 67.8	8.9
Site 16	30.0	178	70-90, 110-163	1.1 - 12.7	4.0

SMTZ = sulfate-methane transition zone

BGHSZ = base of the gas hydrate stability zone

GHOZ = gas hydrate occurrence zone

S_h = gas hydrate saturation

Figure 2

Figure 3

Site 7

Figure 4

Site 10

Figure 5

Site 14

Figure 6

Site 15

Figure 7

Figure 8

Figure 9

Reactions occurring in each panel

Methanogenesis	Yes	Yes	Yes
Silicate weathering	No	Yes	Yes
Carbonate precipitation	No	No	Yes