

THE RELATIONSHIP BETWEEN THE DEPTH OF THE SULFATE-METHANE TRANSITION AND GAS HYDRATE OCCURRENCE IN THE NORTHERN CASCADIA MARGIN (IODP EXP. 311)

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ABSTRACT

In a transect of four sites drilled by IODP Exp. 311 across the northern Cascadia margin, the depth of the near-seafloor sulfate-methane transition (SMT) is correlated to the depth to the top of the gas hydrate-bearing interval below. This relationship is expected if anaerobic oxidation of methane (AOM) is the dominant sulfate reduction mechanism, so that the depth of the SMT is controlled by the diffusive upward flux of methane. Sulfate, however, can also be consumed above the SMT by organoclastic sulfate reduction. This paper quantifies the relative importance of these two sulfate reduction mechanisms with estimates of the methane concentration gradient from pore water data and reaction-transport modeling. The independently estimated methane gradients are consistent at each site and show that at least 1/3 to 2/3 of the sulfate is consumed by AOM. The similar fraction of sulfate consumed by AOM in the transect sites explains the observed correlation between the depth of the SMT and the top of gas hydrate occurrence.

Keywords: gas hydrates, sulfate-methane transition, anaerobic oxidation of methane

NOMENCLATURE

AOM Anaerobic oxidation of methane
 C_{org} Organic carbon in sediment [dry weight %]
 c'_m Concentration gradient of methane [mM/m]
 c'_s Concentration gradient of sulfate [mM/m]
 D_m Diffusion coefficient of methane [m²/s]
 D_s Diffusion coefficient of sulfate [m²/s]
 F_s Fraction of sulfate consumed by AOM
GHOZ Gas hydrate occurrence zone
GHSZ Gas hydrate stability zone
mbsf Depth below the seafloor [m]
SMT Sulfate-methane transition

INTRODUCTION

A four-site transect drilled across the northern Cascadia continental margin during Expedition 311 of the Integrated Ocean Drilling Program [1] provides a unique data set to advance our understanding of marine gas hydrates (Figure 1).

The three seaward sites of the transect (U1326, U1325 and U1327) contain hydrates in a gas hydrate occurrence zone (GHOZ) whose top deepens moving landward [2]. There is no clear evidence of gas hydrate in the most landward site (U1329). The transect sites also display a shallow sulfate-methane transition (SMT), where sulfate and methane concentrations approach zero. As the SMT also deepens systematically moving landward, the depths of the SMT and of the top of the GHOZ are correlated (Figure 2).

Explaining this correlation is the focus of this paper. The relationship in Figure 2 is expected if pore water sulfate is mostly reduced by anaerobic oxidation of methane (AOM). In this case, sulfate will be consumed quickly if the upward diffusive flux of methane is high, with higher methane fluxes corresponding to shallower SMT depths. A relatively high methane flux requires a high

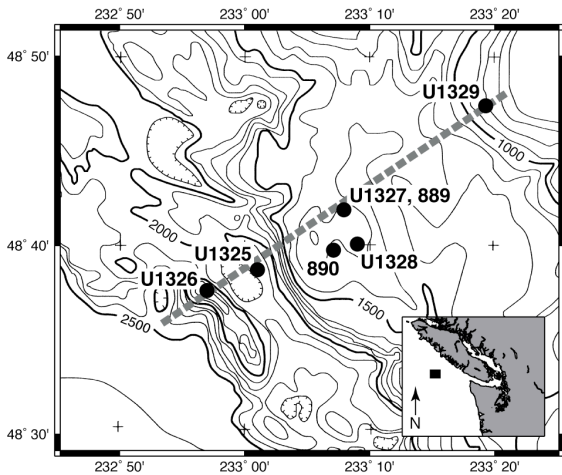


Figure 1. Sites drilled on the northern Cascadia margin during IODP Exp. 311 (U1325-U1329) and ODP Leg 146 (889 and 890). The four-site transect studied in this paper is indicated by a dashed gray line.

concentration gradient of methane, which in turn implies a relatively shallow occurrence of gas hydrate [3].

Sulfate reduction, however, can also be coupled with oxidation of particulate organic matter in organoclastic sulfate reduction [4]. If this process dominates sulfate consumption, the depth of the SMT will not be related to the top of the GHZO. If both sulfate reduction processes are active, a relationship such as that in Figure 2 may still hold if the fraction of sulfate consumed by AOM is similar in all sites. Hence, quantifying the relative contribution of AOM and organoclastic sulfate reduction is key to understanding the relationship between the depth of the SMT and the occurrence of gas hydrates below.

The relative contribution of AOM and organoclastic sulfate reduction can be determined by comparing the diffusive fluxes of sulfate and methane at the SMT. If the methane flux matches the sulfate flux, then all sulfate must be consumed by AOM [e.g., 5]; if the methane flux is less than the sulfate flux, some sulfate must be consumed by organoclastic sulfate reduction [e.g., 6]. Prior modeling work estimated that AOM consumes about half of the sulfate at Site U1325 [7]. This paper extends the previous analysis across the northern Cascadia transect. The goal is to test if the observed correlation between the depths of the SMT and of the top of the GHZO can be explained

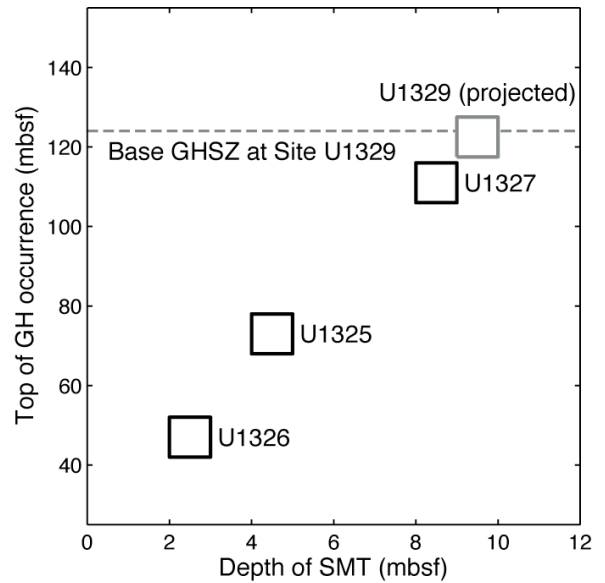


Figure 2. The depths to the top of the GHZO and to the SMT are correlated in the three northern Cascadia transect sites that have gas hydrates (black squares). A projected depth for the top of the GHZO at Site U1329 can be obtained by extrapolating a linear relationship fitted to the other three sites to the SMT depth of Site U1329 (gray square). This projected depth is near the base of the GHSZ (dashed gray line), in agreement with the lack of gas hydrates at Site U1329.

by AOM consuming a similar fraction of sulfate across the whole transect.

METHOD

The fraction of sulfate F_s consumed by AOM at each site is determined from the ratio of the diffusive fluxes of sulfate and methane at the SMT [e.g., 5] as in

$$F_s = -(D_m c'_m) / (D_s c'_s), \quad (1)$$

where D_m and D_s are diffusion coefficients, c'_m and c'_s are concentration gradients, and the subscripts m and s denote methane and sulfate, respectively. The diffusion coefficients in [8] give a ratio $D_m / D_s = 1.568$, and the sulfate gradients are estimated from the sulfate concentration at the seafloor (assumed to be 29 mM as in typical seawater) divided by the depth to the SMT at each site (Table 1).

Site	Sedim. rate (m/Ma)	SMT depth (mbsf)	Depth to top GHZOZ (mbsf)	Sulfate gradient at SMT (mM/m)	Methane gradient at SMT from pore water data (mM/m)	Methane gradient at SMT from model (mM/m)	Sulfate fraction consumed by AOM from pore water data	Sulfate fraction consumed by AOM from model
U1326	366	2.5	47	-11.60	3.13	2.75	0.42	0.37
U1325	302	4.5	73	-6.44	2.17	1.89	0.53	0.46
U1327	187	8.5	111	-3.41	1.43	1.32	0.66	0.60
U1329	98	9.5	-	-3.05	0.88	0.65	0.45	0.33

Table 1. Key parameters at each site in the northern Cascadia transect. Sedimentation rates are averages in the GHSZ after [9], depths of the SMT are after [1], and depths to the top of the GHZOZ are after [2]. Concentration gradients and sulfate fractions consumed by AOM are estimated in this study.

Two methods are used to estimate the methane concentration gradients, based on pore water chemistry analyses and on reaction-transport modeling.

Methane gradients from pore water chemistry

A fundamental difficulty in using pore water analyses is that the low atmospheric solubility of methane causes loss of methane in recovered core samples. The methane concentration gradients from pore water chemistry listed in Table 1 were obtained from the first few samples immediately below the SMT that had concentrations below atmospheric solubility (~2 mM, [5]). Only 2-3 measured pore water concentrations could be typically used at each site, so that these methane gradients have large uncertainties and are likely underestimated.

Methane gradients from reaction-transport modeling

Methane concentration gradients at the SMT were estimated by applying the analytical reaction-transport model in [10] for a uniform sediment lithology. This model assumes steady-state conditions, constant porosity, and no upward water advection. The only source of methane is microbial in situ production. Modeling calculates a methane concentration profile whose gradient at the SMT can be used to estimate the fraction of sulfate F_s consumed by AOM (Equation 1). This methane gradient estimate is likely a minimum because it does not account for upward pore water advection, which can cause a steeper increase in methane concentration with depth [2].

Key parameters used in the modeling at each site are listed in Table 1. At all sites, modeling used an average porosity of 50%, a tortuosity of 2.4 to compute the diffusion coefficients in bulk sediment, and a methane solubility profile computed from the local temperature gradient following [11].

The parameters that control in situ microbial methane production and the resulting methane concentration profile are the amount of metabolizable organic carbon (C_{org}) at the SMT and the reaction rate of methanogenesis. The amount of metabolizable C_{org} can be estimated as the difference between the observed C_{org} at the SMT and the amount that remains at depth, assumed to be the refractory fraction [12]. A conservative estimate for the metabolizable C_{org} content in the northern Cascadia transect sites is a range 0.25% to 0.5% (dry weight fraction).

Previous modeling studies in the Cascadia margin estimated a methanogenesis reaction rate on the order of 10^{-13} s^{-1} [4, 13]. The rest of this section describes the method used to estimate the methanogenesis reaction rate at each site.

Sites U1325, U1326, and U1327

Gas hydrates have been detected at these sites, and the depth to the top of the GHZOZ constrains the methanogenesis rate for a given metabolizable C_{org} content [10]. In practice, a methanogenesis rate that is too low will mean that the depth where the modeled methane concentration reaches the solubility and gas hydrates start to form will be deeper than the observed top of the GHZOZ. Conversely, if the rate is too high, the predicted

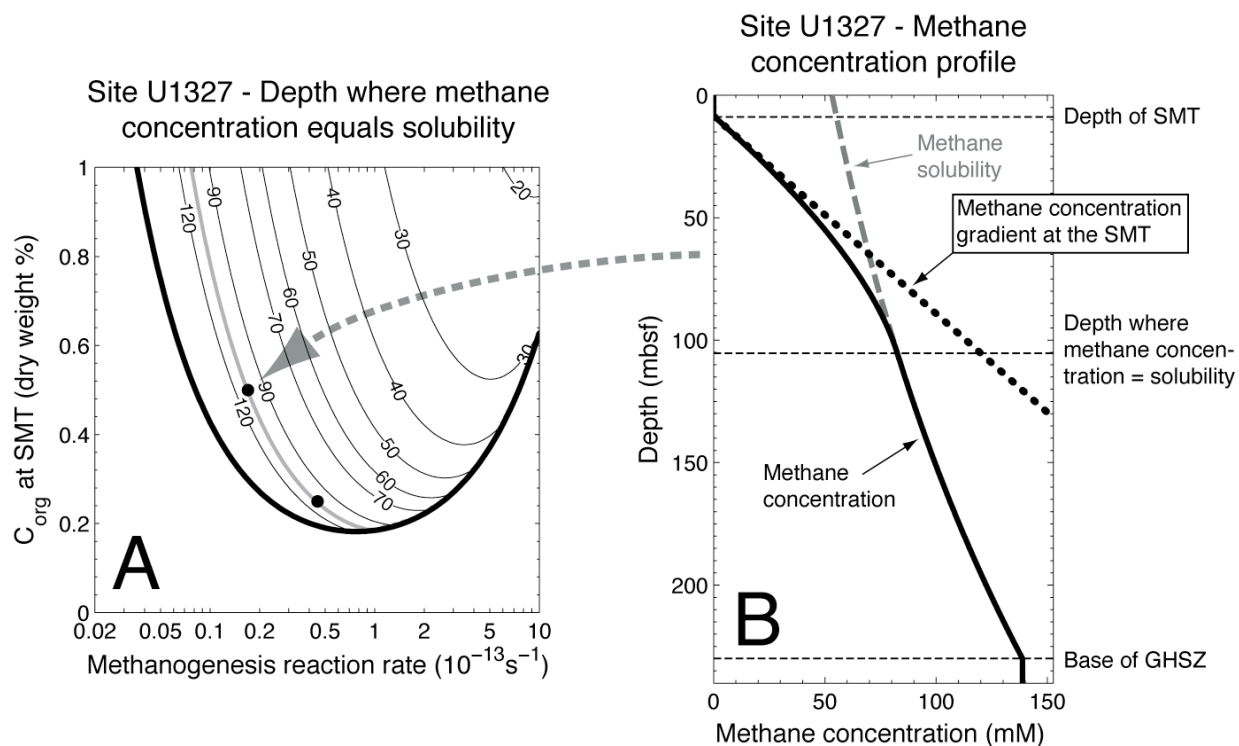


Figure 3. (A) Contour map of the depth where modeled methane concentration reaches solubility at Site U1327 for a given methanogenesis reaction rate and C_{org} content at the SMT. The gray contour is a depth 5 m above the top of the GHOZ at this site. The two black dots mark the methanogenesis reaction rates that fit the observed top of the GHOZ for C_{org} contents of 0.25% and 0.5%. (B) Methane concentration profile corresponding to the values of reaction rate and C_{org} content indicated by the dashed gray arrow in Figure 3A. The modeled methane concentration profile (solid black line) gives a gradient at the SMT indicated by the dotted black line.

top of the GHOZ will be too shallow. The methanogenesis rates estimated at these sites are the rates that make the methane concentration reach solubility at a depth just above the observed top of the GHOZ for the assumed range of metabolizable C_{org} content (0.25%-0.5%; Figure 3). Two values of the metabolizable C_{org} content and of methanogenesis rates result in two values for the methane concentration gradient at the SMT; the differences in gradient, however, are small (at most 11% of the average). The average concentration gradients are listed in Table 1.

Site U1329

There is no clear evidence of gas hydrates and no GHOZ at Site U1329, so the method used for the other three sites cannot be applied. Instead, methanogenesis rates at this site are predicted on the basis of their relationship to sedimentation rate. Methanogenesis rates have been proposed to

be proportional to the square of the sedimentation rate [12], with higher sedimentation rates resulting in better preservation of organic matter. The methanogenesis rates estimated at the three transect sites with gas hydrates are indeed proportional to the square of the sedimentation rate (Figure 4). An extrapolation of the best-fit power law relationship to the sedimentation rate at Site U1329 gives predicted methanogenesis rates. Modeling results are consistent with the observed lack of gas hydrates at Site U1329, because the methane concentration calculated from these predicted rates does not reach saturation in the GHSZ of Site U1329.

RESULTS AND DISCUSSION

The methane concentration gradients estimated independently from pore water data and reaction-transport modeling are similar at each site (Table 1). Methane gradients from modeling are lower

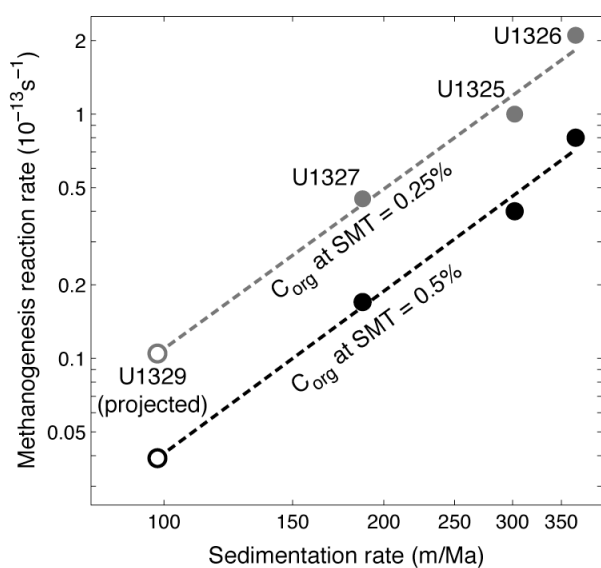


Figure 4. The methanogenesis reaction rates estimated at the three northern Cascadia transect sites that have gas hydrates (filled circles) are approximately proportional to the square of the sedimentation rate. Best-fit power laws (dashed lines) have exponents of 2.17 and 2.2. Extrapolating the best-fit power laws to the sedimentation rate of Site U1329 give estimated methanogenesis reaction rates at this site (white circles).

than those from pore water data, possibly because the modeling did not account for upward pore water advection.

The fraction of sulfate consumed by AOM estimated in the transect sites varies between 1/3 and 2/3 (Table 1). At least part of this variation in sulfate fractions may reflect uncertainties in the estimated concentration gradients. The estimated sulfate gradients have uncertainties due to nonlinear concentration trends with depth and to uncertainties in the depth to the SMT. In most sites, methane concentration gradients from pore water measurements are computed from only 1-2 samples with methane concentrations below atmospheric. Hence, even a small error in sample depth or measured concentration can significantly affect the estimated gradient. Uncertainties of the methane gradients from modeling are also likely to be significant because of uncertainties in sedimentation rate and because pore water advection was neglected.

These uncertainties can lead to changes in the estimates of the sulfate fraction consumed by

AOM made at any one site that are as large as the total variation across the whole transect. For example, consider the fraction of sulfate consumed by AOM at Site U1325. An error of only 20 cm in the depth of the sample below the SMT that controls the methane gradient from pore water data gives a range of estimated sulfate fractions of 0.42 to 0.7.

Given these uncertainties, the results in Table 1 are consistent with a fraction of sulfate consumed by AOM that is about the same in all the transect sites and is approximately equal to the fraction consumed by organoclastic sulfate reduction. A similar fraction of sulfate consumed by AOM at all sites explains the observed relationship between the depth of the SMT and the depth of the top of the GHOZ in the northern Cascadia transect (Figure 2). As the estimated methane gradients are likely to be lower bounds, the estimated fractions of sulfate consumed by AOM are minimum values and could be higher.

The relationship between depth of the SMT and gas hydrate occurrence reported here is not universal. For example, no such relationship has been observed in sites drilled on the Bengal sea margin of India [14]. A possible explanation is that in this setting the fraction of sulfate consumed by AOM is more variable than in the northern Cascadia transect.

CONCLUSIONS

In a transect of sites drilled across the northern Cascadia margin, the depth of the near-seafloor sulfate-methane transition (2.5-9.5 mbsf) is correlated to the depth to the top of the gas hydrate-bearing interval below (47-111 mbsf). This relationship is expected if anaerobic oxidation of methane dominates sulfate reduction or consumes a similar fraction of sulfate at all sites. Methane concentration gradients estimated independently from pore water data and reaction-transport modeling show that at least 1/3 to 2/3 of the sulfate is consumed by anaerobic oxidation of methane in the transect sites. The similar fraction of sulfate consumed by AOM across the transect explains the observed correlation between the depths of the SMT and of gas hydrate occurrence. Modeling also shows that microbial methanogenesis reaction rates are proportional to the square of the sedimentation rate, as previously suggested [12].

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