A kinetic-model approach to quantify the effect of mass transport deposits on pore water profiles in the Krishna-Godavari Basin, Bay of Bengal

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Abstract

Mass transport deposits (MTDs) in the Krishna-Godavari Basin from the eastern Indian margin are common sedimentary features over the modern continental slope. Quantitative understanding of the scale and age of these MTDs is relevant to understanding their triggering mechanisms and environmental feedbacks, as well as for interpreting pore water chemical profiles. Pore water profiles in sediments recovered during the 2006 Indian National Gas Hydrate Project (NGHP-01) expedition suggest that MTDs are present at seven of the ten sites cored in the Krishna-Godavari Basin. Kinetic modeling of the S-shaped pore water sulfate and ammonium profiles from these sites provides quantitative estimates of the individual MTDs thickness, time elapsed after the event, rate of organic matter-fueled sulfate reduction, and time required to reach a new steady state. Model results suggest that the MTDs at the seven study sites are 8 to 25 meters thick and are 300 to 1600 years old. Within the MTD sections, the organic matter-fueled sulfate reduction rates are 130 to 1200 mmol/m²/yr and the time needed to reach a new steady state ranges from

2000 to 3800 years. In comparison to depth-integrated sulfate reduction rates estimated in other regions, our estimates are relatively high reflecting the much thicker sulfate reduction zone that results from the MTDs. A positive correlation is observed between water depth and the MTD activity index defined as thickness of MTD package divided by its emplacement age. This correlation suggests the close relationship between MTD activity and water depth which agrees with previous studies of MTDs in this region and elsewhere. We caution against using the pore water data from sites experiencing significant MTDs to infer metabolic processes and to quantify steady-state reaction rates as our model results confirm the remarkable influence of transient MTDs on pore water profiles.

Introduction

The Krishna-Godavari (K-G) Basin on the eastern margin of India is characterized by extensive mass-transport deposits (MTDs) formed by sliding/slumping of river-delivered sediments (Forsberg et al., 2007; Ramana et al., 2009; Shanmugam et al., 2009; Ramprasad et al., 2011). MTDs in the K-G Basin may be related to variations in regional climate and changes in sediment discharge from the Krishna and Godavari rivers (Forsberg et al., 2007; Ramana et al., 2009; Ramprasad et al., 2011). However, the regional variability, magnitude, and age of the individual events are poorly constrained. Furthermore, sediments deposited by these abrupt events likely alter the pore water geochemical records in the shallow sediments, and hinder development of quantitative models for early diagenetic processes in this margin.

Pore water composition is very sensitive to localized and recent slumping events, as previously shown by Hensen et al. (2003) and Holsein and Wirtz (2010). The pore water profiles sampled during the recent Indian National Gas Hydrate Project (NGHP-01) expedition (Figure 1) provide a unique opportunity to quantify the timing and magnitude of these deposits. In this study, we apply a transport-reaction model to pore water data from seven sites drilled in the K-G basin (Table 1) to quantify the thickness of the deposits and the time elapsed for each event. This information is potentially important for future studies focusing on the control and/or feedback mechanisms of these episodic sediment transport events. Our work also highlights the importance of these events on the shape of pore water solute profiles and on their interpretation.

Study region

The modern K-G Basin in the eastern passive margin basin of India receives large

sediment inputs from the Krishna and Godavari Rivers. The delta fronts exhibit MTDs, scars and irregular topography over the modern upper continental slope formed by sliding/slumping (Forsberg et al., 2007; Ramana et al., 2009; Ramprasad et al., 2011). Sediments transported through large canyons also contribute to the total sediment accumulations (Kotha, 2002; Bastia, 2004; Murthy, 1999). Recent seismic and bathymetric surveys in this area imaged widespread MTDs (Solheim et al., 2007; Forsberg et al., 2007; Shanmugam et al., 2009; Ramprasad et al., 2011), and were used to guide drilling during the NGHP-01 expedition in 2006.

Sediment thickness in the K-G basin varies from 3 to 5 km and may exceed 8 km in the offshore region (Prabhakar and Zutshi, 1993). Drilling during NGHP-01 sampled the upper 200-300 meters at 10 sites, aimed at characterizing the gas hydrate potential of this region (Figure 1). In this study, we focus only on the first 40-60 meters of the sediment column (Table 2), in an effort to unravel the relative magnitude and age of MTD events, as their effect on pore water profiles impact ongoing efforts to quantify organic carbon cycling and methane dynamics in this passive margin (Solomon et al., 2014). The sediments studied all correspond to the same Quaternary lithostratigraphic unit primarily composed of clay (>70%), with variable amounts of carbonates, and trace amounts of quartz, feldspar, mica, and iron sulfide (Collett et al., 2008). Frequent silt/sand beds are observed at each site (Collett et al., 2008). The distribution of authigenic carbonate is not necessarily correlated with the current sulfate-methane-transition-zone (SMTZ), defined by the pore water sulfate and methane profiles, suggesting migration of the SMTZ in the past (Collett et al., 2008) or simply burial of authigenic carbonates produced at the SMTZ through time, perhaps punctuated by sediment slumping.

Effect of MTDs on the pore water data

Shipboard pore water analyses, including sulfate concentration, were reported in Collett et al. (2008). Shorebased pore water ammonium analyses were reported in Solomon et al. (2014). Pore water profiles in seven of the 15 sites drilled in the K-G basin suggest a non-steady-state condition (Figure 2). The concentration of all pore water species, especially sulfate, at these seven sites changes rapidly over relatively short depth intervals, indicating the importance of non-diffusional processes. A rapid drop in sulfate content and the concordant increase of both ammonium and dissolved inorganic carbon (DIC) concentrations at the first ~5 meters in the sediments (Collett et al., 2008; Solomon et al., 2014) are indicative of sulfate consumption due to organic matter degradation (abbreviated as POCSR, particulate organic carbon sulfate reduction, hereafter). As no methane is present in this interval, POCSR should be the only reaction consuming sulfate. Between 15 to 25 meters below seafloor (mbsf), sulfate content remains constant until it is again consumed by methane through anaerobic oxidation of methane (AOM) and POCSR at greater depths (Figure 2). We hypothesize that these sulfate profiles reflect recent mass transfer events at each site, and that the MTDs are too recent for diffusion to smooth the dissolved sulfate distribution between the two sulfate reduction zones.

In this work, we define MTD as a fluidized sediment block whose pore water is well mixed with seawater during sediment transport. The pore water composition in the MTD section is set to be seawater value to reflect the homogenization process. Before an MTD event, sulfate supplied by diffusion from overlying seawater is consumed by both POCSR and AOM, which forms a distinct SMTZ (Figure 2A). In environments devoid of MTD these processes act together to generate a smooth decrease in dissolved sulfate with depth (e.g., Claypool and Kaplan, 1974; Froelich et al., 1979;

Borowski et al., 1999; Hong et al., 2013; Figure 2A). If then a layer of MTD with reactive organic matter tops the original sediment surface (Figure 2B), the SMTZ is buried deeper while the reactive organic matter in the newly deposited sediments also consumes sulfate, leading to the shallow-most drop in sulfate content and effectively separating both sulfate consuming processes (Figure 2C). This produces the S-shaped profiles observed and clearly indicates that the system is out of steady state.

Eventually, the persistent bottom methane supply will move the SMTZ upward until a new steady state is reached (Figure 2D). We use a kinetic modeling approach to explore the conditions leading to the S-shape of sulfate profiles from these seven sites to unravel the effects of MTDs on pore water geochemistry.

Model architecture

Reaction formulation

In these simulations we use the FORTRAN routine CrunchFlow, as described in Steefel (2009). Hong et al. (2013; 2014) has listed the various reactions involved around the SMTZ, among which we focus only on POCSR and AOM. Above the SMTZ, where there is no methane present, POCSR is responsible for all of the sulfate consumption; AOM becomes more significant closer to the SMTZ. These two reactions can be summarized as:

where x is the stoichiometry of nitrogen in the organic matter and was calculated from the C/N ratio at each site (Table 3; data from Phillips and Johnson, 2014). We are aware that such a calculation may only be a first-order estimation of the elemental balance, as the amount of ammonium released from organic matter degradation depends on the C/N ratio in the pool of reactive carbon instead of the bulk organic matter. However, the good agreement with the NH_4 data, as we will show later, indicates that this is a reasonable approximation.

In order to constrain the rate of organic matter degradation in the first sulfate reduction zone (Figure 2C), we simulate pore water ammonium, which can be described as a function of both organic matter degradation and ion exchange on mineral surfaces (Von Breymann et al., 1988a, 1988b, 1990; Wallmann et al., 2006; 2008). To formulate ion exchange with CrunchFlow, we chose the *Gaines-Thomas* activity convention and specify a cation exchange capacity for the bulk sediment. Solid density is calculated based on the sum of mineral volume fractions. In the K-G Basin, ~80-90% of the sediment is composed of clay minerals (Collett et al., 2008), ~50-80% of which is smectite (Venkatarathnam and Biscaye, 1973; Pattan et al., 2008; Underwood, pers. comm.). Using a CEC for smectite of 80-150 meq/100 g of sediment (Hang and Brindley, 1970; Jaynes and Bigham, 1986), we estimated the CEC of K-G Basin sediments to range from 32 to 80 meq/100 g of sediment. The values used at each site were further constrained by data fitting using pore water measurements, and are specified for each site in Table 2.

POCSR was formulated as a Monod-type reaction with one Monod term (half saturation constant of 100 μM for sulfate was adopted; Wegener and Boetius, 2009). AOM was formulated as a double-Monod-type kinetic reaction with (half-saturation

constants of 500 μM were used, Wegener and Boetius, 2009). Detailed formulation for the reactions is given in Hong et al. (2014). The *Dirichlet*-type boundary conditions were used for all species, including methane. A fixed concentration of methane was assigned at the bottom of the simulation frame at each site (Table 2). This concentration is constrained by the observed methane and sulfate profiles as this bottom supply of methane induces AOM at a rate, which together with POCSR, leads to the observed methane and sulfate profiles. It is important to note that the observed methane concentration can only partly constrain (*i.e.*, as minimum constraint) the model, as the shipboard measurements of gas concentrations are affected by degassing during core recovery.

Model logistics

The sediment depth modeled (L in Figure 2) varies from site to site and was estimated based on its dissolved sulfate profile (Table 2). In order to constrain the thickness of each MTD package (defined as the sediment thickness from the onset of the MTD to the seafloor, and denoted by Δx in Figure 2B) and the time elapsed since deposition of this interval (Δt_I in Figure 2C), we evolved the model simulation in two steps. In the first step (Figure 2A), we used bottom seawater composition as the initial condition. We used a sediment deposition rate at all sites of 0.15 meter per thousand years, based on estimates listed in Collett et al., (2008) and Mazmudar et al. (2009). Giosan (pers. comm., 2009) has reported variations in sedimentation rates among the different sites ranging from 0.15 m/kyr at Site 10 to 0.85 m/kyr at Site 5. A range of sedimentation rates was therefore used to test its influence on the model results. We observed no significant effect when varying sedimentation rates from 0.15 to 0.85 m/kyr, which is not surprising since the time scale considered in this study is only on the order of several thousand years. The time length for the first step was calculated by dividing

the modeled depth of each sediment column, L , by the sedimentation rate of 0.15 m/kyr. The resulting time spans (200 to 400 kyrs) are long enough for sulfate profiles to reach steady state. The assigned activities for organic matter and minerals (*e.g.*, calcite and pyrite) were kept constant among all sites. We adjusted the bottom methane flux to match the observed sulfate and methane gradients at the lower sections of the profiles. After this time span, when the system has reached steady state, we assume an instantaneous deposition of a sediment package with a thickness denoted as Δx (Figure 2B).

The second step of model was initiated from the steady state conditions and SMTZ depths established during the first step with a new instantly deposited layer of sediments (*i.e.*, the MTD package) bearing reactive organic matter and sea water sulfate content of 28 mM (Figure 2B). From these initial conditions, we let the model evolve until it fits the observed pore water profiles. The thickness of this organic matter-rich layer (Δx in Figure 2B) can be estimated by simulating the pore water sulfate profiles. The amount of time required to reach the current observed profile (Δt_1 in Figure 2C) provides an indication of the time spanned since the MTD at each site. The assigned bottom methane supply was kept constant between the two steps.

Porosity, formation factor, and formation temperature

We assume that the pore water species migrate primarily by diffusion. This assumption can be verified by calculating the *Péclet* (P_e) number:

$$P_e = \frac{vL}{D} \quad (3)$$

where v is pore water burial rate, D is diffusion coefficient, and L is length scale. For the sedimentation rate (0.15 m/kyr or $1.14 \times 10^{-8} \text{ cm/sec}$) and diffusion coefficients (1.06×10^{-5} to $1.98 \times 10^{-5} \text{ cm}^2/\text{sec}$) considered in this study, diffusion outcompetes advection if the length scale is smaller than ~ 15 meters. Due to the importance of diffusion under such depth scale, its rate has to be accurately constrained.

To provide a realistic estimate of the diffusion rates, the porosity, tortuosity and the in-situ temperature of sediments need to be thoroughly considered. The porosity profile at each site was obtained by fitting the observed profiles (Collett et al., 2008) with the equation for depth-dependent porosity (Boudreau, 1997):

$$\phi(z) = \phi_f + (\phi_0 - \phi_f) \exp(\gamma z) \quad (4)$$

where ϕ_f and ϕ_0 are the asymptotic porosity and porosity at the water-sediment interface, respectively. γ is an empirical constant obtained from data-fitting of the depth interval that covers the modeled depth (*i.e.*, L in Figure 2). The best fitted parameters are reported in Table 2.

In order to account for the different diffusivities of solutes in pure fluid and porous media, a tortuosity value is required to adjust the diffusion coefficients in non-porous medium. One way to quantify the effect of tortuosity is by calculating the formation factor (FF) from the resistivity log data. Logging of the electrical resistivity tracks the electrical current, which is assumed to be analogous to fluid transport in the porous medium. In CrunchFlow, this can be included by providing a parameter named cementation factor (m). This value can be calculated using the FF data obtained from

resistivity logs obtained from logging while drilling (LWD) and shipboard laboratory measurements with a four-pin Wenner array and a temperature probe (Collett et al., 2008). The m values calculated for each site through Archie's law (Steefel, 2009):

$$FF = \phi(z)^{-m} \quad (5)$$

and are listed in Table 2.

In-situ temperatures were measured at each site during coring operations with the APCT-3 (advanced piston corer temperature tool 3) (Collett et al., 2008). Several temperature measurements, which include seafloor temperature, were made at each site to determine the geothermal gradient. This information is also included in Table 2.

Sensitivity tests

We performed a sensitivity test to constrain the variability of Δx , Δt_I and k_{OM} using data from Site 5C. Δx and Δt_I are primarily estimated from the sulfate profile, whereas k_{OM} was estimated using both sulfate and ammonium profiles. In this exercise we used the best fit values for Δx , Δt_I and k_{OM} , which are 13m, 1600 years and $10^{-9.3}$ mol/m²/sec (blue lines in Figure 3), and run the model by varying these parameters from 8 to 18m (Figure 3A), 1300 to 1900 years (Figure 3B) and from $10^{-9.5}$ to $10^{-9.1}$ mol/m²/sec (Figure 3C). The results of this exercise indicate that our model is able to estimate the three parameters with good sensitivity, and therefore provide a reliable quantification of the magnitude and timing of the most recent MTDs, as well as provide information on the k_{OM} in KG basin sediments.

Results and discussion

Model-estimated MTD scale and age

Our model assessment, in light of the geological background of this area, confirms our hypothesis that the S-shaped sulfate profiles result from organic matter degradation driven by a rapid and recent input of reactive organic matter associated with MTDs. Our model reproduces the observed sulfate and ammonium profiles at the seven sites where sulfate profiles indicate that the system is out of steady-state (Figure 4). The MTD thickness (Δx) and the time elapsed (Δt_1) since the mass transfer event are summarized in Table 3. We also ran the model until it reached a new steady state after the MTD event (Figure 2D), to estimate the maximum time the anomalous sulfate profiles can survive (Δt_2). These values are also listed in Table 3.

The thickness of the MTDs estimated from the model ranges from 8 to 25 meters. Seismic profiles at Sites 10 and 12 image a shallow debris flow (Collett et al., 2008), which supports our results, although the thickness is different from what we infer here (<25 m). High resolution multibeam bathymetry profiles also document prevalent and widespread distribution of mass transfer deposits in the upper and midslope areas of the K-G basin (Ramprasad et al., 2011), with a thickness similar in magnitude to what we estimated with our model. Frequent observations of silt/sand laminae in the cores were also attributed to the influence of MTDs in the basin (Collett et al., 2008). However, our results show no correlation between the magnitude of the model-derived Δx and the frequency of laminae (Figure 4), suggesting processes other than MTD may have led to the formation of these laminae.

We introduce an index named MTD activity index, which we define as the thickness of the MTD package divided by the time elapsed since its deposition onset ($\Delta x / \Delta t_1$) (Table 3). This index measures the activity of a single MTD event, as an active MTD

should deliver more sediment (*i.e.*, high Δx) more recently (*i.e.*, small Δt_I) comparing to a less active MTD event. Although this index has the same unit and similar magnitude (55.6-8.1 m/kyr; Table 3) as the sedimentation rate determined by ^{14}C dating approach (Ramprasad et al., 2011; Mazumdar et al., 2012), they are fundamentally different as sedimentation rate measures the accumulation of sediments for a period of time while our index represents the activity of a single MTD event. For the seven MTD events we investigated in K-G basin, the activity index is positive correlated with water depth, if we excluded Site 15A (Figure 5a). This correlation is better ($r^2=0.55$ with Site 15A and 0.89 without Site 15A) than the correlation between age of MTD and water depth ($r^2=0.43$, Figure 5b). No obvious correlation ($r^2=0.17$) is observed between MTD thickness and water depth (Figure 5c). Such results suggest that MTD age is the primary component of the good correlation observed between the activity index and water depth and MTD thickness is of secondary importance. This correlation exercise suggests that the activity of MTD, which is determined by both the age and the thickness of the MTD package, is closely related to water depth. This result not only agrees with previous observations in this region (Ramprasad et al., 2011), but is also consistent with the general observations along US margins (McAdoo et al., 2000).

Sulfate reduction dynamics in the MTD sections

At all sites except for Site 15A, the model is able to reproduce the observed ammonium and sulfate profiles using k_{OM} values ranging from $10^{-9.1}$ to $10^{-9.5}$ moles /m²/sec. These values result in a depth-integrated POCSR rate (R_{POCSR}), which reflect to the total sulfate reduction rate in the MTD section, of 150 to 620 mmol SO_4^{-2} /m²/yr (Table 3). POC (particulate organic matter) degradation rates estimated by Wallmann et al. (2006) from the sediments of the Sea of Okhotsk and Blake Ridge range from

2.8 to 122 mmol $\text{SO}_4^{-2}/\text{m}^2/\text{yr}$. Dale et al. (2008) estimated the organoclastic sulfate reduction rate from the coast of Denmark to be as high as 1150 mmol $\text{SO}_4^{-2}/\text{m}^2/\text{yr}$. Chuang et al. (2013) recently estimated the contribution of sulfate reduction from organic matter degradation to be 4.2 to 47 mmol $\text{SO}_4^{-2}/\text{m}^2/\text{yr}$ offshore Taiwan. Hong et al. (2014) estimated the rates of POCSR in the sediments of Ulleung Basin to be in the range of 0.5 to 74.7 mmol $\text{SO}_4^{-2}/\text{m}^2/\text{yr}$. The rates we estimated for the K-G basin are on the high end of these estimates, which may be due to the fact that we estimated the R_{SR} by integrating over the 8 to 25 m-thick MTD sections. These depth sections are two to five times thicker than the typical thickness of the sulfate reduction zone, which are only a couple meters at these other sites.

The sulfate profile from Site 15A is distinctly different from the other six sites in two ways. First, the first measurement at 1.4 mbsf yielded only 8.27 mM of sulfate (Figure 4), which is significantly lower than the bottom seawater value (28 mM). Such low sulfate content together with the low initial porosity measurement (69.8% at 0.78 mbsf, Figure 6A) suggests that the top of the sediment column at this site may have been removed by a recent erosional event. Second, the drop of sulfate concentration in the upper 9 m of the hole is more dramatic compared to other sites (Figure 4). In order to match the observed unique sulfate and ammonium profiles at Site 15A, we have to assign a distinctly higher k_{OM} that results in a higher R_{POCSR} (1200 mmol $\text{SO}_4^{-2}/\text{m}^2/\text{yr}$; Table 3) at this site. This difference may suggest that the organic matter at this site is more labile than other sites; however, the characterization of organic matter composition and provenance (Phillips and Johnson, 2014) at this site does not support this inference.

Another explanation for the higher R_{POCSR} is that the initial sulfate concentration when

MTD package deposited at Site 15A was not seawater value as what we assigned in the model (Figure 2B). Therefore, a R_{POCSR} similar to other sites and lower initial sulfate content can result in the current pore water profile observed at Site 15A. We hypothesized that the pore water composition of the MTD package was unaltered while the sediment deposited at Site 15A. The upper portion of this MTD package may continue the down slope transport during the same event or was later removed by another erosion event. The removal of this part of sediments result in the lower porosity currently observed (Figure 6A). The remaining sulfate in the intact part of the MTD package was consumed by POCSR at a rate similar to other sites (Figure 6B). These combined processes result in the different sulfate profile observed at Site 15A (Figure 6C). This inference, however, assumes unchanged pore water profiles during mass transport, which may not be very realistic. Although no satisfactory conclusion is arrived at this point, the combined data reveal the very dynamic conditions at Site 15A.

Influence of transient state on geochemistry profiles

Transient, or non-steady state condition, poses additional complexity to the interpretation of geochemistry profiles. For example, van Santvoort et al. (1996) documented the formation of a diagenetic Mn front driven by the degradation of a recent sapropel deposit in eastern Mediterranean. The ongoing degradation of poor quality organic matter in the pelagic section was interrupted by the sporadic occurrence of sapropel layers, rich in labile organic matter. The input of reactive organic matter facilitates formation of diagenetic Mn fronts in the sediments.

As demonstrated by van Santvoort et al. (1996), any inferred reaction that assumes a steady state condition will result in erroneous rate estimates. Although in this study

we only modeled the sulfate and ammonium profiles, we expect the MTDs to influence the distribution of all pore water species, since the entire system is still in a transient state (see profiles in Solomon et al., this issue). Our model results therefore question the postulated new metabolic pathway by Schrum et al. (2009). These authors explain the low ammonium concentration observed within the first sulfate reduction zone at Site 14A as indicative of a sulfate-reducing ammonium oxidation reaction. Although their estimates of Gibbs free energies for the reaction support the potential role of this metabolic process, our model clearly demonstrates that the sulfate and ammonium profiles of the K-G basin can be well explained by rapid deposition of sediment (Figure 2B), and do not necessarily require a sulfate-reducing ammonium oxidation reaction.

S-shaped sulfate profiles have been reported by Hensen et al. (2003) in the west Argentine Basin. They explained such profiles as resulting from two independent slides, each of which brought a sediment package with distinct pore water compositions. The different pore water compositions from these two sediment packages, which are also different from the bottom water composition, reflect the different origins of the sediment sections. By numerically simulating this scenario, Hensen et al. (2003) concluded that the sedimentary process that led to the observed sulfate profile must have happened very recently (i.e., several tens of years). Holstein and Wirtz (2010) observed similar sulfate profiles on a tidal sand flat sediment along the northern Germany coast. They explained this observation as resulting from a rapid organoclastic sulfate reduction fueled by a downward transport of labile organic matter during tidal flat progradation. In both cases, the authors agreed upon the transient nature of the observed S-shaped profiles, and propose episodic sediment pulses as their causal mechanisms. The fast sedimentation in the shallow part of

sediment column rapidly buries sulfate before it diffuses out or it is entirely consumed. Such sulfate burial results in a section with almost constant sulfate concentration. If this is the only process altering sulfate profile, then “kink type” profiles of sulfate (Zabel and Schulz, 2001; Hensen et al., 2003) may be expected. Consumption of sulfate through POCSR in the section with rapid sedimentation is required for the S-shaped profiles, as have been observed in the K-G Basin, Argentine Basin, northern Germany coast, and potentially elsewhere along continental margins worldwide.

The MTDs inferred from our analyses of pore water data from the K-G basin are much larger in scale and significantly older than those discussed previously, which span only 2-8 meters in thickness and are thought to reflect events that occurred several tens of years before sampling (Hensen et al., 2003 and Holstein and Wirtz, 2010). By simulating the profiles until they reach a new steady state (Figure 2D), we estimated the maximum amount of time (Δt_2) that these anomalous sulfate profiles can survive to range from 2000 to 3800 years (Table 3). Mazumdar et al. (2009) observed the similar S-shaped sulfate profile from a site close to the Site 10D in our study. The rapid sedimentation for the first 6 meters of their sediment core suggests influence from MTDs which were dated as ~5 kyr old. Collectively, our results and the dating from Mazumdar et al. (2009) suggest that such S-shaped sulfate profiles may survive longer than previously assumed, if MTDs are large enough in scale. The fact that we observed the influence of MTDs from the seven sites over 90 km in the basin is consistent with the observations of the widespread occurrence of MTDs in the K-G Basin. However, our modeling approach identified the influence of MTDs at some sites that were not recognized by geophysical or core observations, and points to the value of this technique in identifying MTDs and quantifying their magnitude and age.

Conclusions

By simulating the pore water sulfate and ammonium concentrations measured at seven sites drilled in the K-G Basin during the NGHP-01 expedition, we provide a quantitative description of how the MTDs can affect the pore water geochemical profiles. Our model provides reliable estimates of the thickness of the MTD packages ($\Delta x=8\text{-}25$ meters), the time elapsed after the most recent event ($\Delta t_1=450$ to 1600 years), and the organoclastic sulfate reduction rate ($R_{POCSR}=126$ to 1215 mmol $\text{SO}_4^{2-}/\text{m}^2/\text{yr}$) at these seven sites. We also estimated the time required for the system to reach a new steady state after the MTD events ($\Delta t_2=2000$ to 3800 years).

If we exclude site 15A, we observe a positive correlation between water depth and the MTD activity index ($\Delta x/\Delta t_1$), in agreement with the previous observations of mass transport processes in this basin and elsewhere. The depth-integrated sulfate reduction rates estimated here are higher than published values from other sites. This is because the rates in the K-G basin were estimated by integrating over sediment depths that correspond to the thickness of the entire MTD packages, which are two to five times thicker than the sulfate reduction zone in other studies. Site 15A is anomalous in its sulfate and porosity data which suggest that sediment deposition at this site may be more dynamic than the other study sites.

We caution against using the pore water profiles of sites experiencing significant MTDs to infer metabolic processes before considering the role that sediment transport can have on the pore water distributions. In particular, our results suggest that the sulfate-reducing ammonium oxidation pathway postulated by Schrum et al. (2009), is not the primary cause of the low ammonium concentrations observed within the first sulfate reduction zone at Site 14A. The results from our model show that the shallow

pore water solute profiles at Site 14A reflects a non-steady state condition triggered by emplacement of a recent mass transport deposit.

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editor, Dr. Tim Collett, for handling the manuscript.

Figure caption

Figure 1: map of the study area

Figure 2: Schematic diagram showing the steps involved in the transport-reaction model to simulate the effect of MTDs on pore water sulfate profiles. (A) The pre-MTD pore water profiles (step 1) were set by simulating a L-meter long sediment column to steady state using sea water composition as the initial condition. Methane flux assigned here is estimated by both sulfate and methane profiles (i.e., the assigned methane flux has to be at least higher than the observed flux). (B) The MTD (the grey rectangle) with fresh labile organic matter is deposited instantaneously onto the sediment column and buries the SMTZ to a greater depth. (C) In step 2, the pore water profiles and methane flux resulting from step 1 are used as the initial condition. Due to the addition of reactive labile organic matter in the MTD, sulfate is consumed at shallow depth through POCSR only (the first sulfate reduction zone) whereas methane exhausts sulfate from below by AOM and POCSR (the second sulfate reduction zone). The SMTZ in (B) and (C) illustrate this non-steady-state condition, which is observed at seven KG basin sites. The Δx (thickness of MTD) and Δt_1 (time required to reach present observed profile) are estimated by fitting data at each site and are reported in Table 3. (D) The system is expected to reach another new steady state condition after Δt_2 years (Table 3).

Figure 3: Simulation conducted at Site 5C to test the sensitivity of the model to the Δx , Δt and k_{OM} parameters. Blue lines in each panel indicate the best fit to the data, and red lines show changes that would result from small variations in the values assigned

to these parameters. As the results indicate, the three parameters can be well constrained by fitting the observed sulfate and ammonium profiles.

Figure 4A: Model results and the observed sulfate (blue lines and circles), methane (red lines and squares), and ammonium (pink lines and diamonds) profiles at the seven study sites. The depths where thin silt laminae and beds (grey lines) were observed at each site were also plotted for comparison although no apparent correlation was observed between the frequency of laminae and the thickness of MTDs (Δx , Green lines).

Figure 5: Correlation between water depth and the MTD activity index ($\Delta x/\Delta t$). (a) The positive correlation, if Site 15A is excluded, suggests that the MTD activity is closely related to water depth. In order to fit the sulfate profile in Site 15A, a higher k_{OM} is required which may suggest more dynamic conditions at this site as described in the text. (b) Ages of MTD correlate well with water depth suggesting this is the primary component of the good correlation observed in (a). (c) No obvious correlation is observed between MTD thickness and water depth.

Figure 6: Conceptual model to explain the sulfate profile at Site 15A. (A) Comparison of porosity profiles between Site 14A and 15A, the two adjacent sites. The first measurement at Site 15A is ~5% lower than that at Site 14A suggesting that the MTD section in Site 15A may have undergone recent erosion. The two red lines mark our estimated thickness of MTD at Site 15A. In contrast to the initial homogenous sulfate content in the MTD sections at all other sites (Figure 2B), the initial sulfate profile in the MTD section at Site 15B may already be low in sulfate and the total depletion of sulfate within the MTD suggests that this sediment column had

experienced POCSR for a period of time before the emplacement at Site 15A. Such that immediately after emplacement, the system had a sulfate distribution as shown in (B) The continuous consumption of sulfate by POCSR in the MTD section after depositing result in the present observed sulfate profile at Site 15A, as shown in (C)

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Table 2: Input parameters for model simulations.

		Sea floor	Geothermal		ϕ_0^b	ϕ_f^b	γ^b	C/N	CEC ^c
	L (m)	Temperature	gradient	m	(%)	(%)			(meq per
		(°C)	(°C/m)						100 g sed.)
Site 5C	50	7.1	0.044	2.75	77.5	57.5	-0.04	13	80
Site 7B	60	5.3	0.052	2.75	77.5	52.5	-0.04	8.5	80
Site 10D	40	6.5	0.045	3.5	77.5	63	-0.1	8.5	80
Site 12A	40	6.5 ^a	0.045 ^a	3.5 ^a	80	60	-0.07	12	80
Site 14A	40	7.9	0.038	2.5	77	50	-0.03	13	80
Site 15A	60	7.7	0.04	2.5	70	57.5	-0.05	14	50
Site 20A	50	5.5	0.049	2.25	80	55	-0.12	10	70

^a Assuming the same as Site 10.

^b These parameters were estimated from the first 40 to 60 meter of the core sediments

^c cation exchange capacity

Table 3: Model-derived results (Δx : thickness of MTD; Δt_1 : time elapsed after the MTD event; Δt_2 : times requires to reach a new steady state; k_{OM} : kinetic constant for POCSR; R_{POCSR} : depth-integrated sulfate reduction rate)

	Δx (m)	Δt_1 (yr)	Δt_2 (yr)	k_{OM} (10^x moles/m ² /sec)	$\Delta x/\Delta t_1$ (m/kyr)	R_{POCSR} in Δx (mmol SO ₄ ⁻² /m ² /yr)
Site 5C	13	1600	3350	-9.3	8.1	204
Site 7B	25	450	2200	-9.1	55.6	623
Site 10D	11	800	3800	-9.3	13.8	173
Site 12A	15	1050	2100	-9.5	14.3	149
Site 14A	13	1400	3800	-9.3	9.3	204
Site 15A	18	525	2000	-8.65	34.3	1215
Site 20A	8	300	3800	-9.3	26.7	126

Table 1: Water depth and the location of the seven study sites.

	Water Depth (m)	latitude	longitude
Site 5C	945	16° 01.722N	82° 02.677E
Site 7B	1285	16° 31.2785N	82° 40.8672E
Site 10D	1038	15° 51.8609N	81° 59.0749E
Site 12A	1038	15° 51.8609N	81° 59.0749E
Site 14A	895	16° 03.5577N	82° 05.6218E
Site 15A	926	16° 05.6983N	82° 09.7467E
Site 20A	1146	15° 48.5671N	81° 50.5760E