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Numerical Modelling Research on the Mineral Alteration Due to the Methane Leakage at the Seabed

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In order to investigate the response of authigenic minerals to gas hydrate geo-systems, the biogeochemical processes and its induced mineralization were predicted by employing the comprehensive reactive transport modelling approach. On the available data basis, a 1-D vertical column model was built. Three cases with different upward methane flux rates were designed to investigate the effects of variations in the depth of sulfate methane transition zone (SMTZ) on the formation of authigenic minerals. The results indicate that the SMTZ depth is significantly influenced by the upward methane flux rate. During the simulations, oligoclase, k-feldspar, smectite-Na, smectite-Ca, chlorite dissolved. The AOM (Anaerobic Oxidation of Methane) reaction was strong at the interface, and the precipitation amount of calcite is large, which indicates that the formation of calcite at the interface is mainly controlled by AOM. When the methane leakage rate is 20 times higher than the basic case, aragonite starts to precipitate. During the simulation, oligoclase, k-feldspar, smectite-Na, Smectite-Ca, chlorite dissolved.

1. Introduction

Natural gas hydrate found in marine sediments has attracted much attention in the world, because it could become a major future energy resource. Authigenic rocks or minerals associated with methane seeps from gas hydrate are widespread in hydrate occurrence regions, so-called cold-spring deposits. Several numerical models have been developed, which concentrated mainly on the characterization of AOM rate (Anaerobic Oxidation of Methane) (Regnier et al., 2011), the effective leakage rate of methane emission from sediment to seawater (Liu and Wu, 2014), and the relationship between the rate of methane leakage and the type of self-generated minerals (Luff and Wallmann, 2003).The currently existing works are mainly focused on the control of AOM by biological and bioenergy and the relationship between the rate of methane leakage and the type of self-generated minerals. Much less attention was paid to the relationship between AOM-SR reaction and diagenesis. In this study, a model coupling AOM, solute transport and diagenesis was used to explore the AOM biogeochemical processes and its inducing mineralization. One-dimensional (1D) column model was built to investigate the response of AOM and authigenic minerals to the methane leakage rate. Three cases were designed to investigate variations in the depth of sulfate methane transition zone (SMTZ) and the mineral composition induced by varying flux rates of methane leakage.

2. Methodologies

2.1 Numerical simulator

All simulations were performed using a reactive transport modelling tool, TOUGHREACT (Xu et al., 2006; Xu et al., 2011). This code is a numerical simulation program for chemically reactive non-isothermal flows of multiphase fluids in porous and fractured media, The program was written in Fortran 77 and developed by introducing reactive chemistry into the multiphase fluid and heat flow simulator TOUGH2 (Pruess et al., 1999).

2.2 Biodegradation kinetics and parameters

A single microorganism capable of catalyzing AOM has not yet been isolated in pure culture (Knittel and Boetius, 2009). In contrast, several studies have reported a close association between methane oxidizing

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archaea and sulfate-reducing bacteria in the AOM environments (Regnier et al., 2011). The rate of consumption of CH_4 can be expressed using a double Monod kinetics as

$$r_{AOM} = k_{AOM}\left(\frac{C_i - C_{min}}{K_s + C_i}\right)\left(\frac{C_j - C_{min}}{K_a + C_j}\right) \tag{1}$$

where r_{AOM} is the rate of CH_4 consumption (M/s, M = mol/L), k_{AOM} is the maximum consumption rate of CH_4 (M/s), K_s is the half-saturation constant for the substrate CH_4 (M), K_a is the half-saturation constant for the electron acceptor SO_4^{2-} (M), c_{min} minimum concentration of chemical components, and c_i denotes concentration of chemical components (M). Parameters used in this modelling study are listed in Table 1.

Table 1: Biogeochemical parameters used in the model.

Parameter	Description	Value	Unit	Source
K_{CH_4}	Half-saturation constant for methane	1.5×10^{-3}	M	Dale et al., 2008
$K_{SO_4^{2-}}$	Half-saturation constant for sulfate	1.0×10^{-3}	M	Dale et al., 2008
K_{AOM} in Eq. (1)	Maximum rate of AOM	1.62×10^{-9}	M/s	Dale et al., 2008

3. Model Setup and condition settings

3.1 Conceptual model and boundary conditions

The simulation assumed that the major gradients of concentrations and transport within the sediment are in the vertical direction, so a one-dimensional (1D) model (Fig.1a) with a cross-section area of 1 m^2 was used in this study. The 20 m thick was chosen according to the field information reported by Wu et al. (2013). According to the study of Liu and Wu (2014), the upper boundary acting as the interface between the sea water and the sediment was discretized with uneven spacing (Figure.1b). The length of i-th cell Z_i was calculated by:

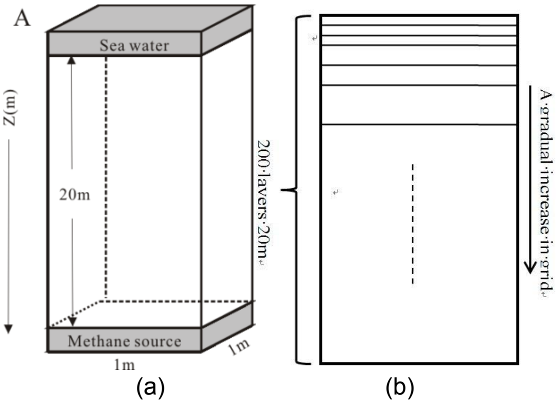
$$A = \frac{L}{n - \sum_{i=1}^{n} \frac{i}{1 + e^{((1-n/2)/c)}}} \tag{2}$$

$$\Delta Z = A - \frac{A}{1 + e^{((1-n/2)/c)}} \tag{3}$$

$$Z_i = Z_{i-1} + \Delta Z \tag{4}$$

where L (in m) is the tall length of the sediment column, n (-) is the number of grid, c is the attenuation coefficient (=10), and Z_i is the cell length of i-th layer.

The top boundary of the modelling domain is defined at the sea bed, and the bottom boundary is at the base of the model column 20 m below the sea bed.



(a) (b)

Figure 1: Conceptual model and grid spacing schematic.

3.2 Physical parameters setting

The pressure along the column was calculated hydrostatically with a pressure gradient of 10 bar/100, and a top pressure of 60.5 bars. The initial temperature of the top boundary was taken from Han et al. (2008, 2013, 2014). The methane enters the column from the bottom of the model, and its flux is 3.80×10^{-3}mmol cm^{-2} a^{-}

[1](Wu et al., 2013). The other geophysical parameters used in the simulations, such as, porosity, and permeability, were taken from previous studies (Liu and Wu, 2014) and summarized in Table 2.

Table 2: Physical parameters used in the model.

Parameter	Description	Value	Unit
Z	Overlaying water depth	605	m
L	Length of modelled column	20	m
T	Sea-bed water temperature	6	℃
△T	Temperature gradient	0.042	℃ m^{-1}
φ	Porosity	0.6	
K	Permeability	10^{-15}	m^2
n	Number of grid	200	

3.3 Initial water chemistry

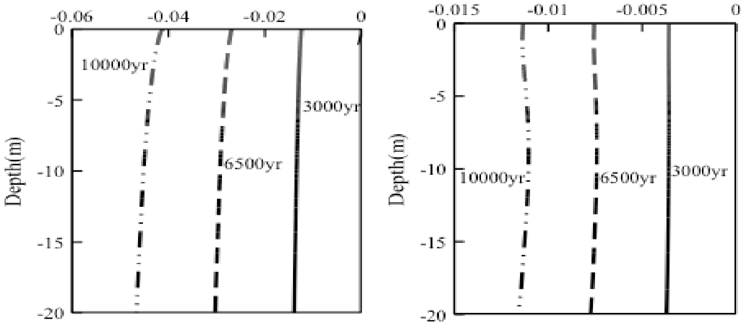
The initial water and boundary water compositions used in the present study are taken from Wu et al. (2010), and the mineral composition was referenced to Lu et al. (2011).

4. Results and Discussion

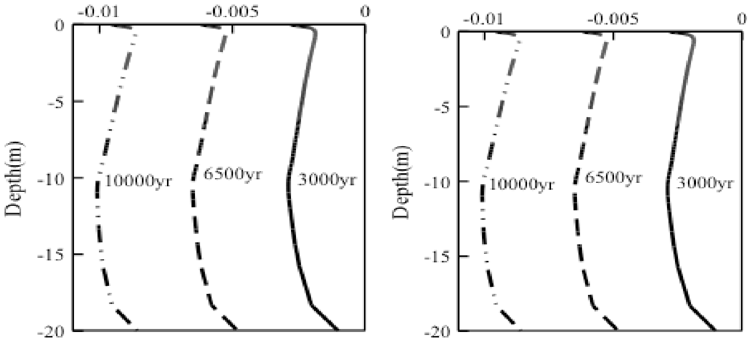
The methane flux of simulation 1 (base-case) is 3.80×10^{-3} mmol cm^{-2} a^{-1} according to Wu et al. (2013). Then two additional methane flux rate were designed, increasing from the base-case by 20 and 50 times.

4.1 Mineral dissolution and precipitation

The increased HCO_3^- generated from the AOM reacted with Ca^{2+} released from the dissolution of certain minerals (e.g., oligoclase and Ca-smectite) in the sediment and from the seawater, resulting in the precipitation of calcite. At the same time, the increased HS^- produced from the SR, associated with Fe to form pyrite. Precipitations of calcite and pyrite are able to strongly affect the distribution of dissolved species in sediment pore waters. In what follows, mineral alterations are discussed. During the simulation, oligoclase, Ca-smectite, chlorite showed dissolution trends (Figure.2a-c).



(a) oligoclase (b) smectite-Ca



(c) chlorite (d) calcite

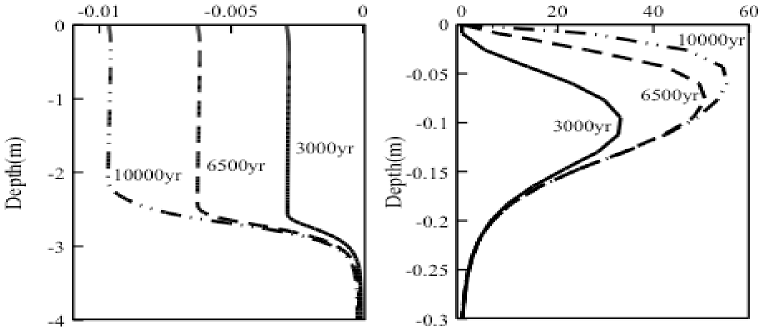
Figure 2: Changes of mineral volume fractions (in vol.%, negative values for dissolution, positive for precipitation) obtained from the base-case simulation

Dissolutions of oligoclase and Ca-smectite provided Ca^{2+} for the precipitation of calcite (Figure, 2d). Calcite precipitation occurred mostly near the bottom of the seabed (Figure.2d), with a volume fraction of 1.5% after 10,000 yrs, because another source of Ca^{2+} is the downward diffused seawater.

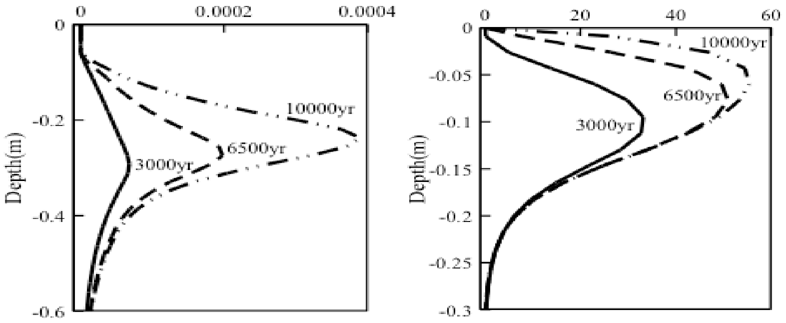
4.2 Mineral dissolution and precipitation under different methane flux rates

Different methane leakage rates affect the AOM reaction, making the difference between the ion concentrations in the pore water, which affects the formation of carbonate minerals. When the methane flux rate in Case 2 is 20 times larger than that in the base-case, the modelled chlorite dissolution accounted for 0.001–0.009% in volume fraction at the top of 3 m in the sediments (Figure. 3a). The SMI position of Case 2 was 0.201 m bellow the seafloor, at which the maximum HCO_3^- concentration was predicted. This led to the maximum precipitation of carbonates in this position (Figure.3c).

With 20 times higher methane flux than the base-case, tiny amounts of aragonite precipitation was observed (Figure. 3d), which appeared only at depth 0.3-0.4 m bellow the sea floor over the simulation time of 400-1000 yrs. Similar to the precipitation of calcite, magnesite precipitation amounts had a maximum value at the same place, with 0.00015–0.00039% volume fraction (Figure. 3c).



(a) chlorite (b) calcite

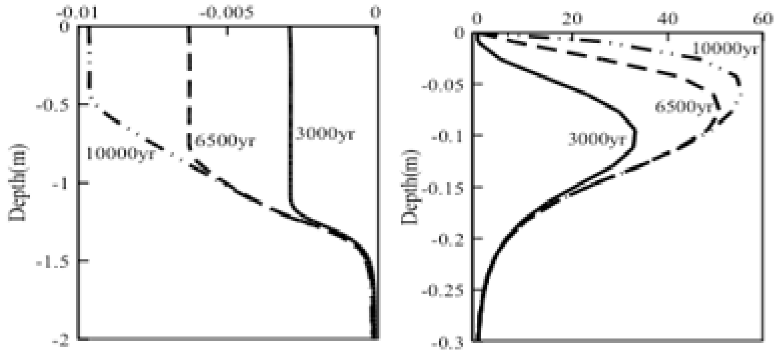


(c) magnesite (d) aragonite

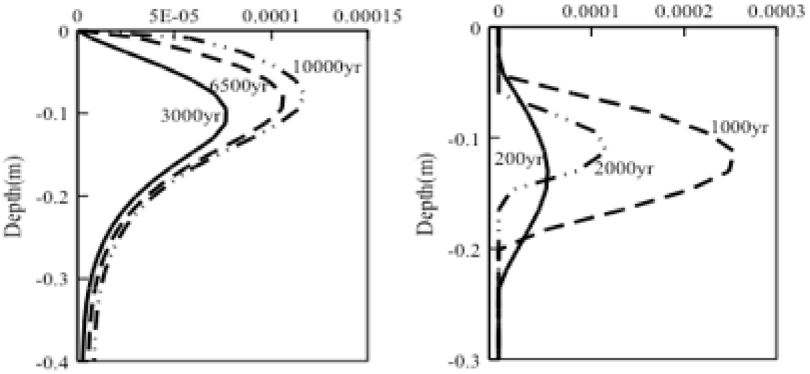
Figure 3: Changes in mineral volume fractions (in vol.%, negative values for dissolution, positive for precipitation) and porosity obtained from the Case2

When the methane flux rate in Case 3 is 50 times larger than that in the base-case, the modelled chlorite dissolution accounted for 0.0017–0.009% in volume fraction at the top of the 1.5 m in the sediments (Figure. 4a). The maximum precipitation of carbonates occurred at about 0.05 m bellow the seafloor after 10,000 yrs (Figure.4b), with a volume fraction of 57%. In the Case 3, the modelled aragonite precipitation amount is larger than that in Case 2 (Figure. 4d). The maximum magnesite precipitation occurred near the depth 0.1m, with 0.00012% volume fraction (Figure. 4c).

The formation of authigenic, magnesite etc. carbonates are influenced by many factors such as temperature, organic, upward methane flux, seawater sulfate content, redox environment and microbial activities.



(a) chlorite (d) calcite



(c) magnesite (d) aragonite

Figure 4: Changes in mineral volume fractions (in vol.%, negative values for dissolution, positive for precipitation) and porosity obtained from the Case 3

5. Conclusions

In this study, anaerobic oxidation of methane together with sulfate reduction and its associated mineralization processes were investigated. On the basis of physico-chemical conditions extracted from the South China Sea, a 1-D vertical column model was developed to represent the marine sediment under sea bed. Three simulations with different upward methane fluxes and three ones with varying initial mineral compositions were performed. This paper is focused on a theoretical study, and the parameters used in the simulations were taken from the NE South China Sea, near the bottom of the continental slope of Taiwan Island. However, the method presented here and the model built in this study can be used for other sites with similar conditions. Major findings can be drawn as follows.

1. The simulation results show that the generation of carbonate in sediments illustrates the richness of HCO_3^- in the sediment. Bicarbonate generation and carbonate precipitation were caused by the AOM. Enhanced pyrite formation near the SMI due to sufficient supply of methane is able to serve as a useful indicator for methane flux in the sea bottom.
2. The methane flux rate influence the reaction rate, the higher the leakage rate, the higher the AOM-SR reaction rate appears. The occurrence of different types of carbonate aggregates appeared to be closely related to the intensity of seepage. Aragonitic crusts apparently precipitated under higher methane concentrations. Small SMI depth and aragonitic crusts are able to reflect large methane migration, and indicate potential gas hydrates occurrence at depth.

The range of problems concerning the process in methane-bearing marine sediments is very broad. The present modelling results are specific to the conditions and parameters considered. The “numerical experiments” do give a detailed understanding of the dynamic evolution, and provide useful insight into fluid flow, biogeochemical and mineralization processes along the vertical column below the sea bed.

Acknowledgments

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