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Experimental Verification of Anomalous Chloride Enrichment Related to Methane Hydrate Formation in Deep-Sea Sediments

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Anomalous chloride concentration enrichment has been detected in marine sediments comprising methane hydrates (MHs). In this study, we designed an electric circuit system linked to the high-pressure resistance cell in which the chloride ion concentration can be directly measured within reliable accuracy under in situ *conditions of the deep-sea floor pressure and temperature. Chloride concentration increased under a fast MH formation rate, but no noticeable concentration change was detected under a relatively low-rate. Furthermore, we suggested that the MH formation rate must be maintained at least* $\sim 10^2$ *mol* m^{-2} *yr*$^{-1}$ *so as to efficiently enrich chlorides and retain the acquired chlorinity. The present experimental system dose not fully reflect the relatively minor effective variables such as vertical advections in real system, but the results seem to be sufficient for revealing chloride enrichment phenomena induced by fast MH formation rate with free methane gas.* © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 322–328, 2012

Keywords: methane hydrate, chloride enrichment, methane hydrate formation rate, ion exclusion

Introduction

Several different processes have been proposed to account for the origin of saline pore fluids in the natural deep-sea environment.[1–3] Among these, of particular interest is a process that involves active methane hydrate (hereafter, MH) formation with the exclusion of dissolved ions. When MH forms in the subseafloor, salt ions dissolved in seawater are excluded from the crystalline MH matrix, in which water molecules are incorporated. The concentration of dissolved ions in the saltier solution decreases by diffusive loss or advective fluid exchange.[3] Accordingly, the chlorinity pattern of pore fluids can be identified by detecting the balance between exclusion and diffusion or advection.

Recently, highly enriched chlorinities (positive Cl^- anomalies) with massive hydrate deposits have been

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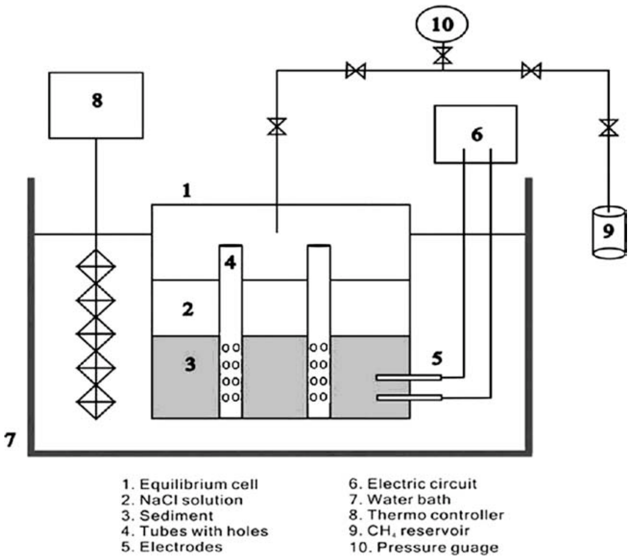

Figure 1. Experimental scheme for measurements of choride enrichment under *in situ* conditions.

observed in several sites. At the summit of a hydrate ridge (Ocean Drilling Program (ODP) Sites 1249 and 1250), the pore fluids were found to be highly enriched with dissolved chloride over a zone that extends from near the sediment surface [$\sim$1 mbsf (meter below sea floor)] to depths of 25 mbsf.[4] This chloride enrichment was also reported to occur in other regions, including U1328 on the Northern Cascadia Margin.[5] In efforts to obtain reasonable explanations of this phenomenon, several model studies have been carried out focusing on the exclusion and diffusion mechanism. Torres et al.[6] used a one-dimensional transport-reaction model, anticipating that the transport of methane as free gas through the MH stability zone results in highly enriched chloride ions. Haeckel et al.[7] also developed a simple transport-reaction model, which they successfully applied to simulate the observed chloride profile, and they, thereupon, calculated high-hydrate formation rates (0.15–1.08 mol cm^{-2} yr^{-1}). They concluded that the methane amount required for building up sufficient MH and achieving chloride enrichment exceeds the methane solubility in pore water. Thus, most of the MH is likely to form from methane gas bubbles rather than dissolved methane. Although the formation of gas hydrate from dissolved gas in natural porous media was revealed experimentally by Buffett and Zatsepina,[8] dissolved methane seems to be not enough for reported positive Cl$^-$ anomalies. As Milkov et al.[9] suggested based on a geochemical analysis of the Southern Summit, the free methane gas trapped by the MH seal at the base of the MH stability zone (Gas Hydrate Stability Zone (GHSZ)) migrates upward from the deep sediments, causing MH to form stably in shallow sediments. However, the accurate relationships between chlorinity and MH formation have not yet been revealed experimentally. For the lab-scale chlorinity detection, we designed an electronic circuit and determined the unique relationship between chloride level and MH formation rate. To the best of our knowledge, this study is the first to carry out appropriate experiments under *in situ* conditions to understand how the free gas affects chloride enrichment.

Experimental Set-Up

Figure 1 shows the overall experimental scheme. In equilibrium cell (1) linked with electric circuit (5, 6), we first set the three tubes with open holes (4). Subsequently, we place the sediment sample around the tubes and finally, fill the NaCl solution to possibly prevent the contact between methane gas and sediment layer. The pressure and temperature in the cell were maintained at 100 bar and 275–276 K, respectively. In the sediment layer, the electrodes were positioned just adjacent of the tubes ($\sim$0.5 cm apart from the tube).

For the analysis of chloride anion concentrations under *in situ* conditions, we assembled a readily accessible electronic circuit system. The voltage relationships in the circuit are simply expressed by the following equations.

$$V_{\text{total}} = V_{\text{sample}} + V_{\text{resist}} \tag{1}$$

$$V_{\text{j}} = I_{\text{j}} \times R_{\text{j}} \tag{2}$$

where V_{sample}, V_{resist}, and V_{total} represent the voltage drop on the sediment sample, the external resistance, and the total circuit, respectively. The current in the series circuit, I_{j}, is constant. We used the 5 kΩ external resistance and 9 V DC power (Figure 2). It was confirmed that the higher ion concentration results in the lower-resistance and voltage drop. According to the voltage relationship, the voltage drop at the

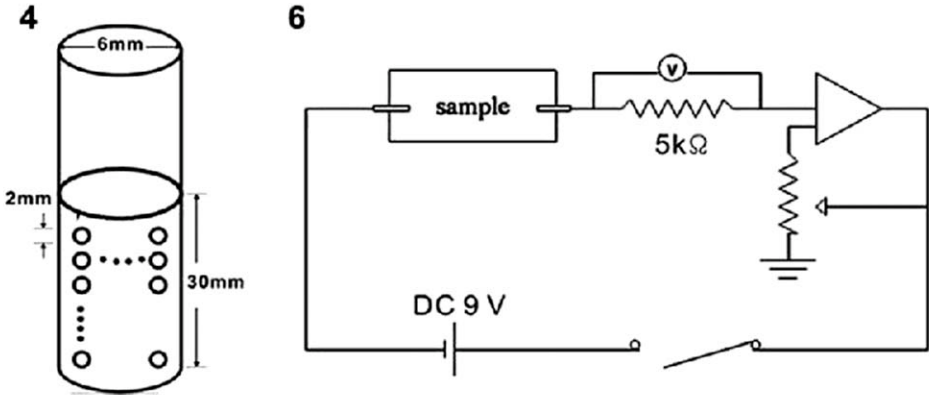

Figure 2. Details of tube (4, left) and electronic circuit (6, right).

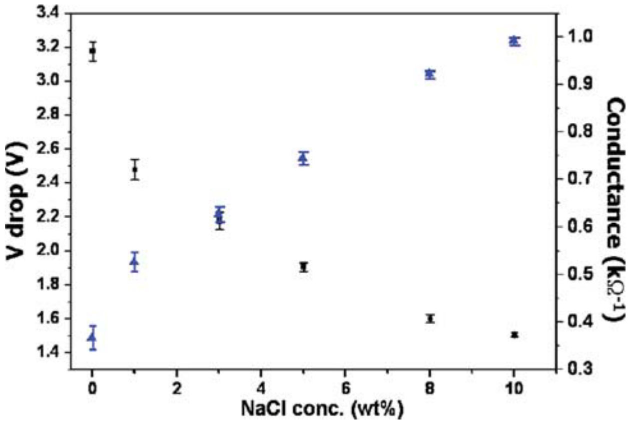

Figure 3. Calibration data of 50 wt % Na-MMT + 50 wt % aqueous solution (0–10 wt % NaCl inside) at 274 K.

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external resistance becomes higher when the sample voltage drop lowers, due to the overall constant current in a closed circuit. The electrodes are placed in a high-pressure resistance cell and care is taken to ensure perfect seal. A small electrode (1.2 mm diameter and 5 mm length) was used to promote the required accuracy in the specified site, possibly minimizing ion consumption during measurements. Before the application of the circuit under *in situ* conditions, calibration was carried out to determine the relationship between chloride concentration and voltage drop, particularly at 274 K. A nearly linear relationship was obtained for the sample of 50 wt % dry Na-montmorillonite (Na-MMT) + 50 wt % aqueous solution (0–10 wt % NaCl inside). At each concentration, the measurements were repeated several times within an error range of 0.03 V (Figure 3). The displacement between two electrodes was maintained at 1 cm and measurement was performed during a period of 3–5 s. The electronic circuit used in this study is only activated during this short-time interval, which was confirmed to be sufficient for measuring the expected chlorinity range. This isotherm data could be applied for a temperature range of 270–277 K without any loss of accuracy. The present approach for precise ion-level determination is expected to provide considerable experimental advantages such as ready accessibility, reliable reproducibility, analysis under *in situ* conditions, and negligible consumption of chloride anion during the short time required to carry out the measurement.

The overall experimental scheme is given as follows. First, we prepared 50 wt % clay swollen with 50 wt % aqueous solution (3.5 wt % NaCl inside) during 1–2 h. This sample was then kneaded until a homogeneous phase appeared at room-temperature. When artificially mixing two or more clay sediments, the uniformity of the mixture could affect the measured voltage, and, thus, we used only one type of clay minerals, Na-MMT, to avoid any complexity. The clay sample was then placed in a high-pressure resistance cell, filling the cell to roughly one-third of its height and bending the sensing terminals of the electrodes such that they are located at the positions adjacent (0.5 cm apart from) to the tubes of the clay mixture. Three tubes having holes on their walls were vertically installed within the clay mixture and the electrodes in the cell. The holes were incorporated to regulate to a certain degree, the interface area between methane gas and the clay sample. The viscosity of the sediment mixture was high enough that the mixture remained outside of the tubes. Also, after purging CH_4, no invaded clay sediment was observed, because the pressure on the sediment layer and the pressure inside the tube must be equivalent. The tube details are shown in the Figure 2; the radius of the tube is 3 mm and that of the hole is 1 mm. We inserted the three tubes in the sample simultaneously and repeated measurements with 4, 25, 40, and 80 holes. All holes are located within a length of 30 mm.

The noncontacting surface of the tubes must be inactive for the MH formation. An aqueous solution of 3.5 NaCl wt % (~600 mM) was charged onto the clay sample but did not penetrate the tubes. The cell temperature was maintained at 275–276 K, and was pressurized with CH_4 gas 100 bar (Figure 1). We believe that even at 277 K, the real deep-ocean temperature, the relationship between the chlorinity and MH formation reported here is convincing. Wyoming-type MMT (Wyoming, SWy-2, Wyoming) was obtained from the Source Clays Repository of The Clay Minerals Society. For the sample preparation, CH_4 gas was supplied by Special Gas (Korea) and had a stated purity of 99.98 mol%. Deionized water with an ultrahigh-purity was supplied from Merck (Germany), and NaCl of 99.8% purity was obtained from Ridel. All materials were used without further treatment.

Results and Discussion

We introduced tubes with various hole numbers to regulate the contact area between the methane gas and sediments. The tubes were inserted in the clay samples such that the MH formation system is divided into three parts: a tube hole to allow a passage for methane gas to flow in, an interface between the methane gas and clay sample at which MH formation is first initiated, and the clay sample. The change of chloride concentration is continuously checked in the *in situ* state according to the variation of the interfacial area. The overall scheme and results are shown in Figures 4 and 5. The chlorinity increased with the contacting area over the entire time range and the maximum chlorinity level ranged from 950 to 1300 mM. While at the present stage, a meaningful and consistent proportionality between the contact area and chlorinity cannot be reasonably argued, because it is noted that the maximum chlorinity tends to increase with the contact area. It took 10–15 hr for the chlorinity to reach the maximum observed value, depending on the contact area. Ussler and Paul[3] suggested that, during gas hydrate formation in a geochemically closed system, the chloride concentration could be computed from the following equation

$$C = \frac{C_{\mathrm{i}}}{1 - \left[\frac{V_{\mathrm{h}}}{(w-(w-1)V_{\mathrm{h}}}\right]} \qquad (3)$$

where C_i is the initial ion concentration of the pore fluid and C the ion concentration after filling a volume fraction of the pore volume. V_h represents the volume fraction of the formed gas

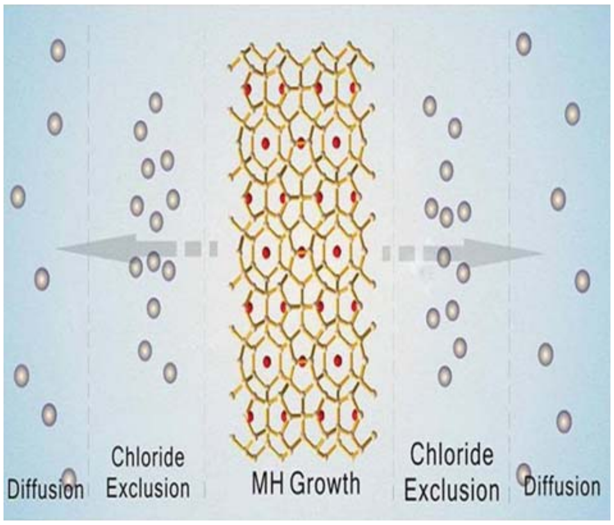

Figure 4. Schematic of chloride enrichment and diffusion.

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hydrate. The term *w* is defined as occupancy density characteristics of the gas hydrate formed depending on guest occupancy with value of 1.264. According to this equation, we attempted to calculate the volume of MH from the experimentally determined chlorinity shown in Figure 5. When the *C* values measured at approximately 10 hr were used, the resulting V_h values were found to be 60, 54, 42, and 6% at contact areas of 251, 126, 75, and 13 mm^2, respectively. Figure 6 shows the relationship between the calculated volume fraction of MH and experimentally measured chloride concentration in time range 0–12 h.

The rate of increase of the chlorinity was quite rapid up to the maximum, and then slowly decreased and stabilized at higher-concentration than the initial level. The decrease of the MH formation rate is closely linked to that of the chloride exclusion rate, and causes the accumulated chlorides to be directly diffused out by concentration gradients, finally resulting in a dynamic equilibrium state. A notable feature among the present experimental findings is that almost two times more than the original chlorinity maintains even after 70 hr. Here, we recognize that this high-value of chlorinity might be caused by two surrounding factors of confined closed space and chloride exclusion due to hydrate formation, but the latter has much more strong effect than the former. Even for this closed experimental system, the MH formation region appears to be relatively small (~0.5 cm apart form the tubes) with respect to the total cell scale (inner diameter of 6.5 cm), which makes the enriched chloride diffusion to proceed for 70 hr. However, a more detailed study is needed to reveal the real nature of ion diffusion pattern. However, as anticipated, at the quite limited contact area on the tube wall (13 mm^2), a noticeable chlorinity change was not observed: an increase of only 20 mM compared with the initial NaCl concentration of 620 mM was detected. As MH forms more actively, more chloride is excluded, leading to an increase of its concentration. Torres et al. indicated that methane transport in the gas-phase, but not in the dissolved phase, must occur to achieve remarkable chloride accumulation, as in the case of site 1249 of the Cascadia margin off Oregon. The enrichment of chloride from 550 to 1000 mM, designated as scenarios 2 and 3 suggested by Torres et al.[6] in their postulation of chloride enrichment from methane-free gas, is described well by their transport reaction model. The maximum chloride level in our experiment is 960–1280 mM, and this is comparatively well matched with the maximum 1000–1100 mM suggested in the model of Torres et al.,[6] within an allowable range of error, with both sets of data indicating that continuous methane gas injection promotes significant chloride enrichment in pore water. Although the kinetic constant vs. seawater depth[6] cannot be fully examined with the present simple cell, the following features are noteworthy. First, a significant amount of

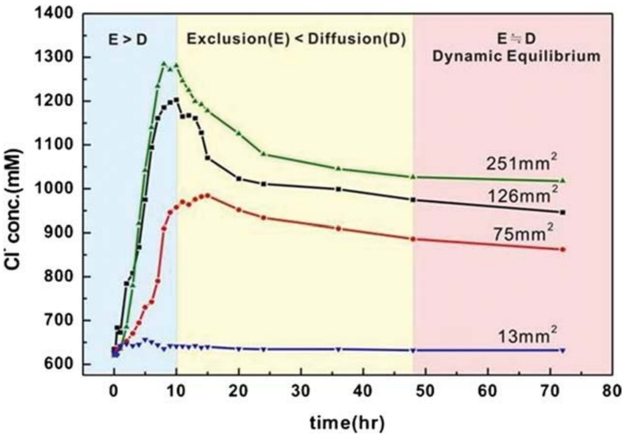

Figure 5. Chlorinity vs. MH formation time at various contacting areas.

The areas are 80 holes in one tube = 251 mm^2 (per tube), 40 holes = 126 mm^2, 24 holes = 75 mm^2 and 4 holes = 13 mm^2. Three tubes were used in each measurement. All steps shown in figure 5 occur simultaneously. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

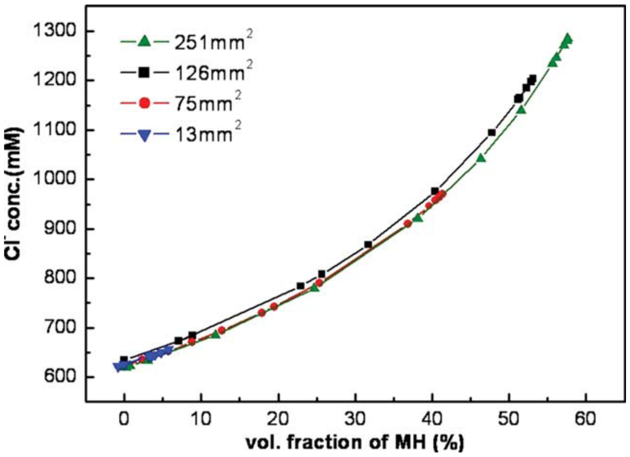

Figure 6. Volume fraction of MH vs. chlorinity calculated with Eq. 1.

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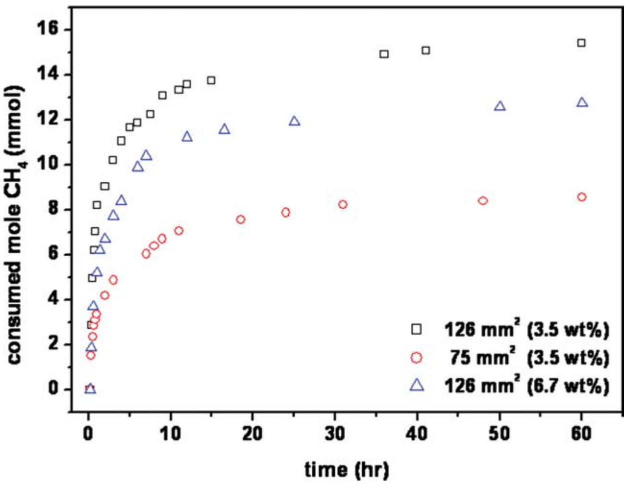

Figure 7. Consumed mole of CH_4 (mmol) with time.

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chloride anions is accumulated at the initial stage (0 ~ about 10 hr), and after 10 hr much higher-chloride concentration relative to that of the original seawater level is observed. Second, the chloride level is strongly affected by the MH formation rate. Here, it must be noted that chloride exclusion seemingly does not occur at a low-MH formation rate in spite of a continuous methane gas supply.

In this experimental system, the water + clay mixture is in direct contact with bulk methane gas, and, thus, we could not physically draw conclusions regarding the principal role of the dissolved methane on MH formation and the resulting chlorinity in sediments. At the present stage, we hoped to observe the relationship between MH formation rate and chloride enrichment regardless of the phase of supplied methane. The low-MH formation rate cannot account for the highly enriched chloride level even if MH formed from gas-phase methane. Also, as can be seen in Site 1249, the effect of dissolved methane appears to be much smaller than that of directly supplied methane gas.[6] Accordingly, this experiment might reflect the main methane gas effect for chloride enrichment in real deepocean surroundings, although the dissolved methane is not taken into account.

Another influencing factor is the degree of compactness in the sediment layer. The porosity of real sediments at Site 1249 is reported as 0.6 to 0.7 beyond about 40 mbsf.[6] On the contrary, the artificial sediments comprising the Na-MMT and NaCl aqueous solution are too compact for methane to transport deeply into the clay sediments along the radial direction in the gas-phase. Although we did not measure the methane concentration in the pore water, no visible hydrate-phase was detected at the final stage of the experiment (~80 hr) far from the tubes (>1 cm). This suggests that MH is actively formed immediately adjacent to the tube in the time scale of our experiment, and, thus, the chlorinity measurements at the region beyond roughly 1 cm are not meaningful. Accordingly, we fixed the positions of tube and electrode at 0.5 cm apart.

The relationship between MH formation rate and time is shown in Figures 7 and 8. We used an aqueous solution with two different initial concentration of NaCl (3.5 and 6.7 wt %). We also included data regarding the consumed moles of CH_4 in Figure 7. A small difference between low- and high-NaCl concentrations was detected for the MH formation rate and CH_4 consumption. First, we measured all the pressure drops according to time, and then determined the slope of the graph divide with the contact area as the methane consumption rates in mmol cm^{-2} hr^{-1}. Finally, we obtained MH formation rates in mol m^{-2} yr^{-1}. In the log–log scale, the MH formation rates almost linearly decrease with time. After 50 hr, the MH formation rates were almost the same for two different contact areas, instead of inversion appearance. However, we placed physical importance on the data measured within 60 hr given their real significance. The decrease of MH formation rate with time results from the MH formation at the interface. Methane supply is gradually hindered by MH formed at the interface, and this behavior seems to be quite natural and could be anticipated in real surroundings. Within the first 10 hr, the MHs significantly form at the rate of more than $\sim 10^3$ mol m^{-2} yr^{-1} while the rates after 10 hr drop to $\sim 10^2$ mol m^{-2} yr^{-1}. As shown in Figure 5, most chloride enrichment was achieved within 10 hr and eventually stabilized after the elapsed time of 50–60 hr. Meanwhile, the direct observation from Figure 8 suggests that MH formation rate must be maintained at least $\sim 10^2$ mol m^{-2} yr^{-1} to efficiently enrich chlorides and retain the acquired chloride level. In the case of the open system of real deep seas, we might expect that a loss of chlorides would occur at a formation rate below $\sim 10^2$ mol m^{-2} yr^{-1}. Interestingly, in the previous report, independent estimates based on seafloor observations at ODP sites 1249 and 1250 indicate MH formation rates at the ridge crest of approximately 10^2 mol m^{-2} yr^{-1}.[6] Also, Haeckel et al.[7] calculated high-MH formation rates (0.15–1.08 mol cm^{-2} yr^{-1} $\approx 10^3$–10^4

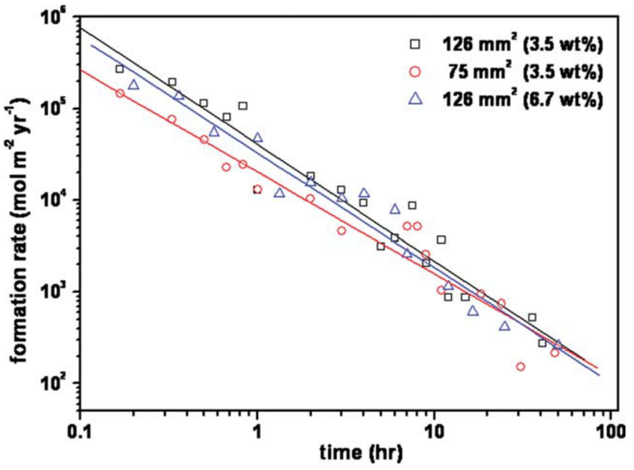

Figure 8. Log–Log plot of MH formation rate (mol m^{-2} yr^{-1}) vs. time (hr).

Linear relationships are shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

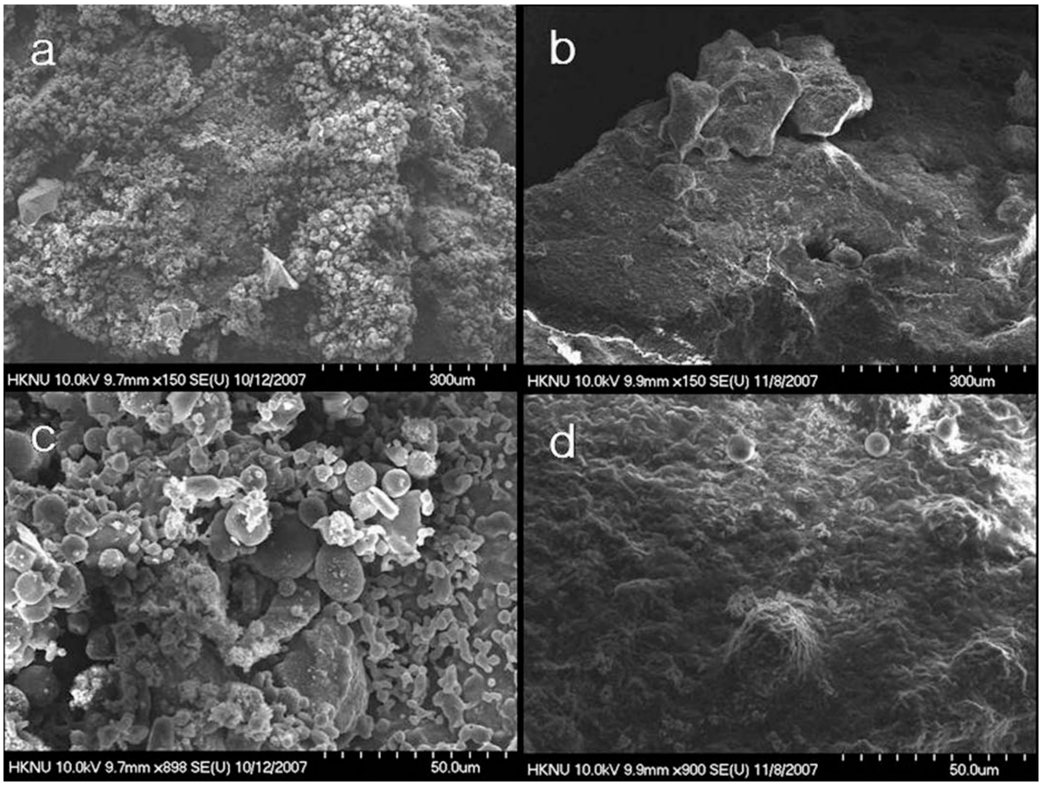

Figure 9. SEM images of Na-MMT 50 wt % + MH with 3.5 wt % NaCl (a), (c) and without NaCl (b), (d).

mol m^{-2} yr^{-1}) for positive Cl^- anomalies observed at the southern summit of the hydrate ridge.

Through a full analysis of present outcomes, we suggest a reasonable scenario to account for the chloride level in natural deep-sea sediments. At the first stage, the chloride anions are enriched continuously and strongly at a high-MH formation rate above $\sim 10^3$ mol m^{-2} yr^{-1}. At the second stage, the accumulated high-chlorinity is kept at an intermediate MH formation rate of $\sim 10^2$ mol m^{-2} yr^{-1}. At the final stage, where the MH formation rate is far below 10^2 mol m^{-2} yr^{-1}, the stably maintained high-chlorinity becomes substantially lowered, eventually reaching the seawater level. Accordingly, the uncommonly high-chlorinity would only be discovered in the region, where the first and second stage prevails but not in the final-stage region.

Another notable feature is that all the experimental (Na-MMT + NaCl) samples comprising chloride anions exhibited quite different viscosity and morphology patterns from pure Na-MMT containing no salts. For (Na-MMT + pure water) hydrates, we observed spheres of 5–10 μm radii on clay-MH surface. As shown in the FE-SEM (Scanning Electron Microscope) results of Figures. 9a, c. On the contrary, for (Na-MMT + seawater) hydrates, their surface texture appeared to be different as shown in the FE-SEM results of Figures 9b, d. This flocculation phenomenon induced by salt ions is possibly explained as follows; in solutions of high-ionic strength, the cloud of counterions becomes so compressed that the particles may approach each other close enough for the van der Waals attraction between them to stick them together.[10,11] However, we must keep in mind that the real marine sediments contain various types of geochemical components whose separate effects on natural gas hydrate or carbon dioxide hydrate formation cannot be clearly defined in such a heterogeneous system of high-complexity. Nevertheless, the preliminary morphology studies strongly suggest that the dissolved ions play an important role in forming/dissociating gas hydrates in the marine sediments.

Conclusion

As the first attempt, we examined (1) the MH formation effect on chloride level and (2) anomalous chloride enrichment induced by ion exclusion in sediment-pore fluids. Also, we attempt to reveal the chloride effect on the clay + MH morphology. Chloride concentration increased under a fast MH formation rate, but no noticeable concentration change was detected under a relatively low-rate. We also conclude that the formation rate of MH should be maintained at least $\sim 10^2$ mol m^{-2} yr^{-1} to enrich chlorides and retain the enriched chlorides. Through a full analysis of present outcomes, we suggest a reasonable scenario for the appearance of abnormal chloride levels in natural deep-sea sediments. Although the present experimental system could not perfectly reflect all the external variables related to real deep-sea sediments such as vertical advections, meaningful outcomes for describing abnormal chlorinity enrichment could nevertheless be drawn. This experimental system could feasibly be simply and widely applied to various types of marine deposits containing ionic salts and to a quantitative analysis of possible ocean water acidity caused by carbon dioxide sequestration.

Acknowledgments

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