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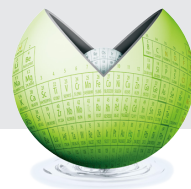
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Anomalous high Cl^- concentration in porewater of marine sediments from the methane hydrate-distributed area off Joetsu, eastern margin of the Japan Sea

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Abstract

We analyzed the chemical composition of porewater extracted from sediment samples collected at shallow methane hydrate fields off Joetsu, in the Japan Sea, during Expedition CK22-03 of the drilling vessel *Chikyu* in 2022. At Joetsu Knoll, where massive methane hydrates were observed, the Cl^- concentrations of porewaters were high (879–1282 mM) at the depth interval between 12 and 60 meters below the seafloor and roughly twice the concentration in the sediment at the top of the core (545 mM). These elevated Cl^- concentrations were observed at greater depths and were higher than those reported in previous studies of this field. We analyzed the δD and $\delta^{18}\text{O}$ of the porewaters and quantitatively confirmed that the hypersaline waters represent residual waters accumulated by rapid formation of methane hydrates. Based on Cl^- concentration, amount of methane incorporated into hydrates in the sediments was estimated to be 51–81 m^3/m^3 at standard temperature and pressure.

Keywords

shallow methane hydrate, hypersaline water, oxygen and hydrogen isotopic compositions

Dates

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Introduction

The eastern margin of the Japan Sea is one of the fields where methane hydrates occur at or near the seafloor. Previous studies in this field have investigated sediments down to several tens of meters below the seafloor, and the porewaters within a few meters of the surface exhibited higher Cl^- concentrations than those in seawater (Hiruta *et al.*, 2009; Matsumoto *et al.*, 2009). Such hypersaline water has also been found at the Hydrate Ridge offshore of Oregon and is concluded to be residual water accumulated by rapid formation of methane hydrates in sediments. The rapid formation of methane

hydrates, occurring faster than the replenishment of seawater or porewater from the surrounding environment, results in the accumulation of hypersaline residual water around the hydrates (e.g., Kvenvolden and Kastner, 1990; Milkov *et al.*, 2004; Torres *et al.*, 2004). During Expedition CK22-03 of the D/V *Chikyu* in 2022, we retrieved sediment cores down to approximately 140 meters below the seafloor (mbsf) in the methane hydrate field off Joetsu and observed higher Cl^- concentrations at greater depths than those reported in previous studies of this field (Hiruta *et al.*, 2009). Our objective was to quantitatively confirm that the hypersaline waters represent residual waters based on hydrogen and oxygen



isotopic compositions and Cl^- concentrations of the porewaters.

Materials and Methods

Coring was conducted at two areas, Joetsu Knoll and Umitaka Spur, and four sediment cores in total, two from each area, were used in this study. In each area, one core was obtained from a site where the occurrence of methane hydrates was expected, based on the presence of a bottom-simulating-reflector (BSR) and gas chimney structures observed in the seismic sections. The other core was obtained from a site where the occurrence of methane hydrates was not expected.

On Joetsu Knoll, Hole C8006A was drilled to a depth of 129 mbsf and penetrated methane hydrate layers at Site C8006 (Supplementary Fig. S1), where a BSR was observed at the interval between 110 and 121 mbsf. Coring at this site was conducted at depth intervals of 0–2, 11–16.8, 47–49.5, 58–60.3, 61–62.2, 111–120, and 120–129 mbsf, avoiding methane hydrate-bearing layers due to the difficulty of coring the massive methane hydrate layers. Hole C8007A, located at the non-methane hydrate site (C8007), was drilled continuously to a depth of 144 mbsf.

On Umitaka Spur, Hole C8009A was drilled to a depth of 122 mbsf and penetrated methane hydrate layers at Site C8009 (Supplementary Fig. S1), where a BSR was observed at the depth of 122 mbsf at the site. Coring at Site C8009 was conducted only at depth intervals of 0–2.8 and 113–122 mbsf, avoiding methane hydrate-bearing layers. Hole C8008A, located at the non-methane hydrate site (C8008), was continuously drilled to a depth of 144 mbsf.

Hereafter, Sites C8006 and C8009, where methane hydrates occur, are referred to as methane hydrate sites, while Sites C8007 and C8008, where no methane hydrates were identified, are referred to as reference sites.

To extract porewater, the subsamples of the sediment were collected as 5–20 cm length whole-round sample from the sediment core samples. Porewater samples were extracted from the subsamples using a Manheim hydraulic squeezer on board (Manheim, 1966).

At the reference sites, the subsamples for the porewater extraction were collected at approximately 5 m intervals from the sediment core samples. At Site C8006, the subsamples were collected only at depths of 12.2, 15.8, 49.0, and 59.5 mbsf. In the interval between 110 and 122 mbsf, where methane hydrate does not exist, and the subsamples were collected every 3–6 m. At Site C8009, the subsamples were collected only at depths of 2.5, 2.6, 115.6, 116.5, and 120.5 mbsf.

The Cl^- concentrations of the porewater samples were analyzed on board by the Mohr method (Gieskes *et al.*,

1991). Stable oxygen and hydrogen isotopic compositions (δD and $\delta^{18}\text{O}$) of porewater were analyzed by using a laser absorption spectrometer (LWIA-24-EP, Los Gatos Research Inc.) (Ijiri *et al.*, 2018). Results are presented here as per mil deviation relative to Vienna Standard Mean Ocean Water (VSMOW). The standard error estimated from repeated analyses of the IAPSO standard seawater (International Association of the Physical Sciences of the Ocean) was in the range of 0.3% to 0.7%. The standard deviations of δD and $\delta^{18}\text{O}$, estimated from repeated analysis of the laboratory standard (deep sea water of Indian Ocean), were 0.5‰ and 0.1‰, respectively.

Results

At the reference sites, C8007 and C8008, the Cl^- concentrations near the seafloor were 545 and 543 mM, respectively, similar to the concentration observed in the bottom seawater off Joetsu (Hiruta *et al.*, 2009). At both reference sites, vertical profiles of the Cl^- concentrations showed decrease with depth and reached values of 460 mM at 143.0 mbsf and 325 mM at 137.4 mbsf, respectively (Fig. 1a, Table 1). Vertical profiles of the δD values at the reference sites C8007 and C8008 showed decrease with depth from -1.2‰ near the seafloor to -7.7‰ and -8‰ , respectively (Fig. 1b, Table 1). Vertical profiles of the $\delta^{18}\text{O}$ values at the reference sites C8007 and C8008 showed decrease with depth from 0‰ near the seafloor to -1.9‰ and -0.7‰ , respectively (Fig. 1c, Table 1). Tomaru *et al.* (2012) documented that the observed decreases in Cl^- concentrations and δD and $\delta^{18}\text{O}$ values with increasing depth are due to dehydration of clay minerals or alteration of Quaternary volcanic ash.

At the methane hydrate site on Joetsu Knoll (C8006), the Cl^- concentrations at the depth interval between 12 and 60 mbsf were high (879–1282 mM), reaching more than twice as high as that of the bottom seawater (Fig. 1a, Table 1). At the depth interval between 112.6 mbsf and 126.8 mbsf, the Cl^- concentrations ranged from 565 to 582 mM and were similar to that of bottom seawater (Fig. 1a, Table 1). The δD and $\delta^{18}\text{O}$ values at the depth interval between 12 and 60 mbsf where the Cl^- concentrations were anomalously high were less than -9‰ and less than -1‰ , respectively. Below 110 mbsf, the δD and $\delta^{18}\text{O}$ values ranged from -4.0‰ to -7.5‰ and from -1.3‰ to -1.4‰ , respectively (Fig. 1b, c, Table 1).

At the methane hydrate site on Umitaka Spur (C8009), the Cl^- concentrations ranged from 557 to 653 mM at depths of 2.5, 2.6, 115.6, 116.5, and 120.5 mbsf (Fig. 1a, Table 1). The δD and $\delta^{18}\text{O}$ value were less than -8.4‰ and less than -0.9‰ at depths of 115.6, 116.5, and 120.5 mbsf (Table 1).

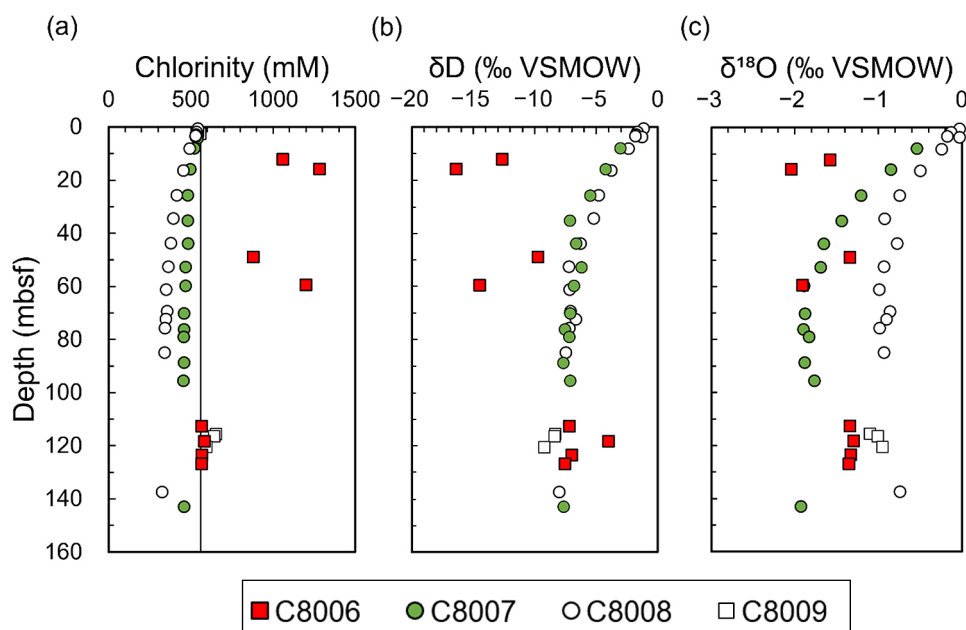


Fig. 1. Vertical profiles of porewater chemistry obtained from Joetsu Knoll and Umitaka Spur. (a) Cl^- concentration, (b) δD , and (c) $\delta^{18}\text{O}$ for sites C8006–C8009. In Fig. 1a, the Cl^- concentration of near-seafloor porewater is shown by the vertical black line.

Discussion

At Site C8006, the Cl^- anomalies were observed at greater depths than those reported by Hiruta *et al.* (2009), with concentrations exceeding their reported values by more than 300 mM. Hiruta *et al.* (2009) documented a maximum Cl^- concentrations of 746 mM at the central part of Umitaka Spur, interpreted as residual water surrounding methane hydrates. The δD and $\delta^{18}\text{O}$ values of the hypersaline waters at Site C8006 indicate that these are also residual waters. The Cl^- concentrations showed a negative correlation with both δD and $\delta^{18}\text{O}$ values (Fig. 2a, b), consistent with the characteristics of residual water around the methane hydrates. During the formation of methane hydrates, water molecules crystallize and form clathrates, and then methane molecules incorporate into the clathrates, Cl^- in the porewater is excluded, and D and ^{18}O are preferentially incorporated into the hydrates (Maekawa, 2004). As a result, the residual water surrounding the methane hydrates becomes enriched in Cl^- , ^1H , and ^{16}O , that is, Cl^- concentration is higher and the δD and $\delta^{18}\text{O}$ values are lower in the residual water than in the porewater prior to the formation of methane hydrates.

Assuming that the δD and $\delta^{18}\text{O}$ values of porewater changed according to Rayleigh-type isotopic fractionation in a closed system, we quantitatively confirmed that hypersaline waters represent residual waters (Fig. 3a, b) by estimating the isotopic variations of porewater following formation of methane hydrate. The equation for Rayleigh-type fractionation can be written as follows using delta notation:

$$\delta - \delta_0 = 1000(\alpha - 1) \ln(f) \quad (1)$$

where δ_0 and δ represent the isotopic compositions of porewater before and after the formation of methane hydrates, respectively; α is the isotopic fractionation factor between the initial porewater (i.e., porewater prior to the formation of methane hydrates) and water incorporated into methane hydrates; and f is the fraction of porewater remaining after the formation of methane hydrates. We used the reported isotopic fractionation factors of hydrogen and oxygen in water between a gas hydrate (Structure I) and NaCl solution ($\alpha_{\text{hydrogen}} = 1.017$; $\alpha_{\text{oxygen}} = 1.0024$; Maekawa, 2004). The value of f was calculated based on the difference between the Cl^- concentration in porewater before formation of methane hydrates ($[\text{Cl}^-_0]$) and the observed high Cl^- concentration ($[\text{Cl}^-]$) as follows:

$$f = \frac{[\text{Cl}^-_0]}{[\text{Cl}^-]} \quad (2)$$

We used two sets of values of Cl^- concentrations and isotopic compositions of porewaters as $[\text{Cl}^-_0]$ and δ_0 values of D and O: Case 1) values similar to those near the seafloor at reference site C8008 (Cl^- : 543 mM, δD : -1.2‰ , $\delta^{18}\text{O}$: 0.0‰ ; depth 0.5 mbsf) and Case 2) values obtained from 59.8 mbsf at reference site C8007 (Cl^- : 469 mM, δD : -6.8‰ , $\delta^{18}\text{O}$: -1.9‰). This depth at site C8007 is equivalent to the deepest depth where hypersaline water was identified at the methane hydrate site (C8006). Case 2 represents a scenario in which methane hydrate forms from porewater similar to that observed at the reference sites, characterized by low Cl^- concentration

Table 1. Depth below seafloor, chlorinity, hydrogen isotopic composition, and oxygen isotopic composition of porewater samples from sites C8006, C8007, C8008, and C8009

Sample	Depth (mbsf)	Chlorinity (mM)	δD (‰ VSMOW)	$\delta^{18}O$ (‰ VSMOW)
Joetsu Knoll Methane hydrate site				
C8006A-2H-2	12.15	1059	−12.6	−1.6
C8006A-2H-8	15.75	1282	−16.4	−2.0
C8006A-3F-2	48.98	879	−9.7	−1.3
C8006A-4F-2	59.49	1199	−14.5	−1.9
C8006A-6H-3	112.63	566	−7.2	−1.3
C8006A-6H-12	118.32	582	−4.0	−1.3
C8006A-7H-7	123.51	568	−7.0	−1.3
C8006A-7H-11	126.84	565	−7.5	−1.4
Joetsu Knoll-Reference site				
C8007A-1H-1	1.00	545	—	—
C8007A-1H-2	1.67	544	—	—
C8007A-1H-4	2.12	543	—	—
C8007A-1H-5	3.13	542	—	—
C8007A-1H-7	4.19	540	—	—
C8007A-1H-10	7.98	522	−3.0	−0.5
C8007A-2H-9	15.86	497	−4.3	−0.8
C8007A-3H-9	25.74	481	−5.5	−1.2
C8007A-4H-9	35.26	481	−7.1	−1.4
C8007A-5H-9	43.87	483	−6.6	−1.7
C8007A-6H-9	52.76	467	−6.2	−1.7
C8007A-7H-8	59.77	469	−6.8	−1.9
C8007A-8H-10	70.22	458	−7.1	−1.9
C8007A-9H-7	76.17	460	−7.5	−1.9
C8007A-9H-11	79.00	457	−7.2	−1.8
C8007A-10H-11	88.75	460	−7.7	−1.9
C8007A-11H-8	95.56	456	−7.1	−1.8
C8007A-12H-9	142.98	460	−7.7	−1.9
Umitaka Spur Reference site				
C8008A-1H-1	0.54	543	−1.2	−0.0
C8008A-1H-3	1.85	535	−1.7	−0.1
C8008A-1H-4	2.77	532	−1.8	−0.0
C8008A-1H-5	3.68	530	−1.3	−0.0
C8008A-1H-5	3.34	530	−1.8	−0.2
C8008A-1H-12	8.14	493	−2.4	−0.2
C8008A-2H-10	16.34	456	−3.8	−0.5
C8008A-3H-11	25.70	415	−4.8	−0.7
C8008A-4H-10	34.41	394	−5.2	−0.9
C8008A-5H-12	43.80	379	−6.3	−0.8
C8008A-6H-9	52.57	363	−7.2	−0.9
C8008A-7H-9	61.18	351	−7.2	−1.0
C8008A-8H-11	69.38	355	−7.1	−0.9
C8008A-9H-1	72.36	349	−6.7	−0.9
C8008A-9H-8	75.67	343	−7.2	−1.0
C8008A-10H-9	84.93	341	−7.5	−0.9
C8008A-11H-4	137.39	325	−8.0	−0.7
Umitaka Spur Methane hydrate site				
C8009A-1H-5	2.49	557	—	—
C8009A-1H-5	2.56	557	—	—
C8009A-2H-3	115.55	653	−8.4	−1.1
C8009A-2H-5	116.45	642	−8.4	−1.0
C8009A-2H-12	120.48	595	−9.2	−0.9

* —: No data

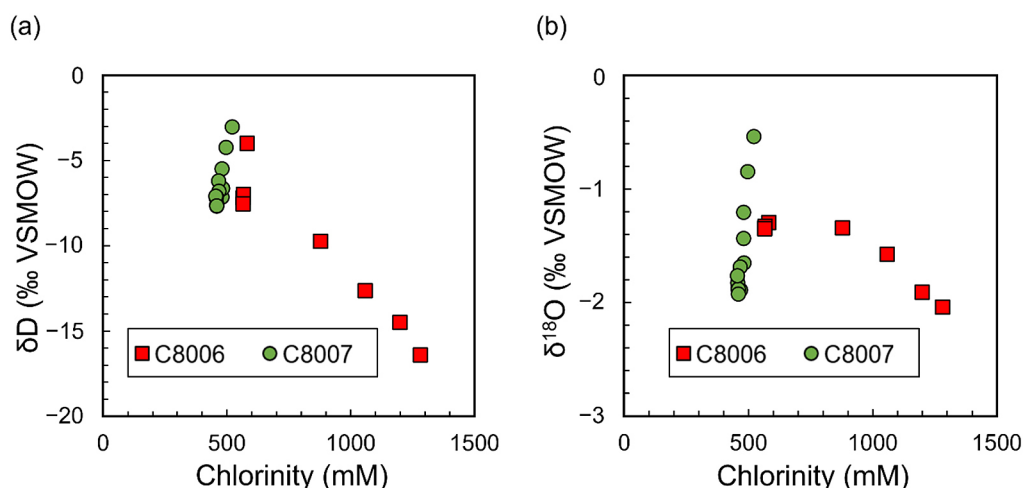


Fig. 2. Plots of stable isotope ratios vs. Cl^- . (a) δD vs. Cl^- and (b) $\delta^{18}\text{O}$ vs. Cl^- for sites C8006 and C8007.

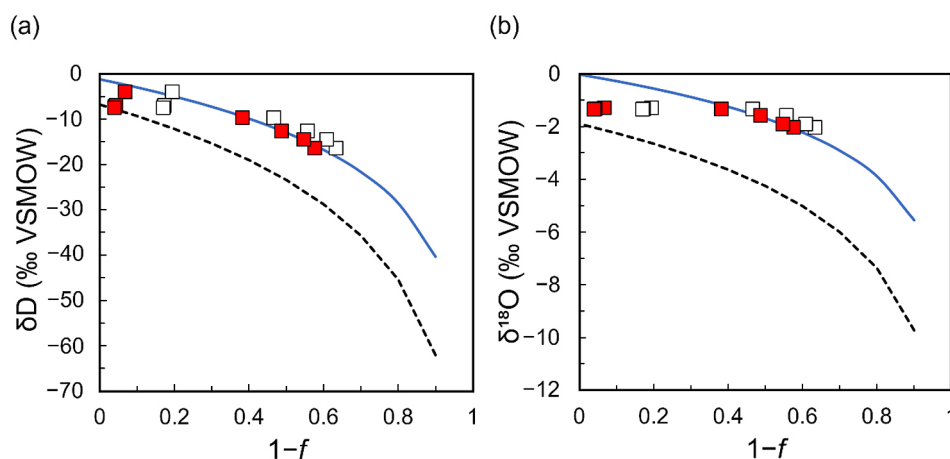


Fig. 3. Estimated variations of (a) δD and (b) $\delta^{18}\text{O}$ of the residual waters associated with formation of methane hydrate. Here, $1-f$ represents the fraction of water molecules incorporated into methane hydrates from porewater during the formation. The red and white squares show the relationship between stable isotope data and $1-f$ during formation of methane hydrate, calculated from the Cl^- concentrations of porewaters observed at methane hydrate site C8006. Red squares represent Case 1, calculated using the Cl^- , δD , and $\delta^{18}\text{O}$ values of porewater observed near the seafloor at the reference site in Umitaka Spur as $[\text{Cl}^-]_0$ and δ_0 values (Cl^- : 543 mM, δD : -1.2‰ , $\delta^{18}\text{O}$: 0.0‰ ; depth 0.5 mbsf). White squares represent Case 2, calculated using the values for porewater at 59.8 mbsf at the reference site at Joetsu Knoll as $[\text{Cl}^-]_0$ and δ_0 values (469 mM, δD : -6.8‰ , $\delta^{18}\text{O}$: -1.9‰). The blue solid and black dashed lines represent the expected isotopic changes during formation of methane hydrate with Rayleigh-type isotopic fractionation using porewater with a Cl^- concentration similar to those observed near the seafloor (543 mM) and at 59.8 mbsf at the Joetsu Knoll reference site (469 mM), respectively ($\alpha_{\text{hydrogen}} = 1.017$, $\alpha_{\text{oxygen}} = 1.0024$; Maekawa, 2004).

and δD and $\delta^{18}\text{O}$ values, likely supplied from deeper strata.

When Case 2 values were used, the estimated isotopic variations as a function of $1-f$ (the fraction of water molecules incorporated into methane hydrates from porewater during hydrates formation) did not match the observed data. In contrast, good agreement with the observed values was obtained when Case 1 values were used (Fig. 3a, b). This correspondence suggested that methane hydrates were formed in a closed system using porewater with a Cl^- concentration and isotopic compositions similar to those observed near the seafloor, rather

than from porewater with a lower Cl^- concentration and the δD and $\delta^{18}\text{O}$ values at the reference sites.

Because our results confirmed that methane hydrates were formed in a closed system from porewater with a Cl^- concentration similar to that observed near the seafloor, we estimated the amounts of water and methane incorporated into the methane hydrates using the f value derived from the Cl^- concentration near the seafloor at the reference site using Eq. 2. The $1-f$ values of 0.38–0.58 indicated that 38–58% of the porewater in the sediment before hydrate formation was incorporated into the hydrates. We then calculated the amount of water in the

hydrates per cubic meter of sediment based on the porosity of the sediment (55–65%) and the proportion of water in the hydrates ($2.35\text{--}3.74 \times 10^5 \text{ g/m}^3$ [$1.30\text{--}2.08 \times 10^4 \text{ mol/m}^3$]). Assuming Structure I methane hydrates (molecular formula: $\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$), the methane concentration of the hydrates fell in the range from 2.27×10^3 to $3.61 \times 10^3 \text{ mol/m}^3$. We consequently estimated the amounts of methane contained in the sediments as hydrates to be $51\text{--}81 \text{ m}^3/\text{m}^3$ at standard temperature and pressure. This amount of methane is markedly higher than that in another area around Japan, such as the mud-volcano field in the Kumano forearc basin ($6.4 \text{ m}^3/\text{m}^3$) (Ijiri *et al.*, 2018). The difference between this study and the Kumano forearc basin could be attributed to the difference of methane hydrate occurrence: massive methane hydrates are found in the sediments off Joetsu, whereas small grains of methane hydrates fill pore spaces and veins in the mud volcano sediments in the Kumano forearc basin.

Similarly high Cl^- concentrations (up to 1370 mM) have been reported at Hydrate Ridge offshore of Oregon within the upper ~30 mbsf in the sediment column because of the extremely high methane flux from deeper layers (Torres *et al.*, 2004). By comparison, at Joetsu Knoll, the occurrence of elevated Cl^- concentrations from approximately 10 to 60 mbsf, a wider depth range than at Hydrate Ridge, implies that methane hydrate formation occurred more extensively likely due to a larger supply of methane than at Hydrate Ridge.

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Supplementary Materials

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