Geochemistry of the interstitial waters of the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well

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Abstract: Interstitial waters were extracted from the sediments of the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well drilled in the Mackenzie Delta, and analyzed for Cl−, SO4²−, Na+, K+, Ca²+, Mg²+, Sr²+, and Ba²+. Cored intervals are divided into zone 1 (low salinity), zone 2 (higher salinity), zone 3 (low salinity), and zone 4 (high salinity), in descending order. Zones 1 and 3 correspond to gas-hydrate-bearing sandstone, whereas zone 2 is a gas-hydrate-free mudstone and zone 4 a gas-hydrate-free sandstone below the base of gas hydrate stability. Anomalies of low Cl− and Na+ concentrations indicate that gas hydrate saturations (Sh) are 60 to 85%, which is not always consistent with Sh values obtained from logging data. This is because of a build-up of either saline or fresher residual water during the formation/dissociation of gas hydrate in a closed system. An unusually higher concentration of SO4²− in organic-rich, deep-seated sediments suggests a likely invasion of seawater and contamination by drilling fluids.

Résumé : Nous avons mesuré les teneurs en Cl−, SO4²−, Na+, K+, Ca²+, Mg²+, Sr²+ et Ba²+ d’eaux interstitielles extraites de sédiments provenant du puits de recherche sur la production d’hydrates de gaz JAPEX/JNOC/GSC et al. Mallik 5L-38, situé dans le delta du Mackenzie. Nous avons subdivisé les intervalles carottés en quatre zones, soit, en ordre de profondeur croissante, la zone 1 (à faible salinité), la zone 2 (à salinité plus élevée), la zone 3 (à faible salinité) et la zone 4 (à salinité élevée). Les zones 1 et 3 sont constituées de grès renfermant des hydrates de gaz, alors que la zone 2 se compose de mudstone dépourvu d’hydrates de gaz et que la zone 4 est constituée de grès également dépourvu d’hydrates de gaz, situé sous la base de la zone de stabilité des hydrates de gaz. A partir de teneurs anormalement faibles en Cl− et en Na+ dans certains intervalles, nous avons estimé des saturations en hydrates de gaz (Sh) s’échelonnant entre 60 et 85 %. Ces valeurs ne correspondent pas toujours aux valeurs Sh obtenues à partir des données diagraphiques, en raison de la présence d’eau résiduelle plus salée ou plus douce dans certains intervalles. Les accumulations d’eau plus douce proviennent peut-être de la dissociation d’hydrates de gaz, alors que celles d’eau plus salée pourraient être le résultat de la formation d’hydrates de gaz en système fermé. Des teneurs exceptionnellement élevées en SO4²− dans des sédiments profonds riches en matière organique suggèrent qu’il y a eu pénétration par de l’eau de mer ou contamination par des fluides de forage.
INTRODUCTION

The JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well was drilled in January–March of 2002 in the Mackenzie Delta. The objectives of the drilling program were to 1) understand more about the occurrence, distribution, and amount of gas hydrate in sediments below the permafrost; 2) develop new methods and technology to evaluate gas hydrate deposits; and 3) conduct production tests of natural gas from gas hydrate reservoirs (Dallimore and Collett, 2005).

Because of the ephemeral nature of gas hydrate, the amount of subsurface gas hydrate is not directly evaluated from the recovered core samples. Among several established proxy methods, the freshening effect (i.e. low chloride anomaly resulting from gas hydrate dissociation during core retrieval and sampling) has been frequently used as a reliable proxy (e.g. Paull and Matsumoto, 2000; Matsumoto et al., 2000). This proxy method is based on the assumptions that 1) the gas hydrate deposits develop in an open system with respect to water; 2) the interstitial water chemistry does not change greatly during the formation/dissociation of gas hydrate; and (3) the overall geochemistry of the in situ interstitial waters is known and nearly constant throughout the gas-hydrate-bearing units. These assumptions are applicable to marine gas hydrate deposits, but not readily applicable to the gas hydrate deposits in the Mackenzie Delta. The host sedimentary rocks, the Oligocene Kugmallit and Miocene Mackenzie Bay sequences, are composed of interbedded freshwater fluvial to coastal plain sediments without any marine microfossils (Jenner et al., 1999; Medioli et al., 2005). Units with pore-filling gas hydrate and intercalations of impermeable, organic-rich claystone may hamper or even protect fluid flow, generating local closed-system environments. The purpose of this paper is to provide a fundamental geochemical data set on the interstitial waters for modelling the origin and evolution of the interstitial waters in relation to formation of gas hydrate in an arctic, terrestrial, subpermafrost environment.

STUDY METHODS

Sampling

Continuous coring was conducted for the interval 885.6 to 1151.4 m of the Mallik 5L-38 gas hydrate production research well (Dallimore et al., 2005b; Fig. 1). Gas hydrate zones were expected to occur between 890 and 1100 m, assuming that the base of gas hydrate stability (BGHS) occurs at approximately 1110 m, as was observed in the Mallik 2L-38 gas hydrate research well, drilled in 1998 (Dallimore and Collett, 1999; Uchida et al., 1999).

Recovered core sections were taken into a cold laboratory at the well site for initial observation, description, and sampling. Samples of whole round core, approximately 10 cm long, were collected every 1 to 2 m for study of the sediments and water geochemistry. Approximately 2 cm were shaved off these samples to remove any potential contamination from drilling fluids during core drilling and retrieval. These prepared samples were then sealed in gas-tight plastic bags, labelled, and transported to the Inuvik Research Centre, where they were squeezed to extract interstitial waters using a Manheim-type hydraulic squeezing system. Extracted waters were filtered through a 0.45 μm disk filter, stored in glass vials, refrigerated, and shipped to the University of Tokyo for geochemical analysis. A total of 137 interstitial water samples was obtained, plus one Mackenzie River water sample and one drilling-fluid sample for comparison.

Measurements

The samples of interstitial waters were diluted 1:200 with pure water (Milli-Q® Ultrapure Water Purification System) and analyzed for dissolved ions. The concentrations of Cl\(^-\) and SO\(_4^{2-}\) were determined at the University of Tokyo using a Shimadzu PIA-1000 ion chromatograph; Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), and K\(^{+}\) were determined on a Seiko Instruments SPS-7700 inductively coupled plasma–atomic emission spectrometer; and Sr\(^{2+}\) and Ba\(^{2+}\) were determined on a Yokohama–Hewlett Packard ICP-4500 inductively coupled plasma–mass spectrometer. The precision of the measurements was estimated to be approximately ±10% of the amounts present.

CORE-LOG CORRELATION

High-quality wireline logs, such as sonic, resistivity, and fullbore formation microimage (FMI), were obtained for the Mallik 5L-38 well (Collett et al., 2005). Correlation of sample-based data (core analysis) with in situ physical parameters

Figure 1. Location of the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well, Mackenzie Delta, Northwest Territories, Canada.
(logging) should delineate the occurrence, distribution, and evolution of the subsurface gas hydrate system (e.g. Lee and Collett, 1999). It is not easy, however, to correlate logging data with core data because core depths are given by the length of rigid pipes, whereas the depths for logging data are based on the length of an elastic wire. Even after wire-stretch corrections, discrepancies still exist between the two depths. Further depth corrections were therefore carried out on the logging data by comparing visual core descriptions with gamma-ray logs and the FMI log.

The lithological log (Fig. 2) was created from initial core inspection in a trailer at the drill site and from detailed descriptions at the Inuvik Research Centre (Medioli et al., 2005). Note that core depths and log depths do not exactly correspond. The cored gas-hydrate-bearing interval is composed of interbedded sandstone and claystone/siltstone with occasional thick coal seams of mixed fluviodeltaic to shallow-marine environments. The sediment cores were recovered almost continuously by means of conventional core barrels 2 to 4 m in length and 15 cm in diameter (Fig. 2). The core recovery was very good throughout, particularly for methane-hydrate-bearing intervals, where it ranged from 78 to 100%. Nevertheless, there were some gaps due either to missing intervals or to splitting of the cores during core recovery. For consistency and simplicity in core handling, the separated parts were moved to the top of the core interval for cores 3, 5, 17, 22, etc., whereas the split pieces were moved to the bottom of the interval only for cores 2, 4, and 23 (see Fig. 2). Such a field procedure means that the depths of the sediment cores from the intervals of poor core recovery do not always indicate the exact depth. This may also contribute to the discrepancies between core depths and logging depths.

Gamma-ray logs (GR) are useful in identifying lithology and lithological boundaries. Gamma-ray intensities depend on the concentration of potassium, which in turn reflects the abundance of clay minerals. The depth profile of gamma-ray intensities (Fig. 2), ranging mostly between 30 and 135 API, roughly corresponds to the lithology (e.g. low GR values in sand and high values in clay/silt). Abrupt transitions between low- and high-GR responses are expected to coincide with the lithological change between sand- and clay-rich facies, but the boundaries do not always occur at the same depth in the core as on the geophysical log. Such discrepancies have been clearly recognized at 20 horizons (marked as horizons A to T in Fig. 2).

Massive to laminated clayey silt is underlain by fine sand with pebbles at 907.3 m in cores 6 and 7, with the gamma-ray (GR) log showing a sharp drop from high to low values at around 906 m (horizon A). Interbedded sandstone, siltstone, and claystone layers occur at 925.8 to 926.8 m within a pebbly sandstone unit, whereas a high-GR spike appears at about 924 to 925 m (horizon B). Two thick coal beds, at 934.3 m and 941.0 m, in clay and silty clay are represented by sharp drops in GR response at 932.0 m and 939.3 m, respectively (horizons C, D). Medium to coarse sand is underlain by laminated fine sand and silty clay at 951.0 m (horizon E), which overlies fine to medium sand with common pebbles at 953.0 m (horizon F). These transitions are represented by abrupt changes in GR response at 949.0 m and 951.0 m, respectively. Massive to weakly laminated sand overlies silty clay and clayey silt at 963.0 m (horizon G). Gas-hydrate-rich sand was collected at 962.0 m, just above horizon G, from a horizon that gives a high-GR response (implying silty clay). Horizon G of the core must correspond to a sharp increase in GR response and a decrease in resistivity at 961.5 m. Pebby sand is underlain by black clay and silty clay at 982.0 m (horizon H), whereas a transition from low to high gamma-ray log response occurs at 980.0 m. The boundary between laminated silty sand and massive sand at 993.3 m (horizon I) is represented by a sharp contrast in the FMI log at 992.5 m. A 0.4 m thick black coal occurs at 1005.0 m (horizon J), corresponding to a sharp drop in the GR response at 1003.6 m. A drop in GR at 1012.2 m may reflect the occurrence of thin sand at 1013.0 m (horizon K). A coal seam at 1042.3 to 1043.3 m (horizon L) is shown at about 1041.5 m by lower GR values within a high-GR plateau. Such drops in GR also occur at 1053.5 and 1061.8 m, corresponding to coal beds at 1057.5 m (horizon M) and 1063.5 m (horizon N), respectively. A layer composed mainly of silt and clay occurs between 1080.0 m (horizon O) and 1086.5 m (horizon Q), with coal layers occurring at 1081.5 m (horizon P); they are reflected by drastic changes in GR values at 1078.5, 1085.0, and 1079.5 m, respectively. A thin intercalation of silty clay (horizon R) in massive sand at 1099.5 m is reflected by a small but sharp spike in GR at 1098.0 m. Approximately 4 m of sandstone at 1143.0 m (horizon S) to 1147.2 m (horizon T) is clearly recognized as a segment of high-GR response between 1141.5 and 1145.2 m.

As described above and depicted in Figure 2, the gamma-ray profile was observed to be 0.8 to 2.1 m (mean 1.59 m) shallower than the corresponding lithological record throughout the Mallik 5L-38 well. The profile was separated into 20 depth zones in order to make a depth correction to the log by applying the relevant correction factor (0.8–2.1 m) to each depth zone (e.g. a +1.3 m correction for zone A [890.0 m to 915 m], a +1.8 m correction for zone B [915 m to 928.2 m], and a +2.1 m correction for zone C [928.2 m to 935.6 m]). Even after the application of these corrections, there were still some depth discrepancies in shallow cores with poor core recovery. A 2.3 m thick section of sand and clayey silt in core 4 should move up approximately 1.5 m to the top of the core; otherwise, the gas hydrate sample collected from core 4 corresponds to a high-gamma-ray and high-resistivity interval (Fig. 2). Also, a 2.0 m thick section of clayey silt and pebbly sand was moved down 1.3 m in core 4, corresponding to a sharp transition of GR values. Another zone of poor core recovery between 1050 and 1070 m was corrected using coal-bed occurrence. The interval 1115 to 1140 m could not be corrected due to the sandy lithology and low-GR response. Nevertheless, these horizons are all below the gas-hydrate-bearing zone, and the lithology and logging data are straightforward, as shown by FMI.
Figure 2. Correlation of core lithology, downhole gamma-ray log, and FMI log (Collett et al., 2005), JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well. Sampling horizons and core number are also given on the lithological column. Symbols denote sand (red triangle), silt (yellow diamond), clay (grey dot), and gas hydrate (blue dot). Letters A to T show the horizons from which a 0.8 to 2.1 m offset is clearly recognized between core and logging.
Figure 2. (cont.)
RESULTS

Results of geochemical analysis of interstitial waters squeezed from core samples are given in the accompanying Interactive Data Viewer (Dallimore et al., 2005a). Compositions of mean seawater, Mackenzie River water, and drilling fluid taken at the drill site are also given for comparison.

**Potassium concentration and drilling-fluid contamination**

Potassium shows unexpectedly wide variation with sediment facies and extremely high concentrations (up to 929 mM below BGHS, 1116.5 m), although the overall concentration level is lower than 100 mM (Fig. 3a). Considering that K⁺ concentrations are very low in seawater (approx. 10 mM) and Mackenzie River water (approx. 0.03 mM) but extremely high in drilling fluid (approx. 1350 mM), the high K⁺ values observed in ‘interstitial waters’ are probably due to contamination by drilling fluids, as proposed by Cranston (1999) for pore waters from the Mallik 2L-38 well. The degree of contamination is directly related to K⁺ concentration. The degree of contamination (drilling-fluid contamination factor, D) was calculated using the equation and the K⁺ concentration of the drilling fluid (approx. 1350 mM):

\[
D = \frac{K^+}{1350}
\]

As shown in Figure 3b, zones of high contamination (D = 0.25–0.76) are found in gas-hydrate-free sand or sand containing small amounts of gas hydrate at approximately 950 m, 1000 m, and 1082.9 m within the gas hydrate zones, and in water-saturated sand (1110 m to approx. 1150 m) below the gas hydrate zone. Drilling fluids could have easily infiltrated into permeable sand, whereas the contamination was minimal in silt, clay, and those sand horizons containing large amounts of gas hydrate (D < 0.04; Fig. 3b); however, few samples showed high contamination (Fig. 4). All the analytical values in this paper have been corrected for the drilling-fluid contamination.

**Sodium**

Figure 5a shows the depth profile of Na⁺ concentration corrected for drilling-fluid contamination. The profile can be divided into four zones: zone 1, top of cored interval to approximately 1000 m; zone 2, approximately 1000 to 1070 m; zone 3, approximately 1070 to 1110 m; and zone 4, 1110 m to bottom of hole. Zones 1 and 3 are characterized by generally low but

![Figure 3](image-url) **Figure 3.** Depth profiles of the geochemistry of interstitial waters extracted from core samples, JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well: a) K⁺ concentration; b) degree of drilling-fluid contamination estimated from K⁺ concentration, based on the assumption that the in situ interstitial waters are K⁺ free and that K⁺ (mM) in waters was totally derived from contamination by drilling fluid (with K⁺ concentration of 1350 mM). See Figure 2 for explanation of colours in lithological log.

![Figure 4](image-url) **Figure 4.** Histogram showing the degree of contamination of interstitial water samples by drilling fluid, JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well.
variable Na⁺ concentrations, generally between approximately 100 and 300 mM, whereas zones 2 and 4 have concentrations in the relatively narrow range of 350 to 450 mM. Anomalously high concentrations occur in coaly shale units at 1057.2 m in zone 2 and in water-saturated sand at 1116.5 m in zone 4. The overall Na⁺ concentration range seems to fall between Mackenzie River water (0.32 mM) and seawater (468 mM).

**Magnesium**

The depth profile of Mg²⁺ concentration (Fig. 5b) is similar to that of Na⁺. Low and variable concentrations occur at shallower (zone 1) and intermediate (zone 3) depths, whereas the relatively high concentrations occur in the middle (zone 2) and in the water-saturated sand at the bottom (zone 4). Anomalously high Mg²⁺ concentrations in zones 2 and 4 occur in the same horizons as do anomalous Na⁺ values, but moderately high spikes at 891 and 932 m in zone 1 are unique to the Mg²⁺ profile. The concentrations in zones 2 and 4 are roughly comparable to that of seawater (53.3 mM).

**Calcium**

Figure 5c shows zones of anomalously high Ca²⁺ concentration (zones 2 and 4) and one of low concentration (zone 3), similar to the Mg²⁺ profile. The Ca²⁺ concentration for the interval 900 to 1000 m, however, fluctuates widely between 2 and 16 mM, compared with 0.9 mM for river water, 10.3 mM for seawater, and 12 mM for drilling fluid. Calcium concentrations higher than seawater and drilling fluids cannot be readily explained by mixing with seawater or by drilling-fluid contamination. High Ca²⁺ may have been caused by salt exclusion during the formation of gas hydrate or, alternatively, may indicate contamination by drilling fluids of different compositions.

**Strontium**

Strontium concentration generally ranges from 0.01 to 0.1 mM for almost all samples (Fig. 6a), but the depth profile exhibits the same four geochemical zones, with zones 1 and 3 being of lower concentration and zones 2 and 4 of higher concentration. The higher concentrations in zone 4 (0.1–0.15 mM) are similar to that of seawater (approx. 0.15 mM), whereas the concentration in zones 1 to 3 are mostly below that of seawater.

**Barium**

Geochemical zones are not clearly recognized in the Ba²⁺ profile, in which the concentration ranges between 0 and 0.05 mM (Fig. 6b). The remarkable feature of the Ba²⁺ profile is the anomalously high concentration spikes (0.1–0.3 mM) in the depth interval 890 to 930 m. These anomalies cannot be
explained by salt-exclusion effects but may indicate contamination by drilling fluid with high \(\text{Ba}^{2+}\) or the dissolution of barium minerals (\text{barite}) in diagenetic fluids.

**Chloride**

The Cl\(^{-}\) profile is almost identical to that of Na\(^{+}\) (Fig. 6c). Four zones and spiky anomalies are observed at the same depths as those of Na\(^{+}\), the concentration level of each zone being somewhat similar to the corresponding zone in the Na\(^{+}\) profile. As shown in Figure 7, however, Cl\(^{-}\) does not occur in a 1:1 ratio with Na\(^{+}\) but is approximately 25% higher, except for those samples in zone 4 of the gas-hydrate-free zone. Low concentrations are caused by ‘fresh’ waters arising from dissociation of gas hydrate, whereas more saline waters arise from salts excluded from the formation of gas hydrate. The nature and origin of the interstitial waters in the gas-hydrate-bearing zone are therefore different from those in the gas-hydrate-free zone.

**Sulphate**

Sulphate concentration reaches 15 mM (Fig. 6d), approximately half that of seawater (28 mM) and of the drilling fluid (32 mM). Zones 1, 2, and 3 are not distinguished by the SO\(_4^{2-}\) concentration; only zone 4, the free-gas zone, is clearly recognized. Generally speaking, SO\(_4^{2-}\) in the interstitial waters was originally derived from overlying seawater and reduced

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**Figure 6.** Depth profiles of the geochemistry of interstitial waters extracted from core samples, JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well: a) \(\text{Sr}^{+}\), b) \(\text{Ba}^{2+}\), c) Cl\(^{-}\) d) SO\(_4^{2-}\). See Figure 2 for explanation of colours in lithological log.

**Figure 7.** Correlation between the concentrations of Cl\(^{-}\) and Na\(^{+}\), with solid line showing 1:1 ratio of Cl\(^{-}\) and Na\(^{+}\); molar concentration of Cl\(^{-}\) is some 25% higher than that of Na\(^{+}\).
was originally derived from overlying seawater and reduced to generate hydrogen sulphide in the course of microbially mediated diagenesis during burial. In particular, pore-water SO$_4^{2-}$ in organic-rich, gas-hydrate-bearing successions would be rapidly reduced by organic matter and/or upward-migrating methane; it would decrease in concentration with depth and disappear between a few metres and 50 m below the seafloor (sulphate-methane interface, SMI). Considering the behaviour of sulphate in organic-rich sediments, the sulphate profile observed in the Mallik 5L-38 well is unusual and difficult to explain. The authors suspect that sulphate was extracted from sediments; from seawater infiltration, ancient or modern; and from drilling-fluid contamination. The nature and origin of sulphide in sediments and sulphate in the interstitial waters is discussed in detail by Chen et al. (2005).

**DISCUSSION**

**Geochemical zones from the interstitial waters**

The ions Na$^+$, Mg$^{2+}$, Sr$^{2+}$, and Cl$^-$ exhibit four geochemical zones, as described above. Calcium fluctuates widely in zone 1 and Ba$^{2+}$ shows extremely high values in the upper part of zone 1. Sulphate also shows high anomalies in the upper part of zone 1, and the profile clearly defines zone 4. High-concentration anomalies for Ca$^{2+}$, Ba$^{2+}$, and SO$_4^{2-}$ in the upper part of zone 1 suggest the dissolution of Ca-Ba-SO$_4$ minerals, the infiltration of evolved seawater, or contamination with another type of drilling fluid.

Zone 1 is divided into upper and lower subzones by an approximately 12 m thick layer of siltstone/claystone that is relatively higher in salinity and free of gas hydrate (Fig. 5, 6, 9). Both the upper and lower subzones are sand dominated and contain high to moderate amounts of gas hydrate, with gas hydrate saturation ($S_h$) of 60 to 80%, as suggested by the downhole logs (Fig. 2; Collett et al., 2005). Lower salinities are likely due to freshening by gas hydrate dissociation during sediment recovery (e.g. Hesse and Harrison, 1981; Paull and Matsumoto, 2000). Gas-hydrate-free sediments (zone 4) reflect the composition of in situ interstitial waters unaffected by gas hydrate dissociation. Likewise, the higher Cl$^-$ concentrations in siltstone/claystone–dominant units of zone 2 represent the in situ pore waters.

Low salt concentration in zone 3 is ascribed to dense accumulations of gas hydrate in sand/conglomerate–dominant units. The base of zone 3 corresponds to the base of gas hydrate stability (BGHS). Sand-dominant units continue down into zone 4, but the sharp discontinuities were recognized in the downhole logs and the FMI log (Collett et al., 2005; Fig. 2). Higher concentrations in zone 4 may reflect the pristine composition, but anomalously high SO$_4^{2-}$ concentrations in zone 4 require another process. As was discussed for K$^+$, permeable, water-saturated sand in zone 4 is easily infiltrated by seawater and drilling fluids.

**Origin and evolution of the interstitial waters**

The concentration of Cl$^-$ in the interstitial waters of the Mallik 5L-38 well is 60 to 80% of that of seawater in zone 1 and nearly 100% of seawater in zone 4. Likewise, the concentrations of Na$^+$, Mg$^{2+}$, and Sr$^{2+}$ are 55 to 100%, 57 to 90%, and 46 to 90% of seawater, respectively, in zones 1 through 4. Thus, whereas marine gas hydrate successions generally show Cl$^-$ freshening with depth (e.g. Kastner et al., 1995; Eggeberg and Dickens, 2000), Cl$^-$ concentration in the Mallik well generally increases with depth. Considering the geological setting, the depth profile may indicate that the interstitial waters of the Mallik 5L-38 well are a simple mixture of Mackenzie River water and evolved seawater. Salt exclusion during the formation of gas hydrate may have also caused the increase in salinity with depth (Clark et al., 1999).

Moderate to frequent incursion of seawater has been suggested from the SO$_4^{2-}$ concentration of the interstitial waters, the high sulphur content of the sediments, and the occurrence of pyrite (Chen et al., 2005). Even after burial, seawater may have diffused downward into the Miocene-Oligocene sequences through permeable sand. The marine-derived SO$_4^{2-}$ was partly reduced by organic matter and methane to precipitate pyrite, leaving isotopically heavy residual SO$_4^{2-}$. High SO$_4^{2-}$ concentration (approx. 15 mM) in zone 4 below the BGHS implies that the diagenetic invasion of seawater took place even after formation of the present distribution of gas hydrate. High and anomalous concentrations of Ba$^{2+}$, SO$_4^{2-}$ and Ca$^{2+}$ seem to suggest contamination of the drilling fluids with barite and anhydrite, which were used to drill the permafrost sections above.

Oxygen and hydrogen isotopic signatures should provide better constraints on the origin and evolution of the interstitial waters from gas-hydrate-bearing strata (see Tomaru et al., 2005).

**Gas hydrate saturation from chloride and sodium anomalies**

Gas hydrate saturation ($S_h$) can be estimated from the magnitude of freshening effects caused by dissociating methane hydrate, on the assumption that the gas hydrate system is substantially open to the ambient pore waters. The Mackenzie Bay and Kugmallit sequences, which host the gas hydrate in the Mallik 5L-38 well, were deposited in fluviodeltaic to coastal-plain environments (Jenner et al., 1999; Medioli et al., 2005). Thus, the initial interstitial waters (i.e. the depositional waters) should range from marine, brackish to fresh, which leads to difficulty in estimating $S_h$ from observed geochemical anomalies. Fortunately, gas-hydrate-bearing sediments in the Mallik 5L-38 well are frequently interbedded with gas-hydrate-free sediments, which provide a baseline composition for geochemical assessment of gas hydrate saturation. Figure 8 shows baselines for Cl$^-$ and Na$^+$ concentrations. The regression lines were calculated from salt concentrations in samples that were presumed free of gas hydrate.
The relation among the baseline concentration ($C_b$), the observed concentration ($C_h$) of water squeezed from gas-hydrate-bearing sediments, and the volume fraction ($M$) of gas-hydrate-derived water in the squeezed water is given as

$$M = 1 - \frac{C_h}{C_b}. \quad (2)$$

Assuming that the density of gas hydrate is 0.91 g/cm$^3$ (Makogon, 1997), one mole of stoichiometric methane hydrate ($\text{CH}_4$•5.75H$_2$O; mass 119.5 g; volume 131.3 cm$^3$) is calculated to contain 103.5 g (103.5 cm$^3$) of water. This means that 1 cm$^3$ of pure water forms 1.27 cm$^3$ of gas hydrate. Hence, the gas hydrate saturation ($S_h$), or the volume % of gas hydrate in the sediment pore space, is

$$S_h = \left( \frac{1.27 \times 100}{1 + 0.27M} \right). \quad (3)$$

Figure 9 shows gas hydrate saturation, $S_h$ (in per cent), calculated from chloride anomalies (red dots) and sodium anomalies (blue dots). The calculation was based on independent deviations of Cl$^-$ and Na$^+$ concentrations, but the profiles are in surprisingly good agreement with each other, with only one exception in the free-gas zone.

Zones of high gas hydrate saturation (60–85%) have been identified at three intervals: zone A, 890 to 930 m; zone B, 945 to 993 m; and zone C, 1070 to 1108 m. The distribution and amount are controlled primarily by the lithology of the host sediments, but variation in salinity is also an important factor for gas hydrate accumulation. Zone A is developed in a thick conglomeratic sand underlain by organic-rich laminated clay and coal beds. The upper limit of zone B coincides with the clay to sand transition, but the base of zone B occurs within sand. The sand just below the base (995.8 m) is saturated by waters of extremely high salinity (1110 mM Cl$^-$, 460 mM Na$^+$, and 21 mM Ca$^{2+}$). Build-up of such high-salinity waters within sand units with large amounts of gas hydrate was caused by ion exclusion during gas hydrate formation. Salts thus excluded accumulated to form hypersaline waters, which then tended to impede or even inhibit the formation of further methane hydrate.

Zone C begins at 1070 m and continues down through the BGHS at 1108 m. Temperature measurements by distributed temperature sensing system (DTS) have revealed a small temperature disturbance at around 1110 m, strongly suggesting the presence of the phase boundary between gas hydrate and free gas (see Hennings et al., 2005).

**Core $S_h$ versus log $S_h$**

For comparison, depth profiles of $S_h$ estimated from Cl$^-$ anomalies, log parameters (NMR porosity; Kleinberg et al., 2005; Collett et al., 2005), and log resistivity (Ro/Rt) are shown in Figure 10. Values of $S_h$ derived from the NMR porosity log are in generally good agreement with the geochemical estimation, whereas the resistivity log tends to overestimate $S_h$ for the interval of low saturation, showing about 10 to 20% saturation for the gas-hydrate-free zone at 930 to 945 m and the gas-hydrate-poor zone at 993 to 1070 m.

**Anomalies in residual water compositions**

Gas hydrate deposits are composed of gas hydrate, solid sediment particles, interstitial waters (perhaps residual waters), and perhaps methane gas bubbles. The composition of the residual waters can be the same as or different from that of the ambient waters, depending on the fluid flow and water-mixing processes in the system. If the gas hydrate formed in an open system, salts excluded from the gas hydrate should be transported by diffusion and/or fluid flow. High-resolution core analysis from the Blake Ridge and Nankai Trough (e.g. Matsumoto, 2000, 2002) support the open-system model for the formation of marine gas hydrate. Recent Ocean Drilling Program (ODP) drilling at the Hydrate Ridge on the Cascadia Margin, however, has revealed waters of extremely high salinity (e.g. 1400 mM Cl$^-$) at less than 10 m below the seafloor in an area of very high methane flux and dense gas hydrate (Torres et al., 2004).
**Figure 9.** Gas hydrate saturations ($S_h$) estimated from Cl$^-$ and Na$^+$ anomalies. See Figure 2 for explanation of colours in lithological log.

**Figure 10.** Depth profile of gas hydrate saturations ($S_h$) determined from Cl$^-$ anomalies, compared to $S_h$ calculated from a) the NMR porosity log, and b) the resistivity logs. See Figure 2 for explanation of colours in lithological log.
Gas hydrate in the Mallik 5L-38 well is considered to have developed mostly in an open system, but high-salinity residual water have been found in at least four horizons: a) 995.8 m, b) 1057.2 m, c) 1082.9 m, and d) 1116.5 m (Fig. 5, 6). Horizon c occurs in thin, impermeable silt-clay units within hydrated sand, and horizon d occurs in gas-hydrate-free sand about 7 m below the BGHS. Occurrence of high-salinity residual waters implies that fluid migration in Mackenzie Delta sediments is slow, perhaps hampered by gas hydrate accumulation, as well as by original lithology.

Given the $S_h$ of the sediment cores, the salinity of the residual waters can be calculated, using equations 2 and 3, from the concentrations of Cl$^-$ and other ions in water squeezed from the sediment cores. Detailed correlation of core and log data (Fig. 2) has made it possible to combine the interstitial-water-geochemistry data and the log-$S_h$ data. Figure 11 shows the variation in the Cl$^-$ concentration of in situ residual waters (blue dots), squeezed water samples (red dots), and $S_h$ derived from the NMR porosity logs (blue line). Thick red bars at the right margin of the figure show the build-up of saline residual waters, and blue bars show that of fresher residual waters. The upper gas hydrate interval in zone A is associated with fresher residual waters (200–300 mM Cl$^-$) with the exception of one data point. This range of values is nearly 100 to 200 mM fresher than the overall trend of the baseline (approximately 400 mM; Fig. 8a). The fresher residual waters likely suggest dissociation of gas hydrate within a semiclosed system and intermixing of gas-hydrate-derived fresh waters with in situ pore waters. This means that the top horizon of the Mallik gas hydrate deposit has undergone massive dissociation.

In contrast, saline residual waters were identified in zones A, B, and C, in which the Cl$^-$ concentration increases up to 800 mM and 1100 mM, respectively. Residual waters with thick, massive gas hydrate zones develop in a substantially closed environment, and salts excluded during gas hydrate formation increase the salinity of the residual waters. The bottom part of zone C contains lower salinity pore waters, and may suggest a melting episode before the formation of zone C gas hydrate. Repetitive formation and dissociation of gas hydrate around the BGHS suggest that the depth of the BGHS fluctuated temporally, probably reflecting glacial-interglacial cycles.

**CONCLUSIONS**

1) The cored interval of the JAPEX/JNOC/GSC et al. Mallik 5L-38 gas hydrate production research well is divided into four geochemical zones: zone 1, top of cored interval to approximately 1000 m; zone 2, approximately 1000 to 1070 m; zone 3, approximately 1070 to 1110 m; and zone 4, 1110 m to bottom of cored interval. Zones 1 and 3 are characterized by generally low concentrations of dissolved ions, and zones 2 and 4 by high concentrations within a narrow range.

2) Salinity of in situ interstitial waters decreases with depth, from 46 to 60% of seawater concentration in zone 1 to 70 to 100% of seawater concentration in zone 4. The overall trend of the chemical composition of interstitial waters in the Mackenzie Delta sequences reflects a variable mixture of fresh- to brackish-dominated pore waters with seawater.

3) Geophysical downhole log depths are 0.8 m to 2.1 m (mean 1.59 m) shallower than the corresponding lithological records throughout the Mallik 5L-38 well.

4) The sharp contrast in chemical composition between gas-hydrate-bearing and gas-hydrate-free units, and the rather monotonic downhole trend of the pristine pore waters, enabled an estimate of gas hydrate saturation ($S_h$) from the geochemical anomalies. Zones of high $S_h$ (60 to 85%) were identified at three intervals: zone A, 890 to 930 m; zone B, 945 to 993 m; and zone C, 1070 to 1108 m. Gas hydrate distribution is controlled primarily by the lithology of the host sediments, but high salinity may inhibit gas hydrate formation.

5) Both fresher and more saline residual waters have been identified in thick intervals where gas hydrate acts as a sediment-cementing agent. The fresher waters may indicate...
the melting of gas hydrate during dissociation, whereas the more saline waters suggest formation of gas hydrate in a closed system and/or invasion of seawater.

6) Gas hydrate saturations estimated from the NMR porosity logs are in good agreement with those determined directly from geochemical parameters, whereas resistivity logs tend to overestimate $S_h$ for sediment intervals with low gas hydrate saturation.

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