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Possible variation in methane flux caused by gas hydrate formation on the northeastern continental slope off Sakhalin Island, Russia

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Abstract The Sakhalin Slope Gas Hydrate Project (SSGH) is an international collaborative effort by scientists from Japan, Korea, and Russia to investigate natural gas hydrates (GHs) that have accumulated on the continental slope off Sakhalin Island, Okhotsk Sea. From 2009 to 2011, field operations of the SSGH-09, -10, and -11 projects were conducted. GH-bearing and -free sediment cores were retrieved using steel hydro- and gravity corers. The concentrations of sulfate ions in sediment pore waters were measured to investigate sulfate concentration–depth profiles. Seventeen cores showed linear depth profiles of sulfate concentrations. In contrast, eight cores and two cores showed concave-up and -down profiles plausibly explained by sudden increase and decrease in methane flux from below, respectively, presumably caused by the formation of gas hydrate adjacent to the core sampling sites.

Introduction

The Okhotsk Sea is one of the biggest reservoirs of gas hydrates (GHs) worldwide (Soloviev and Ginsburg 1997). The GHs were first discovered at structures close to Paramushir Island (Zonenshayn et al. 1987). Later, in 1991, GH was retrieved within gas-venting areas in the Derugin Basin on the continental slope off Sakhalin Island (Ginsburg et al. 1993). Subsurface GH was again sampled during the Russian-German Kurile-Okhotsk Marine Experiment (KOMEX) Project (Biebow et al. 2002; Matveeva et al. 2003; Obzhirov et al. 2004), from layers at <4.1 m below seafloor (m bsf) in a gas seepage structure later named the Obzhirov Flare (Matveeva et al. 2003). The pore water geochemistry of cores retrieved during the KOMEX II expedition has been evaluated by Wallmann et al. (2000, 2002, 2006) and Matveeva et al. (2003).

In related work, the Hydro-Carbon Hydrate Accumulations in the Okhotsk Sea (CHAOS) I, II, and III cooperative projects were organized by scientists from Japan, Korea, Russia, Belgium, and Germany with the aim of studying GHs in the Okhotsk Sea (Matveeva et al. 2005; Shoji et al. 2005, 2009; Jin et al. 2006, 2011a). The molecular and isotopic compositions of hydrate-bound gas retrieved during the CHAOS projects have been investigated by Hachikubo et al. (2009, 2010), and the geochemical features of pore waters from gas-seepage structures, including GH-bearing

Responsible guest editors: M. De Batist and O. Khlystov

Electronic supplementary material The online version of this article (doi:10.1007/s00367-012-0287-x) contains supplementary material, which is available to authorized users.

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sites, by Mazurenko et al. (2009), Minami et al. (2009), and Tomaru et al. (2009).

The present study was carried out within the framework of the Sakhalin Slope Gas Hydrate (SSGH) Project, which started in 2007 in an international collaborative effort by Japanese, Korean, and Russian scientists to investigate natural GHs accumulated on the continental slope off Sakhalin Island (see cruise reports by Baranov et al. 2008; Jin et al. 2008, 2011b; Shoji et al. 2010). As shown in Fig. 1a and b, the project's study area is located on the northeastern Sakhalin slope near a plate boundary corresponding to the Sakhalin Shear Zone (Baranov et al. 2010). This shear zone forms a strike-slip boundary between the Okhotsk plate and the Amur plate; it is represented by complex fault systems, and can be traced over the entire Sakhalin Island (Shoji et al. 2009). The present study area has a sedimentary infill of

more than 9 km thickness (Baranov et al. 2011). Numerous gas flares/methane plumes have been observed during the SSGH and CHAOS projects (Shoji et al. 2005, 2009; Jin et al. 2011b).

From July to August 2009, in June 2010, and in August 2011, field operations of the SSGH-09, -10, and -11 projects were conducted during the LV47, LV50, and LV56 cruises aboard the R/V *Akademik M.A. Lavrentyev* (see cruise reports by Shoji et al. 2010; Jin et al. 2011b). In the present study, concentrations of sulfate ions in sediment pore waters obtained during the LV47 and LV50 cruises were measured to investigate sulfate concentration–depth profiles down to the depth of the sulfate–methane interface (SMI), since SMI depth and sulfate profiles are reported to depend on the upwelling of methane (Borowski et al. 1996, 1999; Hensen et al. 2003). Most of the methane in sediments is thought to

Fig. 1 **a** Plate boundaries around the Okhotsk Sea: *lines with triangles* subduction zones, *lines with arrows* strike-slip zones, *dashed line* suggested plate boundary. **b** Areas studied during the LV47, LV50, and LV56 cruises: *black symbols* coring sites, *red symbols* GH-bearing, including suggested LV47-29HC
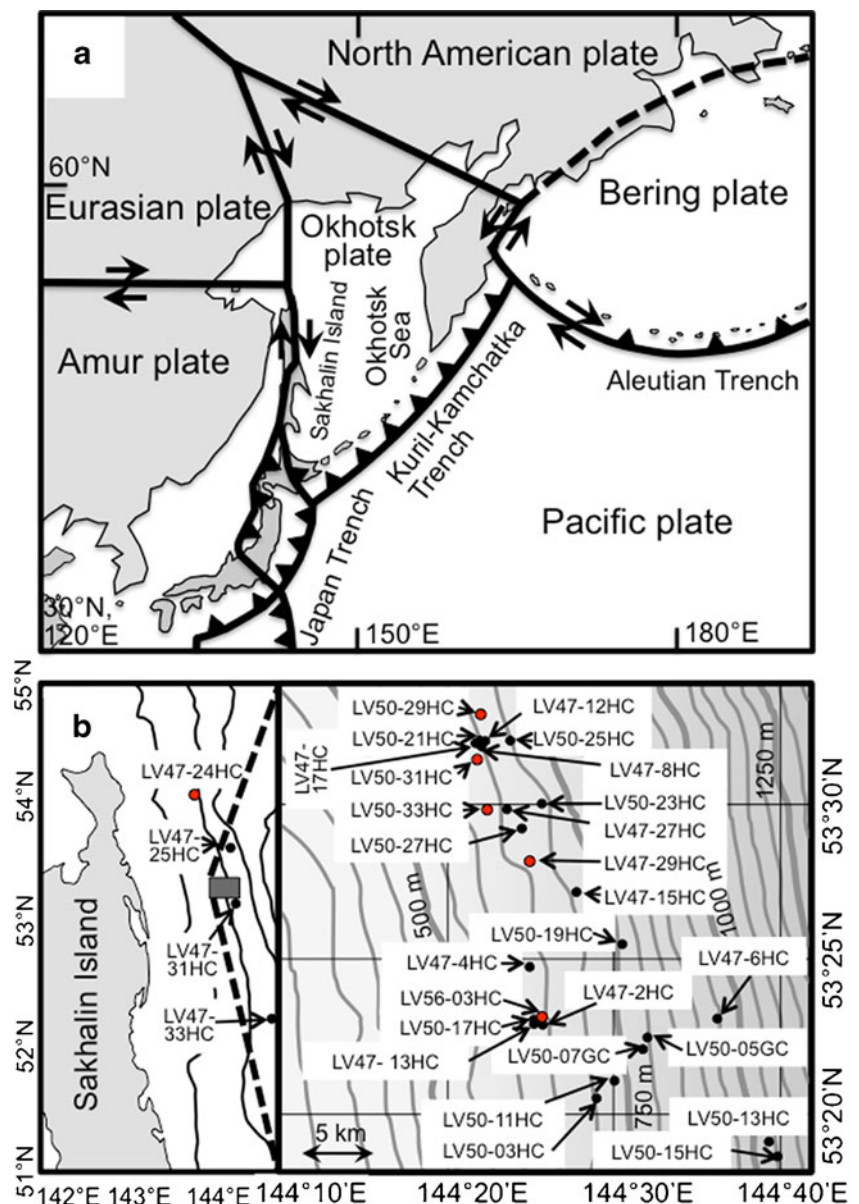
be consumed anaerobically by a bacterial consortium that uses sulfate as an oxidant in the process of anaerobic oxidation of methane (AOM; e.g., Iversen and Jørgensen 1985; Boetius et al. 2000; Knittel and Boetius 2009). Sulfate and methane are consumed at the SMI by the following reaction:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

By observing sulfate concentration–depth profiles, Borowski et al. (1999) categorized sulfate profile shapes in terms of linear and nonlinear, including concave-up and concave-down. They discussed the mechanisms responsible for linear and concave-down profiles, but not for concave-up profiles. Niewöhner et al. (1998) proposed that linear sulfate profiles indicate sulfate consumption mediated primarily by upward-diffusing methane, and Fossing et al. (2000) that sulfate consumption was counterbalanced by an upward methane flux. Based on their computer simulation study, Hensen et al. (2003) suggested that variations in sulfate concentration–depth profiles, such as concave-up/down patterns, could be due to variations in methane flux from below without, however, discussing possible control mechanisms. More recently, Ussler and Paull (2008) reported a concave-up sulfate profile for a sediment core from the Gulf of Mexico, and noted that the profile suggested a sudden increase in upward methane flux. Again, possible driving factors were not addressed. Evidently, the mechanisms responsible for the formation of concave-up/down sulfate profiles caused by sudden increase/decrease in methane flux have yet to be identified, and this forms the context of the present study.

Materials and methods

Sediment core sampling

Thirty sediment cores were retrieved from the seafloor using a 5.5-m steel hydro corer or a 10.5-m steel gravity corer. All cores were from seepage structures, except one reference core located outside of the seepage areas but still on the Sakhalin slope. Lithological descriptions were made, and sediment subsampling was performed on board immediately following retrieval of the cores. Figure 2 shows some photographs of GH-bearing cores.

Water sampling

The pore water was sampled on board from 30 cores using two squeezers designed and constructed at the Kitami Institute of Technology (KIT). A 10-cm depth interval of each sediment core was drawn into the squeezer, and pore water was then directly collected into a polyethylene syringe connected to the discharge tube of the squeezer. The other end of the syringe was connected to a membrane filter cartridge containing a 0.2-μm filter. Seawater samples were obtained from the top of the corer. All water samples were filtered through 0.2-μm filters, and then stored in polypropylene bottles at 2 °C.

### Chemical analyses of water samples

All chemical analyses of water samples were conducted at KIT. The concentrations of sulfate, chloride, and hydrogen carbonate ions were determined by an ion chromatograph (Nihon Waters K.K., Tokyo) equipped with a model 717 plus auto sampler, a model 1525 binary HPLC pump, and a model 432 conductivity detector. A model Z-8230 polarized Zeeman background correction flame atomic absorption spectrometer (Hitachi Ltd., Tokyo) or model SPS 3100 HVUV inductively coupled plasma optical emission spectrometer (SII NanoTechnology Inc., Chiba) was used to determine the concentration of sodium.

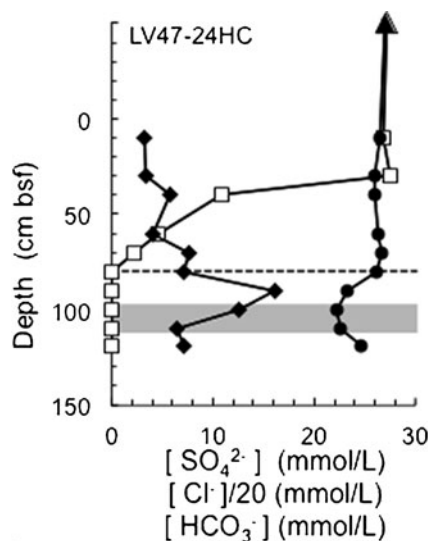## Results

Depth of sulfate–methane interface

Figure 3 shows the concentration–depth profiles of sulfate, chloride, and hydrogen carbonate ions in pore waters from the GH-bearing core LV47-24HC. The depletion of chloride ions observed in the GH-bearing interval was likely caused by dilution resulting from the input of pristine pure water produced by GH dissociation while retrieving/handling the core. The other three GH-bearing cores (LV50-29HC, -31HC, and -33HC) also showed depletion of chloride ions (data not shown; pore waters of the GH-bearing core LV56-03HC were not measured). Other possible processes for freshening of pore waters (cf. Brown et al. 2001, Dählmann and de Lange 2003, and references therein) include (1) clay mineral dehydration, (2) biogenic opal recrystallization, (3) meteoric water input, and (4) clay membrane ion filtration. However, low chloride anomalies were not observed as widespread regional phenomenon in the present study area, but only in GH-bearing intervals. Therefore, processes 1–4 mentioned above are not likely to have been major causes of pore water freshening in the present case.

Niewöhner et al. (1998) and Jørgensen et al. (2001) defined the sulfate–methane transition depth where both methane and sulfate concentrations are less than ca. 0.5–1 mmol/L. Based on their definition, the depth of the SMI was determined for the sulfate and methane concentration–depth profiles of the present study (cf. Obzhirov et al. 2010; Hachikubo et al. 2011). The SMIs of the GH-bearing cores were 0.4–0.8 m bsf, whereas for the 24 GH-free (by visual observation) cores they were 0.9–3.8 m bsf. Since the depth of the SMI depends on the intensity of the upward methane
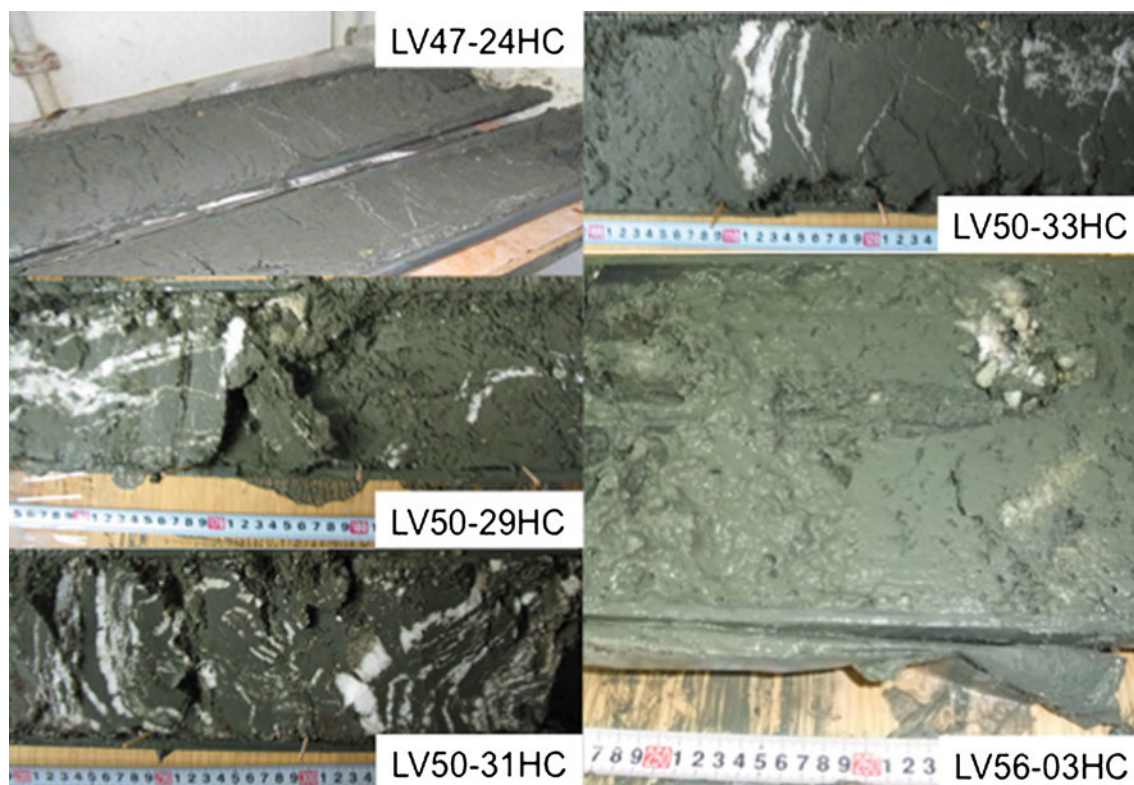
Fig. 2 Photographs of GH-bearing intervals

flux (Borowski et al. 1996), it can be inferred that intensive methane flux was characteristic of the GH-bearing cores. The compiled data including core names and SMI depths are shown in Table 1 in the online supplementary material for this article.
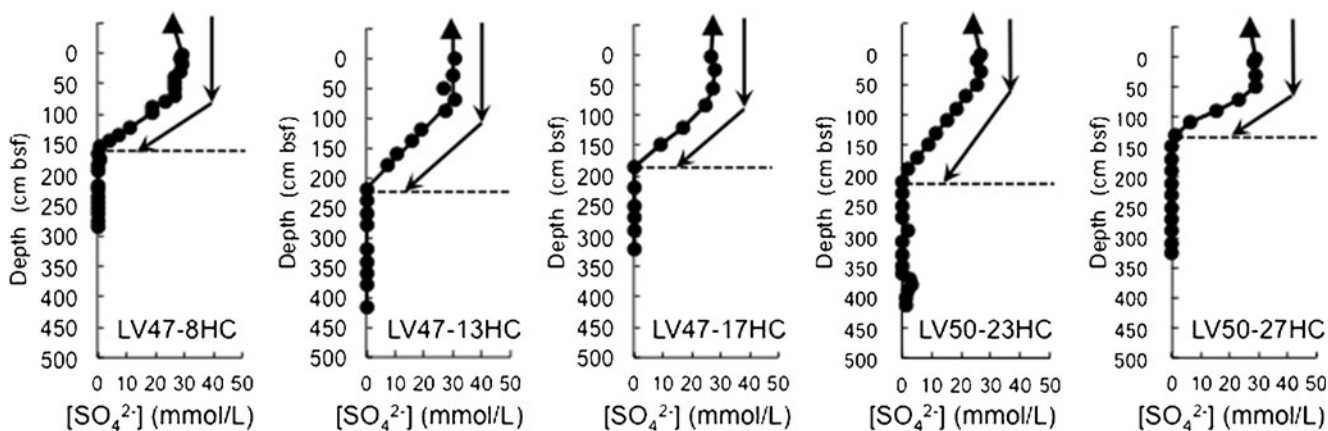

Fig. 3 Concentration–depth profiles of sulfate, chloride, and hydrogen carbonate ions: *squares* sulfate, *circles* chloride, *diamonds* hydrogen carbonate, *triangles* seawater, *dashed lines* sulfate–methane interface, *shaded area* GH-bearing interval

The concentration of sulfate ions was not depleted over the length of two cores, including the reference core LV47-33HC. This was selected as reference because (1) no GH was observed in the core, (2) no gas flare was observed on echograms at the site, and (3) no carbonate was observed in the core. AOM produces hydrogen carbonate ions, and this process is supported by the appearance of a maximum concentration peak of hydrogen carbonate ions around the SMI depth, as shown in Fig. 3.

Sulfate concentration–depth profiles

Figure 4 shows a typical example of linear concentration–depth profiles of sulfate ions for five cores. Sulfate concentrations decreased linearly with depth from ca. 0.5–0.6 m bsf to the SMI. The linearity of these profiles suggests that sulfate depletion is driven largely by an upward flux of methane, rather than by a flux of organic matter from above, and AOM at the SMI (Borowski et al. 1996; Niewöhner et al. 1998; Dickens 2001). Linear sulfate profiles are formed in a steady state based on sulfate and methane co-consumption (AOM) at the SMI, and the balance of sulfate and methane fluxes (Borowski et al. 1996, 1999).

Figure 5 shows concave-up and -down profiles for ten cores. Hensen et al. (2003) simulated such concave-up and -down profiles in terms of sudden increases and decreases in methane flux from below, respectively.
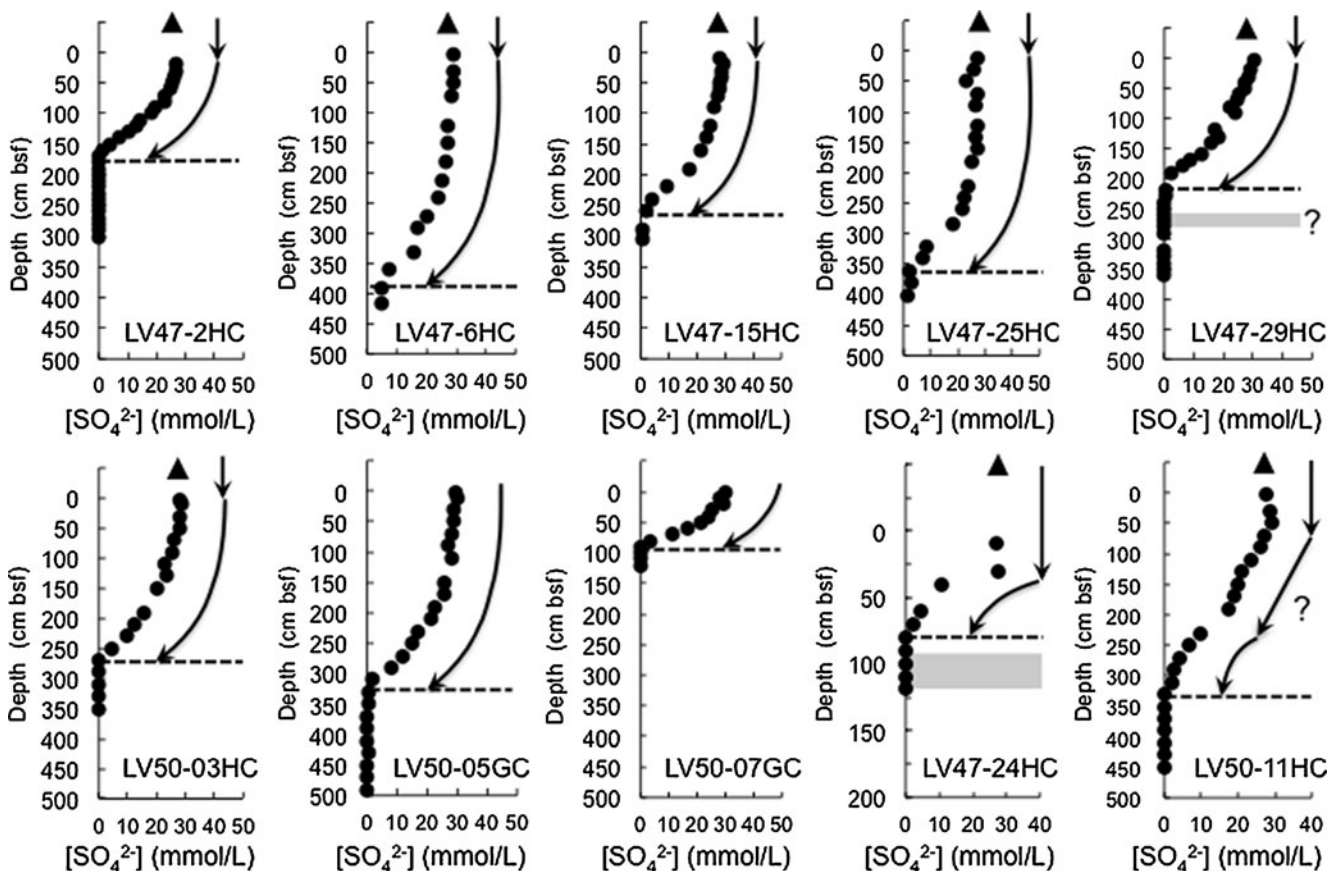
Fig. 4 Linear concentration–depth profiles of sulfate ions: *circles* pore water, *triangles* seawater, *dashed lines* sulfate–methane interface
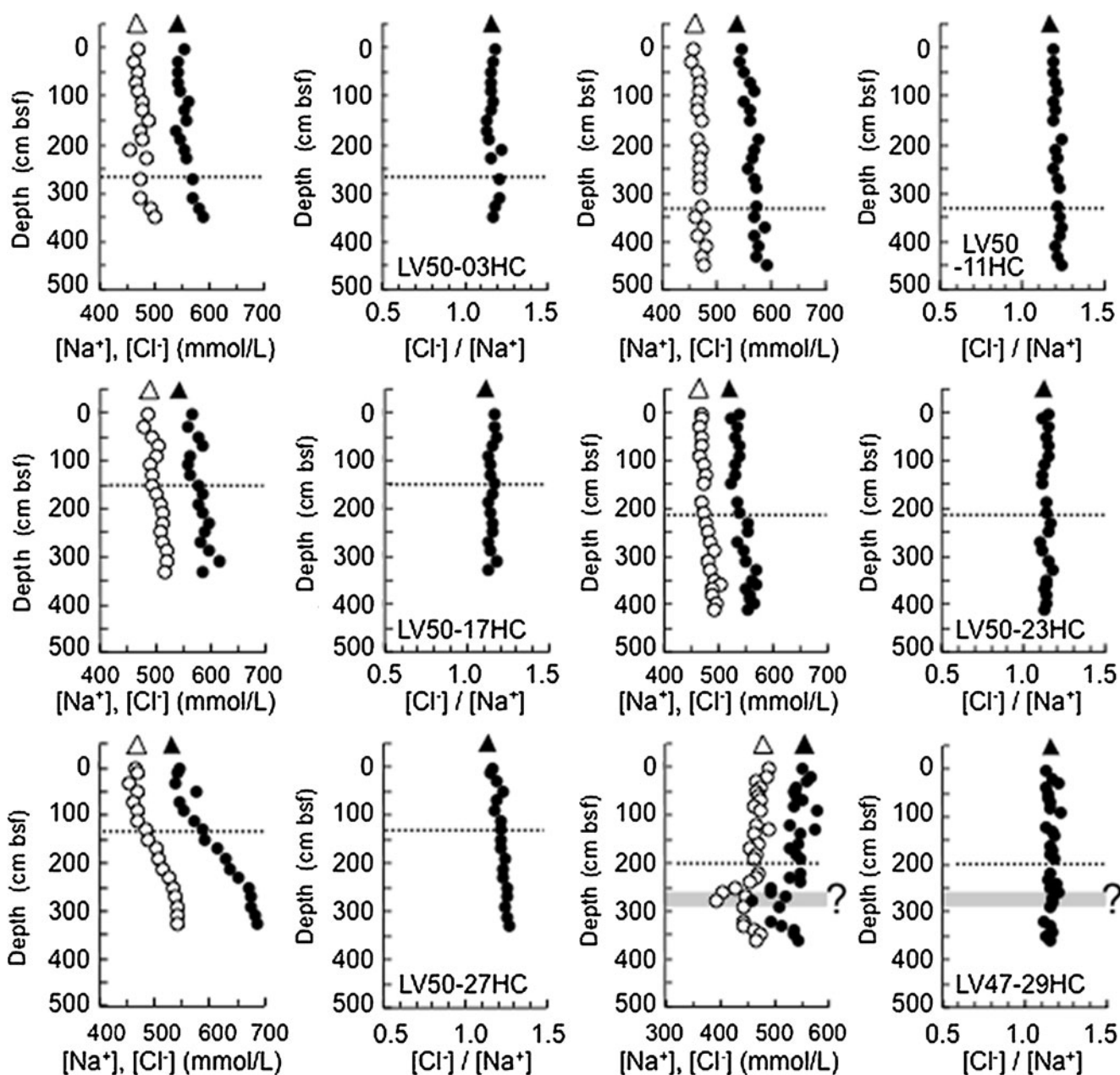
Chloride and sodium profiles

Downcore depth profiles of chloride and sodium ions reveal that their pore water concentrations were initially similar to those of the bottom seawater, and then increased with depth for cores LV50-03HC, -11HC, -17HC, -23HC, and -27HC (Fig. 6). This was particularly

marked in core LV50-27HC (27.3 % increase in Cl⁻, versus 8.1–10.1 % in the other cores; Table 1 in electronic supplementary material). On the other hand, a minimum peak in ionic concentration at 2.8 m bsf was observed for core LV47-29HC. Correspondingly, the ratios of these two ions remained essentially constant downcore (Fig. 6).

Fig. 5 Nonlinear concentration–depth profiles of sulfate ions: *circles* pore water, *triangles* seawater, *dashed lines* sulfate–methane interface, *shaded areas* GH-bearing intervals, including suggested LV47-29HC

Fig. 6 Depth profiles of concentrations of chloride and sodium ions, and their ratios for various cores: *closed symbols* chloride, *open symbols* sodium, *circles* pore water, *triangles* seawater, *dashed lines* sulfate–methane interface, *shaded areas* suggested GH-bearing interval

Discussion

Among 30 cores evaluated in the present study, 17 cores showed linear and ten cores showed nonlinear sulfate concentration–depth profiles in pore waters down to the SMI; sulfate was not depleted over the length of two cores, including one reference core. Categorizing the ten nonlinear profiles based on their features revealed that eight cores had concave-up and two cores had concave-down profiles.

Linear sulfate concentration–depth profiles

The fact that sulfate concentration decreased linearly from ca. 0.5 m bsf down to the depth of the SMI implies that a steady-state situation of methane and sulfate fluxes exists between those depths. The question then arises as to whether the constant sulfate concentration in the upper ca. 0.5 m results from the diffusion of sulfate ions from the seafloor through the pore water, or whether the transportation route of sulfate is ensured as a point-to-point connection. The

lithological interpretation that the presence of hydrotroilite lenses/interlayers is a sign of intensive bioturbation, expressed as a spotted-lenticular texture and high amounts of sandy particles within subsurface sediments of some cores in the present study, is consistent with the bioirrigation suggested by Ussler and Paull (2008) to explain their constant sulfate concentration in the upper 1 m. Almost the same sulfate profile was documented by Schulz et al. (1994); however, they did not discuss any driving mechanism. The reports by Fossing et al. (2000) and Treude et al. (2005) that a downward-directed transport of water due to bioirrigation enables penetration and/or active transport of sulfate ions into deeper sediments suggests that the constant sulfate observed in the upper ca. 0.5 m results from bioirrigation in the present study. Although neither sandy particles nor signs of bioturbation were visually observed in core LV50-23HC, their existence inside this core is suggested by comparison with neighboring cores.

Nonlinear sulfate concentration–depth profiles

Evidence that the sulfate concentration decreased in a concave-up profile down to the SMI suggests that an increase in methane flux from below results in a non-steady state, as simulated by Hensen et al. (2003). The findings of Riedinger et al. (2006), whereby an increase in methane flux could be explained by the burial of high amounts of organic matter below the sulfate–methane transition, resulting in elevated rates of methanogenesis, may not be relevant in the present case because the concave-up sulfate profiles were not a widespread, continuous phenomenon in the study area. Another possible cause of marked increase in methane is the dissociation of GHs. Hensen et al. (2003) pointed out that GH dissociation could add an advective component to the methane flow, thereby increasing methane fluxes. Moreover, observations by Wallmann et al. (2000) of a methane-rich and chloride-depleted ascending fluid from greater depths in the Derugin Basin off northeast Sakhalin Island suggest that a source of ascending fluid may be widespread GH dissociation. Therefore, the existence of an advective component caused by GH dissociation is considered an important possible cause of increase in methane flux in the present study.

The fact (Fig. 6, core LV47-29HC) that the concentrations of both chloride and sodium ions had minimum peaks at 2.8 m bsf, whereas the chloride/sodium ratios did not show any significant downcore change, implies that the concentrations of both ions are affected in the same way. It is speculated that there was GH at about 2.8 m bsf, and that it was dissociated. If the freshening of core LV47-29HC was caused by the dissociation of GH at the base of GH stability (BGHS) during the last glacial maximum (LGM), as reported by Hiruta et al. (2009), then the concentration of

both ions should decrease with depth, and those profiles should be observed widely in the vicinity of this core. This was, however, not the case. On the other hand, the chloride concentration of core LV50-27HC located near core LV47-29HC increased 27.3 % with depth. The dissociation of GH at the BGHS during the LGM cannot explain those phenomena.

Therefore, it can be inferred that (1) although GH was not observed visually in the core, the freshening of chloride ions in core LV47-29HC was caused by the dissociation of GH at about 2.8 m bsf during retrieval/handling of the core, and (2) GH dissociation at about 2.8 m bsf is not the main reason for the sudden, marked increase in methane flux to form the concave-up profile (Fig. 5).

Possible mechanism forming concave-up and -down profiles

Figure 6 (except core LV47-29HC) suggests that only water molecules are consumed to form GHs, since ions are excluded from water when GHs form (Egeberg and Dickens 1999; Ussler and Paull 2001; Hesse 2003; Matsumoto et al. 2004; Sloan and Koh 2008). When GH forms in sediments, at least two possible obvious changes occur: (1) an increase in ionic concentrations, as discussed above, and (2) an alteration of the pathway of upwelling methane from below to the seafloor, since the GH formed acts as a cap/plug of the prevailing methane pathway. A possible mechanism for the formation of concave-up sulfate profiles based on the latter change is proposed as follows (Fig. 7a): (1) subsurface GH is presently being formed near cores that show increases in ionic concentrations; (2) a once prevailing pathway of methane flux from below has been closed off; (3) the methane flux needs to find other pathways; and (4) methane flux close to the GH-bearing areas has increased because the newer methane flux has joined together with the older flux, leading to a concave-up profile. The fact that core LV47-2HC (concave-up profile) was retrieved close to cores LV56-03HC (GH-bearing) and LV50-17HC (increasing in ionic concentration), as shown in Fig. 8, supports this scenario.

It is interesting that core LV50-11HC showed not only increased ionic concentration but also a concave-down sulfate profile. Concave-down profiles have been attributed to sulfate reduction by organic matter degradation (Borowski et al. 1999). If the concave-down profiles observed in the present study were caused mainly by organic matter degradation (not by AOM), then those profiles should be observed widely in the region; however, such is not the case. On the other hand, they can be explained as follows (Fig. 7b): (1) GH is being formed in the sediment just under core LV50-11HC; (2) the concentrations of chloride and sodium ions have increased, since those ions are being

Fig. 7 Schematic scenario for possible variation in methane flux from below caused by GH formation: **a** sudden increase in methane flux, **b** sudden decrease in methane flux
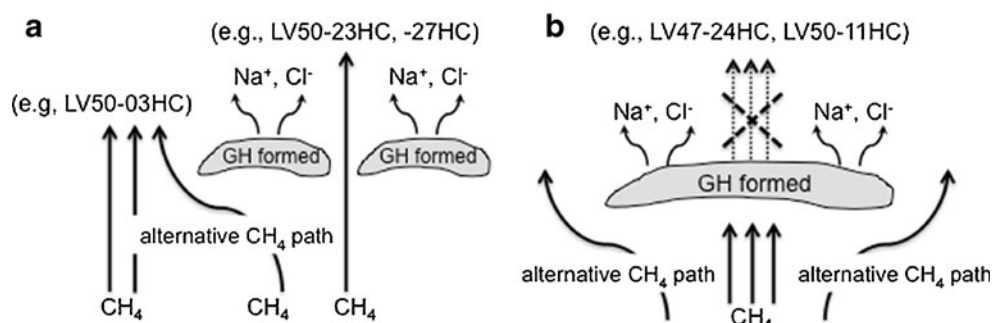
excluded; (3) a once prevailing pathway of methane flux has been closed off; (4) methane flux just above the GH has suddenly decreased; and (5) a concave-down profile associated with increasing ionic concentrations is formed. The finding that GH-bearing core LV47-24HC, as shown in Fig. 3, is obviously concave-down (the sulfate profile shown in Fig. 5 is the same as that of Fig. 3) supports this scenario, since the concave-down profile was found just above the GH-bearing interval. In addition, evidence that the concentration of hydrogen carbonate ion peaked at about the SMI depth suggests that sulfate is consumed mainly not by organic matter degradation, but rather by AOM at the SMI.

Conclusions

Based on the geochemical analyses of pore waters and interpretations discussed above, the following conclusions can be drawn concerning the possible relationship between the variation in methane flux and GH formation.

1. The sulfate profiles are not only linear but also concave-up/-down. This finding suggests possible variations in methane fluxes.
2. Increases in ionic concentrations with depth were observed, whereas the ratios of chloride/sodium remained constant through the cores. This suggests that subsurface GHs are presently forming.
3. The nonlinear sulfate profiles and ionic anomalies were observed in the vicinity of GH-bearing sites. It is concluded that possible variations in methane flux are presumably caused by subsurface GH formation. Dickens (2003) argued that excessive free gas could induce flow through fracturing. If this is applicable to the present study area, then not only a diffusive process but also sulfate-depleted/methane-rich fluid flow as an advective

Fig. 8 Overview of core features at various locations: symbols: *red* GH-bearing, *gray* without GH, *blue* concave-up sulfate profile, *green* concave-down sulfate profile, *magenta* increasing in ionic concentration, *overlapped symbols* both features observed together
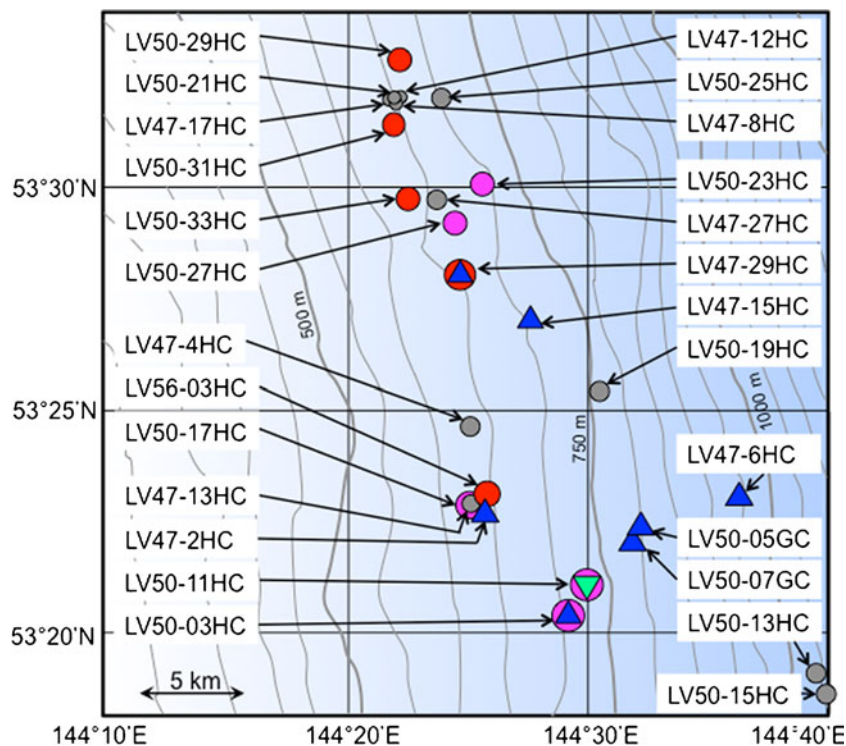
process might contribute to these variations. However, future studies are needed to confirm this interpretation and advance our knowledge of such systems.

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