Terr. Atmos. Ocean. Sci., Vol. 17, No. 4, 961-979, December 2006

Distribution of B, Cl and Their Isotopes in Pore Waters Separated from Gas Hydrate Potential Areas, Offshore Southwestern Taiwan

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(Manuscript received 31 October 2005, in final form 28 April 2006)

ABSTRACT

Boron (B) and chlorine (Cl) are widely distributed on the Earth's surface and show distinctive geochemical behaviors. Cl behaves rather conservatively in oceanic environments while B is an excess-volatile and its distribution is sensitive to sediment absorption and organic matter degradation. The distribution of B, Cl and their isotopes in pore waters provide useful information for distinguishing between shallow circulation and deep origin fluid sources. Thirty-six sediment cores 0 - 5 m in length were sampled from a foreland accretionary prism offshore Southwestern Taiwan where strong bottom simulating reflectors (BSRs) and an abundance of mud diapirs were discovered. More than 350 pore water samples were separated and analyzed for B, Cl and other major ions. Four long cores were selected for B and Cl isotopic analysis. We found that the Cl in all cores varied less than 10%, suggesting no major hydrate dissolution or formation involvement at shallow depths in the study area. However, the B concentration changed greatly, ranging between 360 and 650 μM, indicating a possible sedimentary contribution during the early diagenesis stage. The B isotopic compositions were relatively depleted (~25 to 37‰) in these pore waters, implying the addition of sedimentary exchangeable B with low δ^{11}B. The Cl isotopes showed rather large variations, more than 8‰, possibly related to the addition of deep situated fluids. In summary, the chemical and isotopic characteristics of pore waters separated from piston cores off Southwestern Taiwan suggest strong influence from organic matter degradation

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during diagenesis at shallow depths and the possible addition of deep fluids advecting through mud diapir channels at greater depths, causing a minor degree of hydrate dissolution / formation to occur at shallow depths. Further systematic investigation of pore waters δ^{18}O and δD are needed in a future study.

(Key words: B isotopes, Cl isotopes, Pore waters, Gas hydrate, Organic matter degradation)

1. INTRODUCTION

Boron and chlorine isotopes are powerful new tracers for mud volcano hydro-geochemical studies on land and offshore (Spivack et al. 1987; Goden et al. 2004; You et al. 2004). In particular, the distribution of B and δ^{11}B in pore waters separated from drilling sites at various accretionary wedges (i.e., Nankai Trough, the Barbados Ridge Complex, and Hydrate Ridges) have provided important information on fluid migration along porous sandy layers and the decollement zones (Gieskes et al. 1989; You et al. 1993; Spivack et al. 2002; Teichert et al. 2005). Ransom et al. (1995) also reported large δ^{37}Cl depletions in deep generated fluids separated from the decollement zones during ODP Leg 131 at Site 808. A systematic study of B and Cl isotopes in pore waters is a powerful tool for differentiating between fluid sources and migration processes in subduction zones.

There are two stable B isotopes in nature, ^{10}B and ^{11}B with abundance of 19.82 and 80.18% respectively (Rosman and Taylor 1998). Because of the large relative mass difference between the two isotopes, high elemental mobility, abundances in the upper crust and large isotopic variations (~60‰) on surface Earth environments, B and B isotopes have become unique tracers for studying upper crust recycling, progressive metamorphism, hydrothermal water-sediment-rock interaction, slab derived fluids in subduction zones, pore water expulsion in accretionary prisms, oceanic pH in the past, and environmental pollution issues (Spivack et al. 1987, 1993; Morris et al. 1990; Palmer 1991; You et al. 1993; Ishikawa and Nakamura 1994; Gäbler and Bahr 1999; Rose et al. 2001; Benton et al. 2001; Kopf and Deyhle 2002; Deyhle et al. 2004). B sources in aqueous solutions include seawater, adsorbed or lattice bound, and those released during marine carbonate dissolution. Each of these components displays distinctive B concentrations and isotopic signatures. For instance, seawater has an average δ^{11}B of 39.5‰ compared to +15‰, ~ -5 to -10‰ and ~20‰, for sedimentary exchangeable B, lattice-bounded B and marine carbonates respectively (Spivack et al. 1987; Nakamura et al. 1992; Vengosh et al. 1991; Hemming and Hanson 1992; You et al. 1993, 1995, and 1996). Recently mud volcano studies have also indicated that B and B isotopes may provide a useful tool for methane hydrate formation where solutions obtained from the dissolution of pure gas hydrates show low B and δ^{11}B (Kopf et al. 2000; Hensen et al. 2004).

Chlorine, on the other hand, is the most abundant major element in the ocean and behaves conservatively. The two stable Cl isotopes, ^{35}Cl (75.78%) and ^{37}Cl (24.22%) (Rosman and Taylor 1998), show small isotopic fractionations (~2‰) in surface hydro-geological cycles, including river, groundwater, seawater and basin brines (Desaulniers et al. 1986; Eggenkamp et al. 1994; Liu et al. 1997). The Cl isotopic compositions in basaltic glass and silicate minerals sampled from mid-ocean ridge are heavier than seawater, 0.2 - 7.2‰ and 0.3 - 7.5‰, respectively (Magenheim et al. 1994, 1995). Due to its conservative geochemical characteristics, the variations in chlorine content in pore water often serve as an indicator for estimating the mixing ratios between seawater and other water mass end-members. In an accretionary wedge, possible fresh fluid sources are often involved with gas hydrate dissociation, groundwater addition and clay mineral dehydration (Dahlmann and de Lange 2003; Hesse 2003; Milkov et al. 2004; Toki et al. 2004). Possible brine fluids are often associated with gas hydrate formation, phase separation and halite dissociation (You et al. 1994; Torres et al. 2004; Ruppel et al. 2005). There are four possible mechanisms that may alter the Cl and Cl isotopic compositions in the fluids. First, precipitation, dissociation and evaporation of Cl-containing fluids will lead to ^{37}Cl enrichment in solid phases and change the Cl concentration in the remaining fluids (Magenheim et al. 1994; Eggenkamp et al. 1995). Secondly, differences in the diffusion rate between the two isotopes in groundwater or marine sedimentary column causes ^{35}Cl to become more depleted at depth (Desauliniers et al 1986; Eggenkamp et al. 1994). Clay membrane filtration may also cause Cl isotopic fractionation (Phillips and Bentley 1987). The above mentioned mechanisms, however, will cause only a small degree of isotopic fractionation (less then 2‰). A rather large depletion of δ^{37}Cl, -8‰, observed at the decollement zone at the Nankai Trough, was explained in terms of fluid-rock reactions at depth (Ransom et al. 1995; Spivack et al. 2002). Since gas hydrate dissolution and fresh water dilution will not cause any change in Cl isotopes in fluids, the Cl isotopic ratio has become an interesting tracer to distinguish the origin of fluids at shallow circulation or depth (Ransom et al. 1995).

In this study we measured B, Cl and their isotopes, along with other major ions in pore waters collected from a gas hydrate potential area offshore Southwestern Taiwan. Our main objectives were (1) to understand the down core variation in B, Cl and their isotopes in pore waters possibly affected by large amount of sediment transported from an active orogenic belt. (2) To study the role of sediment diagenesis on the distribution of B, Cl and their isotopes in pore waters. (3) To study the relationships between the redox potential and pore water compositions, and (4) to estimate any potential for gas hydrate formation in this region and the possible fluid expulsion related chemical fluxes to the ocean.

2. GEOLOGICAL SETTINGS

The island of Taiwan is located at the boundary between the Philippine Sea Plate and the Eurasian Plate. There are two plate subduction directions reported at the eastern and the southern part of Taiwan. At the eastern part, the Philippine Sea Plate is subducting in a northwestern direction under the Eurasian Plate along the Ryukyu Arc-Trench system. In Southern Taiwan, the South China Sea oceanic lithosphere or the Eurasian Plate is subducting easterly beneath the Philippine Sea Plate along the Luzon Arc-Manila Trench system. The Taiwan mountain belt was formed by a well-studied arc-continent collision (Biq 1972; Li 1976; Suppe 1980; Teng 1990), with the Luzon Arc moving rapidly in a northeastern direction toward the Asian continent at a speed of 7 cm per year (Yu et al. 1997). This collision has resulted in the formation of a foreland basin filled with orogenic sediments up to 6000 m in Southwestern Taiwan (Covey 1984).

With a complex tectonic background, two distinctive structural patterns were observed in the area off-shore Southwestern Taiwan. The passive South China Sea continental margin is located in the west and active imbricated fold-and-thrust structures are observed to the east (Liu et al. 1997) of the study area with a deformation front situated in between. The active margin in this region can be divided into two structural domains (Lin and Lin 2005), fold domain where sites N8, G23 and G24 are located and a thrust domain where the other sites are located (Fig. 1). Mud diapires and mud volcanoes are widely distributed in this region (Chow et al. 1996; Liu et al. 1997) along with wide spread strong BSRs (Chi et al. 1998; Chow et al. 2000).

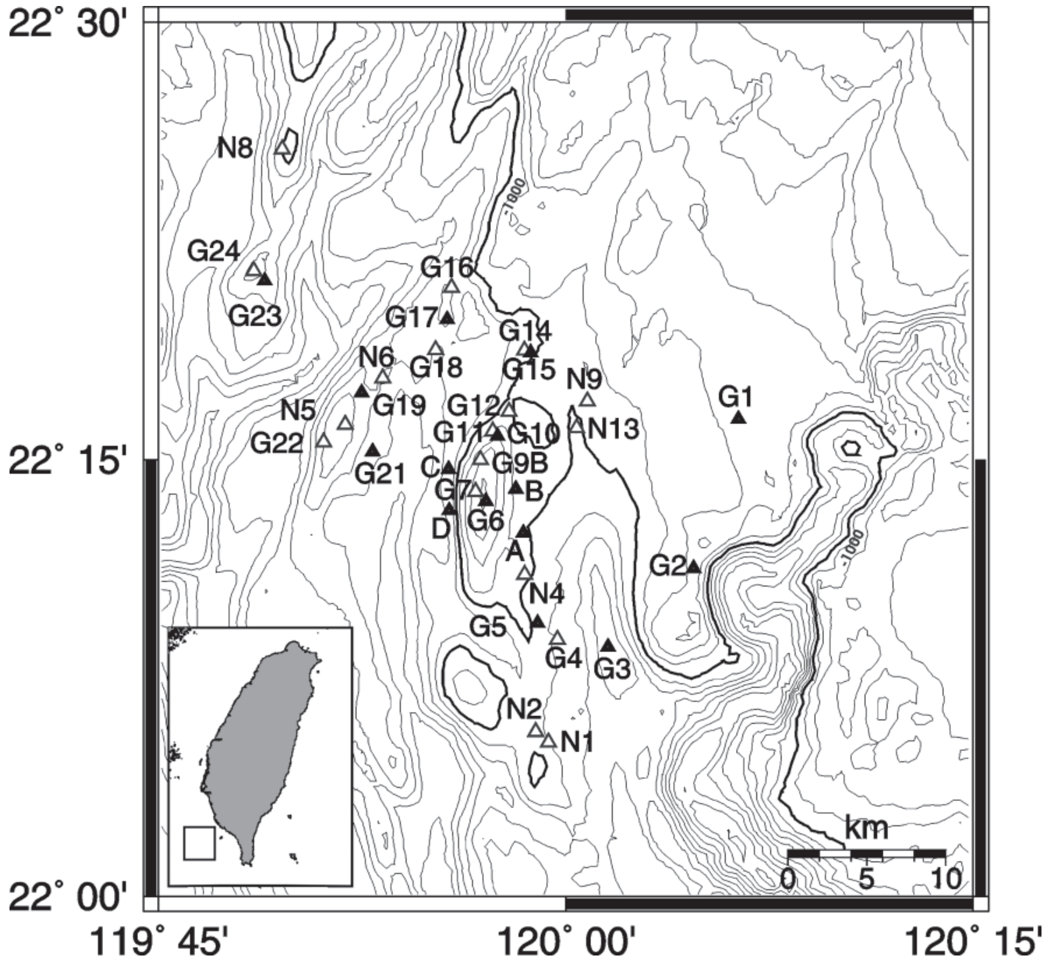

Fig. 1. Site location map of piston cores collected during OR1-697 (close triangle) and OR1-718 (open triangle) cruises offshore southwestern Taiwan.

3. SAMPLING AND ANALYTICAL METHODS

Thirty-six piston cores (up to ~5 m in length) were collected from the potential gas hydrate area off-shore Southwestern Taiwan during two OR1 cruises (OR1-697, 9 to 13 October 2002 and OR1-718, 11 to 16 May 2003). Whole round sediment cores five centimeters in length were sliced and centrifuged to separate the pore fluids. The obtained pore fluids were filtered using 0.45 μm membrane filter on board R/V Ocean Research 1. Core top water was also collected and used as representative bottom water. All pore water samples were stored in acid washed Polypropylene (PP) bottles and refrigerated at 4°C until laboratory measurement.

Chlorine and sulfate concentrations in the pore fluids were determined using ion chromatography with an average analytical precision of 3 and 5% respectively. The dissolved boron concentration was measured by colorimetric technique applying boron-curcumin complex in acidic conditions, modified from Grinstead and Snider (1967) with an external reproducibility of 5%. A few B concentrations in the pore fluids were double checked with sector field ICP-MS. Since most cores are less than one meter in length, we selected pore waters from four long cores, G2, G22, G23, and N4 which showed a major ion anomaly, for B and Cl isotopic measurements. The isotopic compositions of B and Cl were measured using TRITON TI negative-mode thermal ionization mass spectrometry (TIMS) installed at the department of Earth Sciences, NCKU. Approximately one micro liter of pore water was loaded directly on a Re filament and dried with an ion current of 0.8 A. The filament was then heated to 2 A current to burn out possible organic interference. A total of 100 ratios in 10 blocks were measured for each sample run and at least one or two standards were loaded together with unknown samples in the same turret for calibration. The B and Cl TIMS results were normalized to NBS SRM 951 and NASS-5 standards respectively and an average 2σ precision of better than 0.5‰ was obtained for both techniques.

The B and Cl isotopic compositions reported here are represented as per mil (‰) deviation from NBS SRM 951 and NASS-5 standard, respectively.

$$\delta^{11}B = \left[\frac{^{11}B / ^{10}B_{sample}}{^{11}B / ^{10}B_{NBS\ SRM\ 951}} - 1 \right] \times 10^3 \text{‰} \quad , \tag{1}$$

$$\delta^{37}Cl = \left[\frac{^{37}Cl / ^{35}Cl_{sample}}{^{37}Cl / ^{35}Cl_{NASS-5}} - 1 \right] \times 10^3 \text{‰} \quad . \tag{2}$$

4. RESULTS AND DISCUSSION

4.1 Boron and Boron Isotope

B and δ^{11}B are unique tracers for various geochemical and hydrological processes (Spivack et al. 1987; You et al. 1993, 1995, and 1996). In aqueous solution, B can be formed in two dominant species, $B(OH)_3$ and $B(OH)_4^-$. The ratio between the two species was controlled using the solution pH (Palmer et al. 1987). In general, ^{11}B prefers to enter $B(OH)_3$ trigonal structure while ^{10}B prefers $B(OH)_4^-$ tetrahedral structure. For instance, $B(OH)_3$ species has enriched ^{11}B of approximately 20‰ compared to $B(OH)_4^-$ at 20°C (Kakihana et al. 1977). Recent studies have shown even greater fractionation between the two B species (Palmer et al. 1987; Oi et al. 1991). These isotopic characteristics can be applied to study possible sources and the B process in pore water. In shallow marine sediments, the tetrahedral $B(OH)_4^-$ ion, which contains more ^{10}B, is adsorbed onto the surface of detrital clay (Spivack et al. 1987). This makes $B(OH)_3$ become the domain species in seawater and leads to depletion of B with ^{11}B enrichment up to 39.5‰ . Any release of absorbed B into pore waters will cause the B concentration to increase with significant ^{11}B depletion. Release of exchangeable sedimentary B can occur at rather shallow burial depth (You et al. 1996) or associated with organic matter decomposition during the early sediment diagenesis stage (Brumsack and Zuleger 1992; You et al. 1993). At greater depths where in situ temperatures are high and porosity is reduced, release of lattice bound B can occur (You et al. 1996). With increasing burial depth during the late diagenesis, the adsorbed B is incorporated into clay mineral interlayers and then substituted for Si in tetrahedral sites after Si-O bonds are broken during smectite to illite re-crystallization (Williams et al. 2001). These processes alter significantly both B and $\delta^{11}B$ in pore fluids and thus provide useful information for tracing fluid sources and migration passways.

All pore fluids analyzed show slightly elevated boron concentration (up to ~650 μM in core G2) and depleted isotopic composition (as low as ~25‰ in core G22) relative to seawater of 420 μM and $\delta^{11}B$ of 39.5‰ (Fig. 2 and Fig. 3, respectively). It is a rather common and wide spread phenomenon to find high boron content with lower isotopic ratio in pore water at shallow depths due to the addition of sedimentary exchangeable B. At ODP Site 1251 drilled at Hydrate Ridge, B concentration increases up to ~1100 μM with $\delta^{11}B$ of 33‰ (Teichert et al. 2005). Similar observation also reported at various accretionary wedges including the Japan Sea (Brumsack and Zuleger 1992), Nankai Trough (You et al. 1993), Okinawa Trough (Huang et al. 2005), and Costa Rica (Kopf et al. 2000). Organic matter decomposition and/or addition of desorbed sedimentary B are likely mechanisms for explaining the above mentioned high B with low $\delta^{11}B$ feature (Brumsack and Zuleger 1992; You et al. 1993, 1995; Deyhle and Kopf 2002).

The down-core distribution of B and $\delta^{11}B$ in pore waters are summarized in Fig. 4. In general, most of the pore fluids are enriched in B and depleted in $\delta^{11}B$ with a few exceptions. Three end-members can be clearly identified in the plot of $\delta^{11}B$ vs. 1 B^{-1}, namely sedimentary adsorbed B, seawater and gas hydrates. The end-member compositions of sedimentary exchangeable boron is well documented, 1400 μM of B and $\delta^{11}B$ of 15‰ (Spivack et al. 1987). The gas hydrate end-member is poorly studied and may vary with sample locality (Kopf et al. 2000; Huang et al. 2005). So far only limited gas hydrate samples have been sampled and measured for B and $\delta^{11}B$. All pore fluids show a strong mixing relationship between two end-members of seawater and adsorbed B (Fig. 4), indicating addition of sedimentary exchangeable and lattice-bounded B in pore fluids.

4.2 Chlorine and Chlorine Isotope

Chlorine is one of the most abundant and the most conservation anions in seawater and

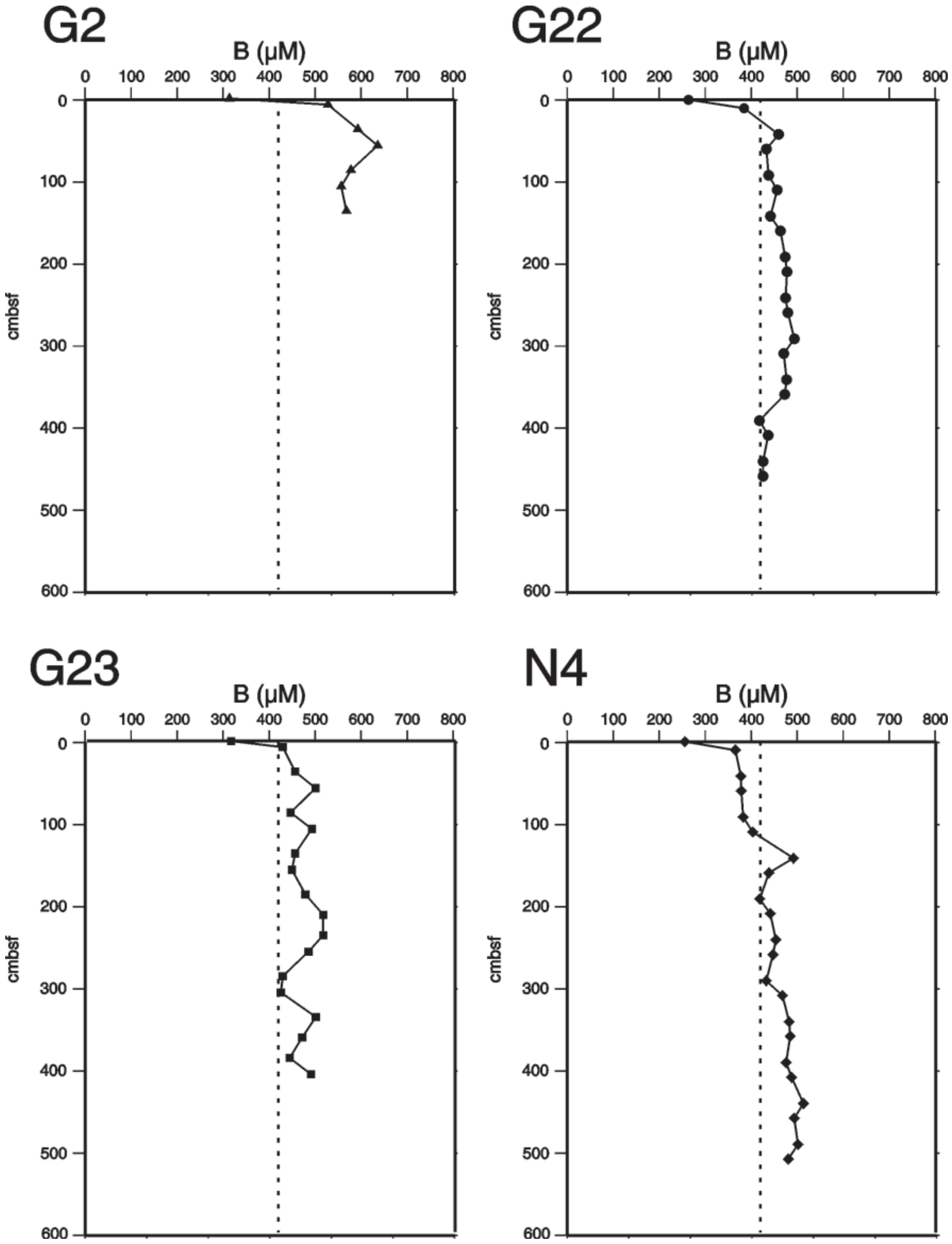

Fig. 2. Down-core distribution of boron concentration in pore waters separated from piston cores G2, G22, G23, and N4. Most samples show slight elevated boron content compared to seawater (dash line).

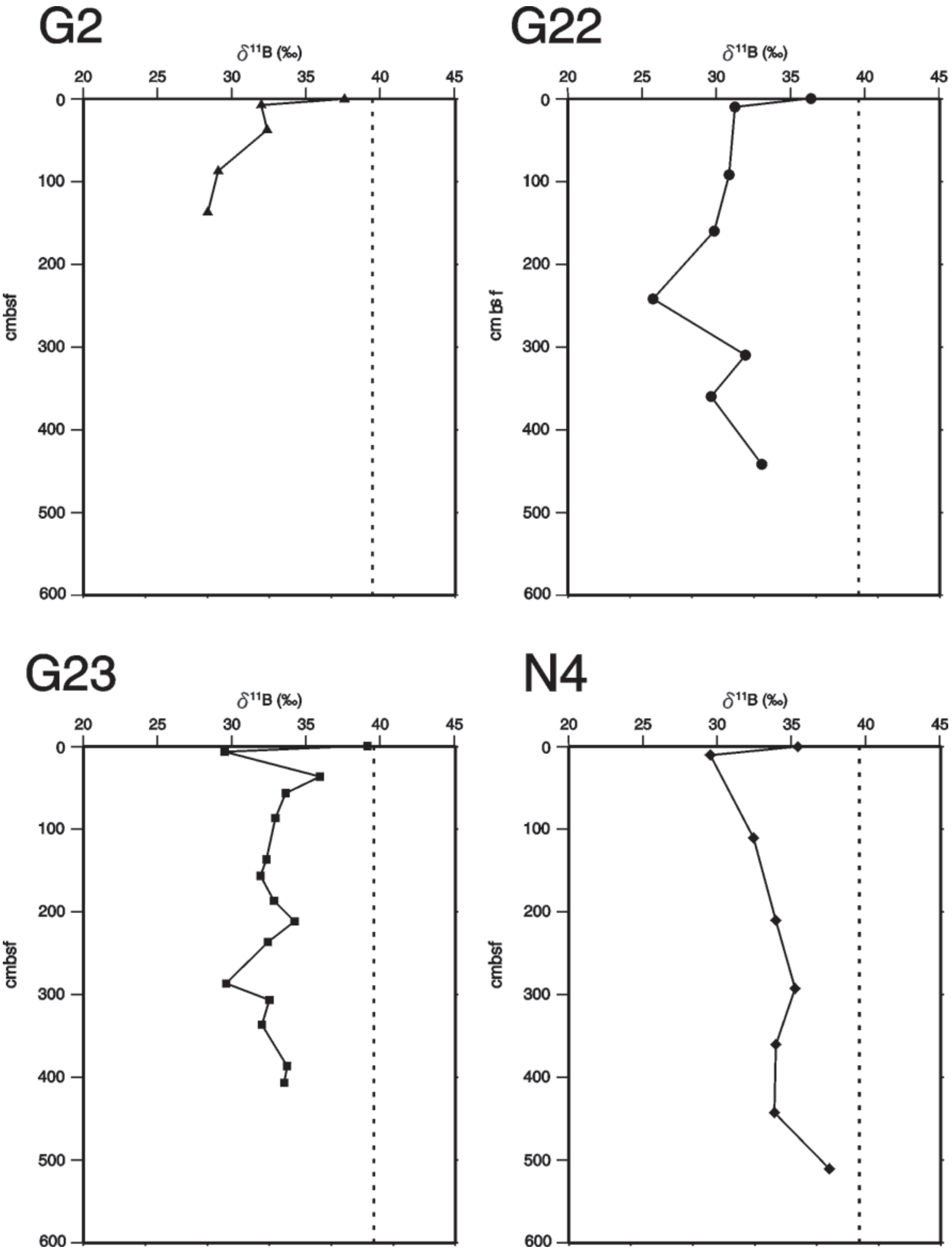

Fig. 3. Down-core distribution of boron stable isotopes in pore waters separated from piston cores G2, G22, G23, and N4. All samples show δ^{11}B lower than an average seawater value of 39.5‰ (dashed line).

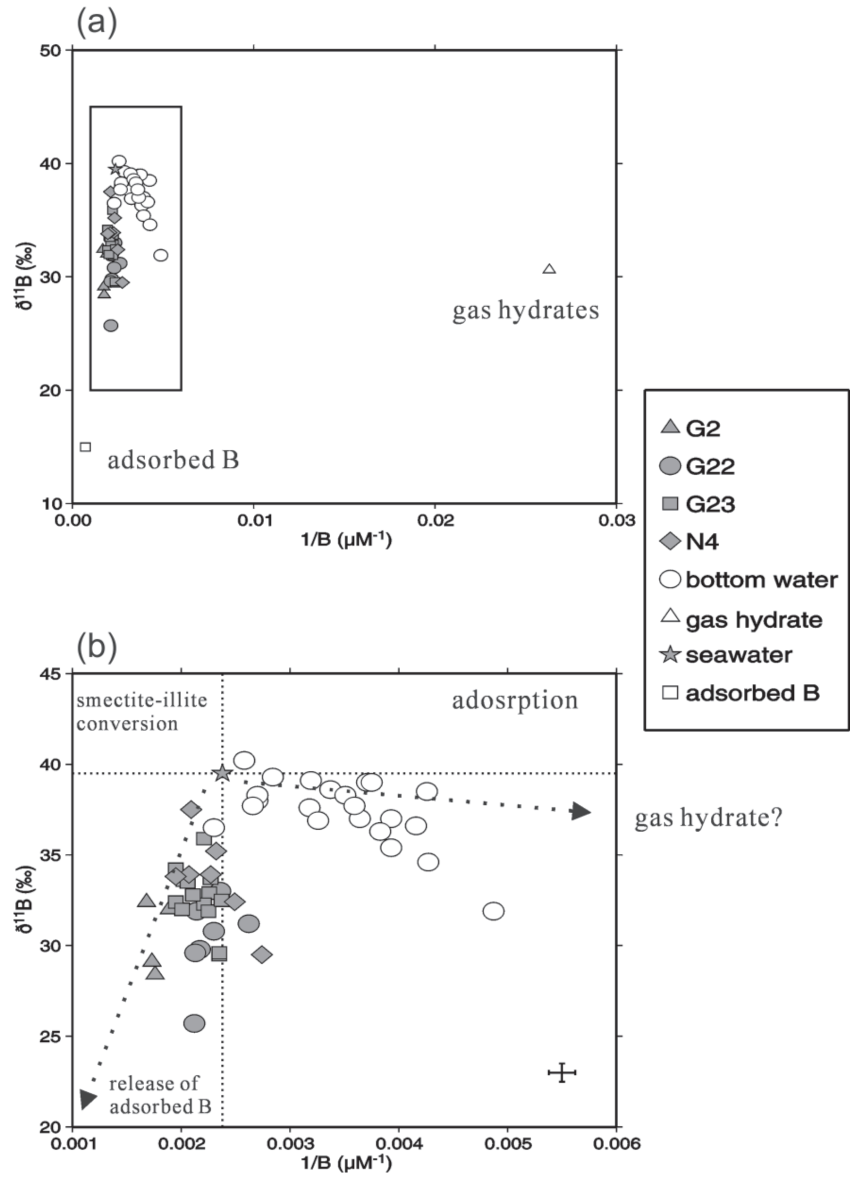

Fig. 4. Correlation plot of δ^{11}B vs. 1 B^{-1} in pore waters separated from piston cores G2, G22, G23, and N4. (a) Three distinctive B sources in pore waters identified are seawater ([B] = 420 μM and δ^{11}B = 39.5‰), adsorbed B ([B] = 1400 μM and δ^{11}B = 15‰; Spivack et al. 1987) and gas hydrates ([B] = 38 μM and δ^{11}B = 30.6‰; Kopf et al. 2000) (b) Four possible mechanism that may affect B and δ^{11}B in pore water are released of adsorbed B, adsorption of B onto clay minerals, gas hydrate dissociation and smectite-illite transformation.

pore water. The Cl concentration in all pore waters analyzed show small down-core variation, less than 10%, for all cores (Fig. 5). However, the down-core Cl isotopes vary largely, in particular more than 8‰ found in G23 compared to less than 4‰ in others (Fig. 6). The most depleted Cl isotopic composition of -6‰ is detected in pore waters separated from 340 centimeters below sea floor (cmbsf) at G23. Due to possible diffusion artifacts, chlorine isotopes are normally in negative values in the pore waters (Magenheim et al. 1994; Eggenkamp et al. 1995). The natural δ^{37}Cl variation in the Earth's surface is smaller than 2‰. The observed large depletion and shallow occurrence ruled out any possibility due to molecular diffusion and/or halite precipitation. Deep generated fluids reported were depleted in δ^{37}Cl (Ransom et al. 1995; Spivack et al. 2002) and this has been used as a sensitive tracer for fluid migration in accretionary wedges.

Fluids separated from seafloor mud volcanoes often show low δ^{37}Cl. For instance, fluids with δ^{37}Cl as low as -6‰ are reported in marine mud volcanoes, Barbados (Goden et al. 2004) and similar observations are reported from the decollement zone fluids at ODP Site 808, Nankai Trough (Ransom et al. 1995; Spivack et al. 2002). Interestingly, the seismic profile at site G23 is indeed a mud diapiric structure, indicating possible involvement of deep generated fluids and the most depleted isotopic composition of -6‰ is similar to fluids emitted from mud volcanoes near the deformation front at Barbados. Deep fluid migration along porous sandy layers or the decollement zone has been reported in various accretionary wedges and could play an important role to chemical budget of B and Ca into the ocean (You et al. 1993, 2004). Other mechanisms like phase separation (Spivack et al. 1990), water-rock interaction (Ransom et al. 1995; Spivack et al. 2002) and ion filtration (Goden et al. 2004) to generate Cl-depleted fluid need further systematic investigation.

4.3 Possible Gas Hydrate Formation

Sulfate is a major constituent in pore water of shallow marine sediment and has a relatively high concentration (~28 mM). Under the aerobic depth of just a few centimeters below subsurface, it is used as an electron acceptor during sedimentary organic matter oxidation using sulfate reducing bacteria (SRB):

$$SO_4^{2-} + 2CH_2O\,(\text{carbohydrate}) \rightarrow H_2S + 2HCO_3^- \quad . \tag{3}$$

This reaction will be accompanied using a methane oxidation reaction in a methane-rich environment (Boroski et al. 1996):

$$SO_4^{2-} + CH_4 \rightarrow HS^- + HCO_3^- + H_2O \quad . \tag{4}$$

The sulfate reduction layer extends downward until the sulfate-methane transition (SMT) depth, which is the sulfate depth entirely consumed by SRB (Borowski et al. 1999). The SMT depth primarily depends on two factors: 1) the sulfate content near the seafloor, which is normally constant, and 2) the amount of organic matter within the sediment or the amount of vertical methane flux. Thus, a relative shallow SMT depth implies higher methane flux from below and a higher possibility for gas hydrate formation since a sufficient supply of methane is the key for hydrates formation.

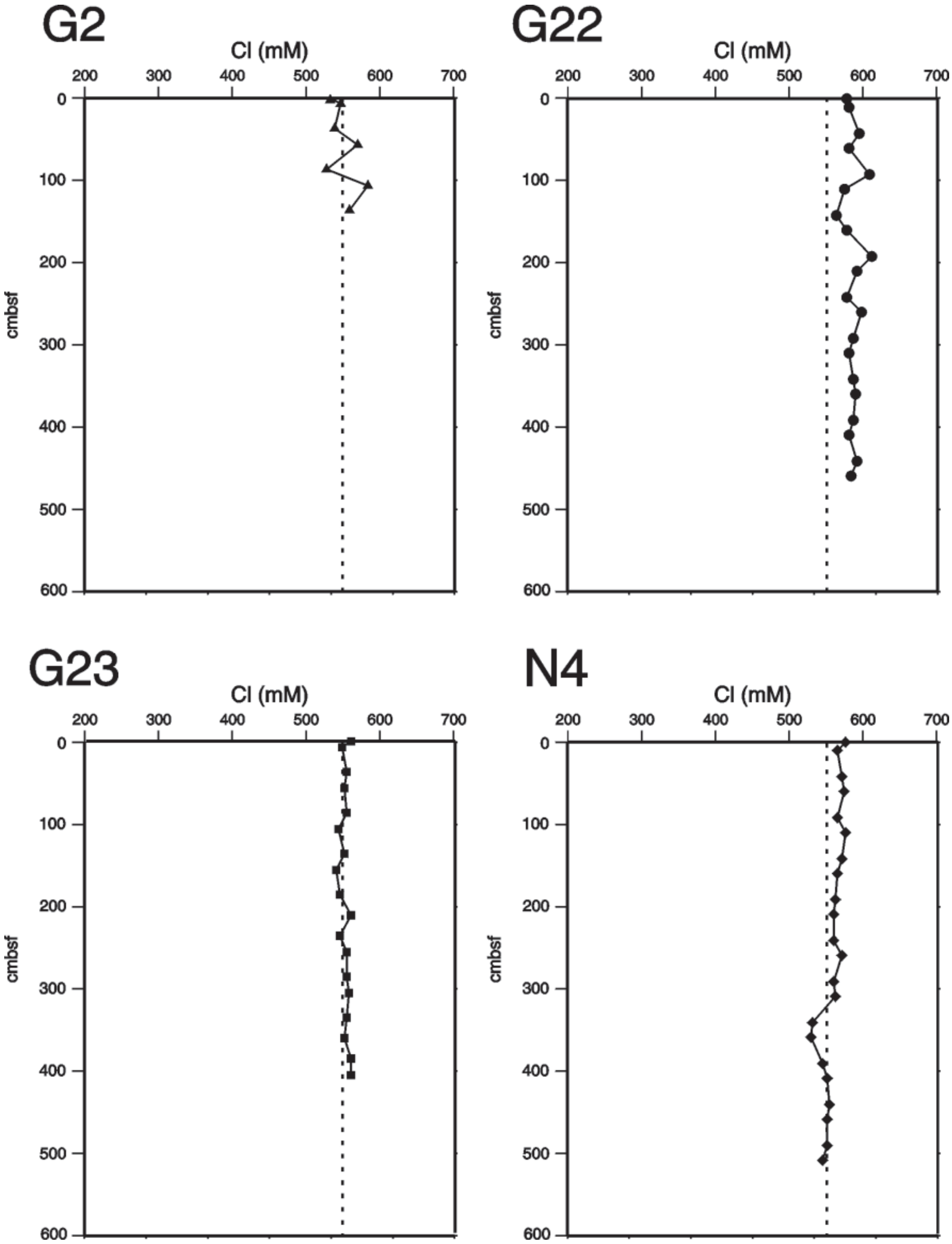

Fig. 5. Chlorine down-core concentration distribution in pore waters separated from piston cores G2, G22, G23, and N4. All samples show minor Cl variations with seawater value (dash line).

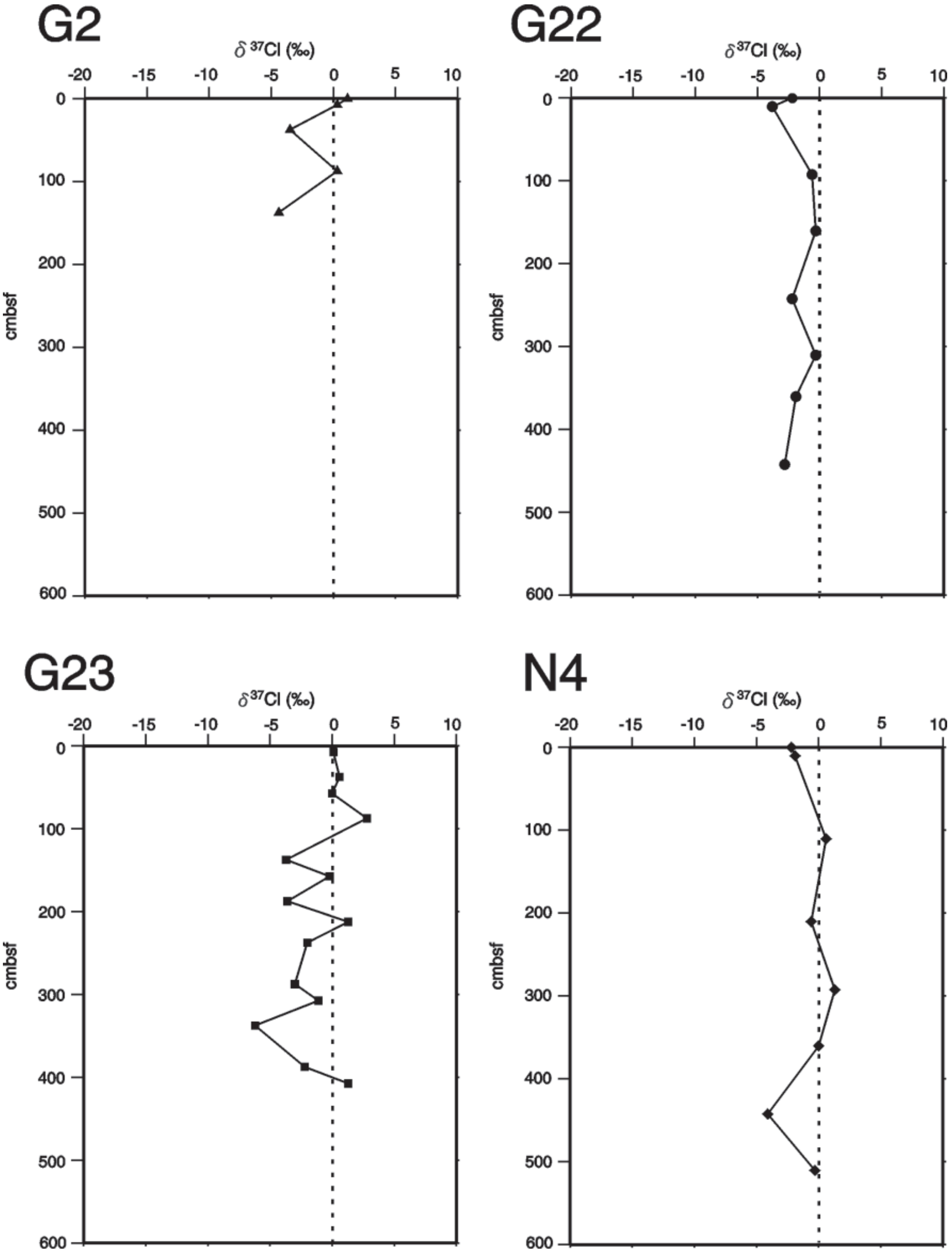

Fig. 6. Chlorine stable isotope down-core distribution in pore waters separated from piston cores G2, G22, G23, and N4. Please note that G23 pore waters display the most depleted δ^{37}Cl at depth, possibly due to addition of deep generated fluids. The dashed line represents the seawater value.

The down-core variations in sulfate show significant decreasing trend due to sulfate reduction. Site G23 has the shallowest SMT depth (~60 cmbsf; Fig. 7), with large amount of upward methane flux due to the fast vertical fluid channel migration from a mud volcano. Since we do not have direct gas hydrate recovery, the possibility of gas hydrate existence is verified judging from the SMT depth (G23, G22, N4, and then G2).

At a depth range between 300 ~ 400 cmbsf at G23, a slight increase in the sulfate concentration was detected. This SO_4 maximum is coincided with large Cl stable isotope depletion. Similar observations in pore waters reported at ODP Site 1202 where high porosity sandy layer contains high sulfate (Huang et al. 2005) possibly due to fluid migration from greater depth.

All core top waters show an interesting boron concentration and isotopic compositions: both B and δ^{11}B are lower than average seawater. No similar observation has been reported, however, it could possibly be a result of gas hydrate dissolution and/or formation. Due to its long oceanic residence time (12 - 20 million years), it is commonly believed that boron in the ocean should be rather uniform. There are two possible causes that may lower the boron concentration in the bottom water. First, any fresh water addition either by freshwater contamination during sampling or gas hydrate decomposition after coring will dilute the concentration. Kopf et al. (2000) reported an end-member gas hydrate dissociated fluids with similar low boron and low δ^{11}B. Similar observations in pore water at ODP Site 1040 and 1041, Costa Rica were explained in terms of hydrate dissolution. Huang et al. (2005) observed low B and δ^{11}B in pore waters at 16.1 and 41.6 mbsf, ODP Site 1202, Okinawa Trough where high porosity sandy layers and low chlorine concentration (~520 mM) fluids were recovered. It was explained in terms of fresh fluid advection along the high porosity sandy horizons or the addition of gas hydrate dissociation fluids. However, they could not clearly separate the effects due to fluid sources or migration processes without further oxygen and hydrogen isotopic analyses. Teichert et al. (2005) reported similar boron distributions in pore waters collected from Hydrate Ridge, where gas hydrate dissolution/formation may have occurred. No strong evidence found to support that B isotopic signals were influenced by hydrate dissociation during core recovery. Any fresh water dilution will lower the Na and Cl sensitivity in pore waters. However, the chlorine concentrations in bottom waters remain rather constant. Secondly, absorption and/or desorption of exchangeable boron in subsurface sediment or during coring disturbance may alter B and δ^{11}B in pore waters. Sediment absorption of B will lead to low concentration with high isotopic ratios of B in fluids. In other words, any released of sedimentary B will raise B but lower δ^{11}B. It is clear that both mechanisms mentioned could not be used to explain the bottom water observations. Advection of deep generated fluids with low B and δ^{11}B and subsequent mixing with shallow fluid sources will be a likely scenario.

5. CONCLUSION

We have analyzed pore water samples collected from potential gas hydrate area off-shore Southwestern Taiwan. Down-core distribution of B, δ^{11}B, Cl, and δ^{37}Cl, as well as sulfate and other ions, show useful information of fluid sources and migration processes. Our major observations are:

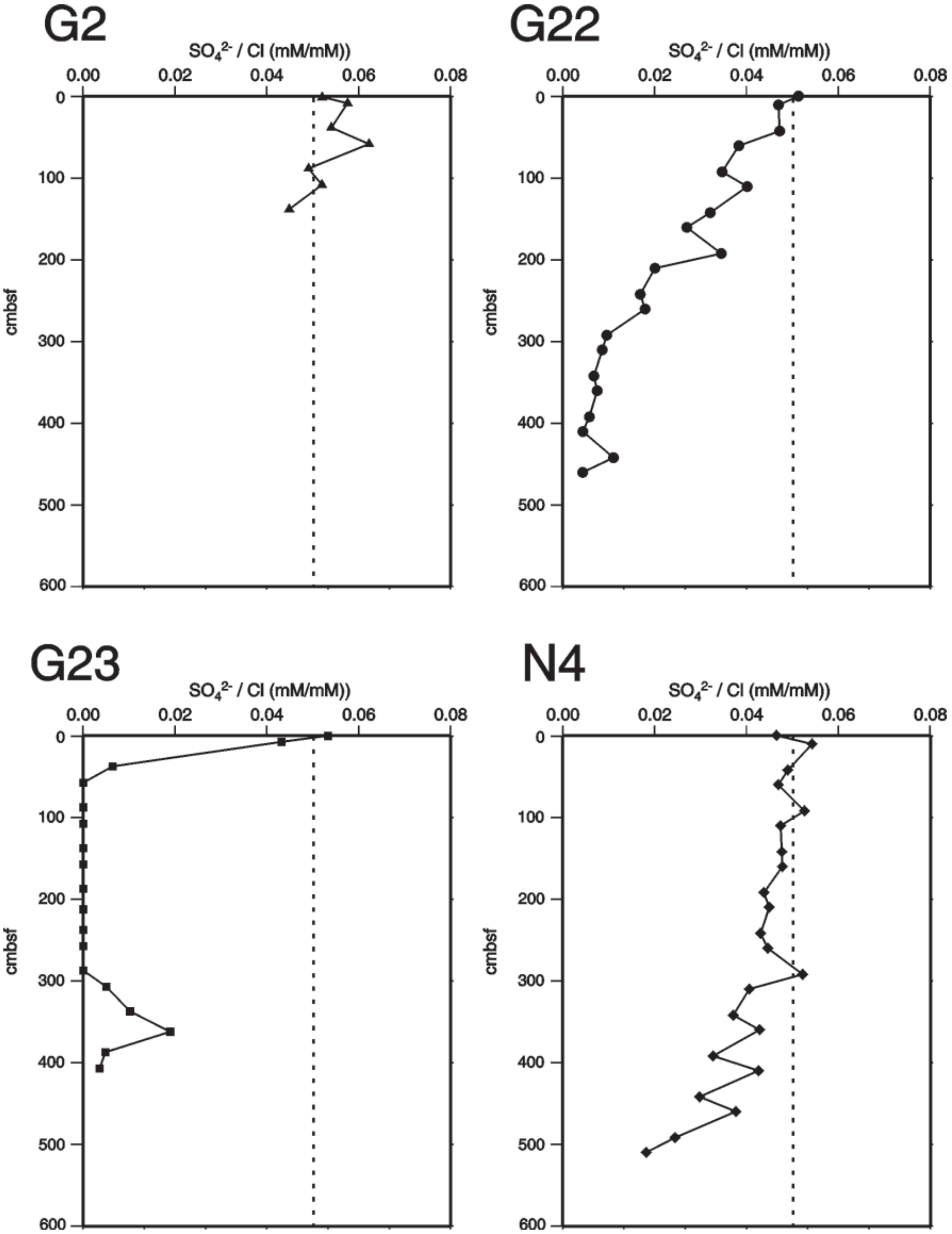

Fig. 7. Normalized sulfate down-core concentration distribution in pore waters separated from piston cores G2, G22, G23, and N4. Most samples show $SO_4\ Cl^{-1}$ ratio lower than average seawater value (dash line) and the ratios vary with depth. It is interesting to note that G23 had the shallowest SMT depth at 60 cmbsf.

1. The down-core distributions of B and δ^{11}B in these sedimentary pore waters show rather large and systematic variations. The B content falls in a range between 360 and 650 μM while δ^{11}B varies from 25 to 37‰.
2. High B concentration with low δ^{11}B in pore water samples indicating the release of sedimentary exchangeable B due to degradation of organic matter during sediment diagenesis.
3. Low B content with low B isotopic compositions in bottom waters is a unique observation, which hasn't been reported before and need further systematic investigation in any future study. Possible cause for such observation is seawater like shallow fluid mixed with deep generated with low B and δ^{11}B.
4. Cl concentration in all cores remains rather constant with seawater value, indicating only minor degree of gas hydrate dissolution/formation at shallow depth. The most depleted δ^{37}Cl occurred at G23 of more than 6‰, possibly related to addition of deep situated fluids at depth.
5. Sulfate concentration varies largely with depth and core location. The shallow SMT depth of G23, which located near the mud volcano conduits implies greater methane upward migration and is a potential drilling target for further scientific study.

Acknowledgements This work is supported by the Central Geological Survey project to YCF. We thank Professors J. C. Chen, C. S. Liu, S. Lin, T. F. Yang, crew and technicians aboard the R/V Ocean Research 1 for wonderful project coordination and cruise assistance during OR1-697 and OR1-718, and K. F. Huang for analytical support and scientific discussion. The constructive comments provided by two reviewers, Professor Y. N. Shieh and an anonymous person have greatly improved this manuscript.

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