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Geochemistry of Major Constituents, Boron and Boron Isotopes in Pore Waters from ODP Site 1202, Okinawa Trough

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ABSTRACT

Forty-one interstitial water samples recovered from ODP Site 1202, Okinawa Trough, were analyzed for major constituents, B and δ^{11}B. The geochemical results show that major constituents and boron content varied largely in pore fluids and possibly were affected by sulfate reduction, recrystallization of biogenic carbonate or silica, ash alteration, and organic matter degradation. Mixing of fluids along high-porosity sandy layers or fracture zones also changes the pore water chemical compositions significantly.

The down-core distribution of B and δ^{11}B in the pore waters are sensitive tracers for assessing fluid migration and water/sediment interaction at various depths. Pore water B content at Site 1202 falls in a range between 0.25 and 1.16 mM compared to that of 0.42 mM in seawater. The δ^{11}B values, however, vary considerably from ~32.7 to 50.9‰ relative to the seawater value of 39.5‰. The δ^{11}B vs. 1/B plot indicates that sedimentary B released from clays is the most important source to pore waters, resulting in elevated B with low δ^{11}B. Other processes including precipitation of calcium carbonate, fluid advection through high-porosity permeable sandy horizons, interaction with terrigenous sediments and/or ash alteration may also modify the B and δ^{11}B distributions.

(Key words: B isotopes; Pore waters; Sedimentary B-desorption; Okinawa Trough)

1. INTRODUCTION

The chemical concentration and isotopic composition of boron in interstitial waters often provide useful diagnostic tools to assess possible solute migration, geochemical interactions,

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and organic matter degradation in sedimentary columns. Work during the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP) in the past three decades has obtained a broad spectrum of high quality chemical data of interstitial waters in various marine environments. These studies, in particular, have shed light on sediment dewatering processes in the frontal part of accretionary wedges around the world and have provided information on potential return flux of volatiles into the ocean at convergent margins (You et al. 1993a,b; Zuleger et al. 1996; Kopf et al. 2000; Deyhle et al. 2001; Deyhle and Kopf 2001). On the contrary, only a little attention has been focused on pore water chemical characteristics in a newly occurring spreading region, e.g., Okinawa spreading center. It is evident from recent seafloor hydrothermal studies that estimated fluxes at ridge flanks possibly have a profound influence on seawater chemistry compared with focused hot springs at mid-ocean ridges (Elderfield and Schultz 1996).

In previous DSDP/ODP drill sites, large down-core changes in pore waters have been reported including major and trace constituents, as well as boron. Some of these components behave conservatively in seawater (e.g., chlorine; Gieskes 1975; Brumsack and Zuleger 1992), but display rather large variation in pore waters. Several mechanisms have been proposed to explain the observed variations in pore water, including reduction-oxidation, sediment diagenesis, diffusion and/or advection of deep generated fluids. Changes in depositional environments, in particular, the reduction-oxidation states affect greatly the distribution and mobility of chemical species in pore waters (Gieskes 1975). Sediment diagenesis generally involves decomposition of organic matter, formation of authigenic minerals, inorganic transformation of clay minerals, volcanic ash or tephra alteration and barite precipitation (Gieskes 1975; Gieskes and Lawrence 1981). Large chemical or isotopic variations also may be related to low-temperature alteration or sulfate reduction and anaerobic methane oxidation by microbiota (Gieskes and Lawrence 1981; Spivack et al. 1987). In some cases, diffusive exchange among pore waters, seawater and the upper oceanic crust also play an important role in pore water gradients (McDuff 1981). On the other hand, mixing of clay dehydration and lateral transport of deep generated fluids affect pore fluid compositions importantly in convergent margins (Gieskes 1975).

Boron and B isotopes are unique tracers for studying hydro-geological processes in subduction zones because of boron’s high mobility and associated large isotopic fractionation on Earth’s surface environments (Palmer 1991; Ishikawa and Nakamura 1994; Rose et al. 2001; Benton et al. 2001; Kopf and Deyhle 2002). Other important B and δ^{11}B applications are oceanic crust alteration (Spivack and Edmond 1987; Spivack et al. 1990; Smith et al. 1995), environmental pollution (Gabler and Bahr 1999), and pH reconstruction in past oceans (Spivack et al. 1993; Sanyal et al. 1997; Palmer and Pearson 2003). Recent studies also demonstrate that B and δ^{11}B provide crucial information on the study of fluid origin and the degree of water/sediment interaction at depth, as well as methane hydrates formation (Brumsack and Zuleger 1992; You et al. 1993a; You et al. 1995 1996; Kopf et al. 2000; Deyhle and Kopf 2002).

In this study, we measured in detail major ions and B content, as well as B stable isotopes, in pore fluids at Site 1202 of the Okinawa Trough. The main objectives are to understand the degree of pore waters chemical variation down-core and to investigate causes for various diagenetic processes at depth.

2. GEOLOGICAL SETTING

The Okinawa Trough is an active, incipient, intra-continental back-arc basin formed behind the Ryukyu arc-trench system in the western Pacific. Site 1202 was drilled at the southwestern part of the Okinawa Trough (24°48.24'N, 122°30.00'E) where the water depth is approximately 1278 m (Fig. 1). The total core recovery at this site is approximately 410 meters. The Okinawa Trough is characterized as a rifting basin associated with incipient arc volcanism opening in the middle of orogenic belt caused by arc-continent collision (Teng 1996). Extensive bathymetry (Liu et al. 1998), gravity and magnetic surveys (Hsu et al. 1998) have shown a series of normal faults dipping toward the center. Preliminary sedimentological results obtained during ODP Leg 195 indicate extremely high sedimentation rates, possibly > 300 cm kyr^{-1}, in the Holocene, and that the sediments mainly consist of dark gray calcareous silt clays and sandy turbidites. This was attributed to large amount of terrigenous inputs from the East China Sea and from the main island of Taiwan (Chen et al. 1992a) by turbidity currents through river canyons. Box-cores in the same region consist of mainly clay to silt-sized terrigenous materials and secondary biogenic carbonates (~20%) or opal, as well as a small portion of volcanic ash (Chen et al. 1992b).

The lithology of the upper 410-m section at Site 1202 is characterized by dark grayish green, bioturbated clayey silt. Abundance of sandy turbidites are observed between 230 and 280 mbsf and occasional thin layer (< 1 cm) of turbidites appeared throughout the rest of the

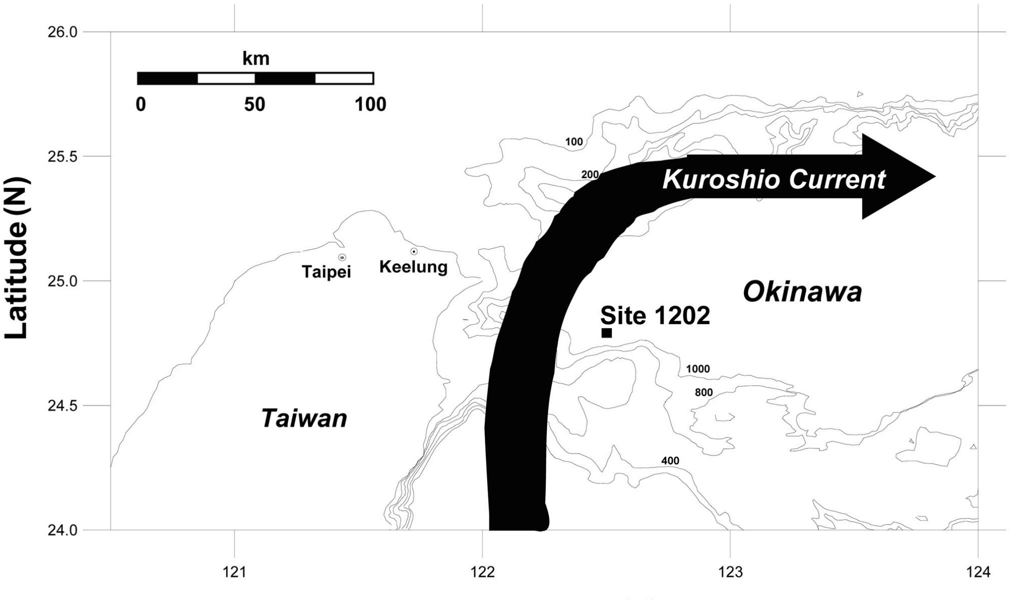


Fig. 1. Location map showing Site 1202. Approximate path of Kuroshio Current also indicated (modified after Shipboard Scientific Party 2002).

core section. The sediments obtained at Site 1202 contain rich organic carbon and charge with H2S. The non-biogenic fractions consist of quartz, feldspar, detrital carbonates, and the sandy turbidites contain micas, heavy minerals, and opaques (Salisbury et al. 2002). The terrigenous components were transported from nearby islands as well as local ash and tephra layers.

3. ANALYTICAL METHOD

Forty-one interstitial water samples were collected from ODP Site 1202 with a depth resolution of 1.5 m and 20 m at intervals of 0 - 41.6 and 41.6 - 410 mbsf respectively. The pore waters were obtained by routine squeezing procedures on board JOIDES RESOLUTION using sediment sections 5 - 10 cm long, which were cut immediately after core retrieval on the deck. Samples of pore water were then filtered through 0.45 -μm filters and acidified for later laboratory analyses. The major ion concentrations including chloride, sulfate, sodium, potassium, magnesium, and calcium were analyzed by ion chromatography installed at NCKU, with an average analytical precision of 3 - 5%. Dissolved B concentrations were determined using a curcumin colorimetric technique modified from Grinstead and Snider (1967) by UV-Visible spectrophotometer with a precision of approximately 3%. B isotopic compositions were determined by meta-borate BO_2^- negative thermal ionization mass spectrometry, and the standard deviation of isotope ratios based on replicated analyses of the NASS-5 standard seawater (38.8‰) and natural pore water samples was about 0.4‰ (2σ). All isotopic compositions reported in this study are expressed in terms of per mils (‰) deviation relative to the NBS SRM 951 standard ($^{11}B/^{10}B = 4.0056 \pm 0.5$‰); i.e.,

$$\delta^{11}B = \left(\frac{\left(\frac{^{11}B}{^{10}B}\right)_{sample}}{\left(\frac{^{11}B}{^{10}B}\right)_{NBS951}} - 1 \right) \times 1000 \ (‰)$$

4. RESULTS AND DISCUSSIONS

4.1 Major Constituents in Pore Waters

The pore waters analytical results are summarized in Table 1 and the distribution profiles of Cl, SO_4, Na, K, Mg and Ca are presented in Fig. 2. The major sediment properties are characteristic of homogenous calcareous and bioturbated clayey sediments, with sandy turbidites at depth intervals between 230 and 280 mbsf (see also Fig. 2). Sulfate reduction, carbonate dissolution, clay dehydration, ash alteration, and organic matter degradation are likely to have occurred at Site 1202. In the following discussion, we describe firstly the down-core distribution of these constituents and subsequently examine possible causes for the variations.

In the uppermost section (0 - 230 mbsf), chlorine varies substantially, from 490 to 560 mM, and becomes less scatter deeper down (Fig. 2a). The large Cl fluctuations can be attributed partly to fluids advection along the sandy horizons at the intervals between 0 and 140 mbsf, where porosity is relatively high (Salisbury et al. 2002). Potential advective flows along high porosity layers or fractures zones have profound effects in pore water chemistry at convergent margins (Gieskes et al. 1998; Deyhle and Kopf 2002). In addition, volcanic ash alteration or fresh water addition also affect Cl distribution (Gieskes 1975; Gieskes et al. 1998). No major tephra layers were reported at this site; however, rare volcanic glass shards do present throughout the entire core (Salisbury et al. 2002). The chlorine content is significantly lower than the seawater value at depth intervals between 230 and 280 mbsf, which coincides with the occurrence of a thick layer of sandy turbidites. Below 280 mbsf, the Cl concentration decreases to 510 - 520 mM, approximately ~8% lower than seawater. On the other hand, potential artifacts due to squeezing procedures cannot be completely ruled out as rather large scattering in Na and K were also presented.

Sulfate decreases rapidly from 26.2 mM near the seawater/sediment boundary to 0 mM at 15 mbsf (Fig. 2b), possibly due to efficient sulfate reduction (Gieskes 1975). Below the sulfate reduction zone, sulfate increases slightly and reaches a peak value ~7.43 mM at 270 mbsf near the sandy turbidite layers. Then, sulfate decreases again toward the deeper sections.

The dissolved Na and K display similar depth distribution patterns at Site 1202 (Figs. 2c, d). Dissolved Na shows large scatter at the uppermost 50 meters with a minimum value at ~97.1 mbsf. It is appropriate to use Na/Cl instead of Na alone, because of the large Cl variations abovementioned. Any dilution or fresh water contamination artifacts will be removed after Cl normalization. The Na/Cl ratio (Fig. 3a) decreases gradually from the sediment surface to 97.1 mbsf, possibly a result of Na uptake into authigenic or detrital minerals (Kastner 1974). For the rest of the core sections, the Na/Cl ratios scatter rather largely. The occurrences of high-porosity sandy layers or turbidites provide potential conduits for mixing of fluids generated at different sources.

In the uppermost 140 mbsf, dissolved K and Cl display interesting correlations (Figs. 2a, d), reflecting changes in sediment porosity. Below 140 mbsf, K increases slightly and reaches a value ~12.0 mM at 270 mbsf where sandy turbidites are located. Previous studies indicate that K was taken into illite after deep burial or co-precipitation with colloidal clays (Kastner 1974; Weaver 1989). Other potential sinks for potassium are authigenic feldspars, chlorite or volcanic ash alteration (Kastner 1974; Gieskes et al. 1998).

The distribution of dissolved magnesium and calcium are plotted in Figs. 2e, f, respectively. The dissolved Mg decreases from 57.1 mM at the core-top to a minimum ~30 mM at 41.6 mbsf. Large Mg variations were detected at the sandy layers between 41.6 to 150 mbsf, possibly due to carbonate precipitation, clay incorporation or dolomitization (Gieskes 1975; Gieskes et al. 1998). Between 150 and 250 mbsf, Mg remains rather constant. Of importance to note is the significant increase of Mg at 250 - 280 mbsf associated with the occurrence of sandy turbidites.

The dissolved Ca concentration decreases rapidly at the uppermost 40 m in response to sulfate reduction (Fig. 2f). Then Ca increases slowly down-core to a maximum value of 7.49 mM at 270 mbsf. Precipitation of $CaCO_3$ associated with organic matter decomposition decreases Ca in pore water (Gieskes et al. 1998). On the other hand, clay and ash alteration or

Table 1. The chemical compositions of interstitial watwrs at Site 1202.

Leg	Site	Core, section, interval (cm)		Depth (mbsf)	Cl^- (mM)	SO_4^{2-} (mM)	Na^+ (mM)	K^+ (mM)	Mg^{2+} (mM)	Ca^{2+} (mM)	Na/Cl	B (μM)	$\delta^{11}B$ (‰)	RSD (‰, 2σ)
195	1202	1H1	145-150	1.44	493	26.2	460	9.55	52.3	9.56	0.93	1166	34.9	0.11
195	1202	1H2	145-150	2.94	538	22.2	466	10.8	55.5	7.78	0.87	731	33.1	0.17
195	1202	1H3	145-150	4.44	501	18.0	444	10.2	53.6	5.16	0.89	755	33.2	0.17
195	1202	1H4	145-150	5.94	506	15.6	456	10.8	57.1	4.23	0.90	701	33.9	0.14
195	1202	1H5	94-99	6.94	505	11.9	451	11.1	52.9	4.18	0.89	749	33.9	0.15
195	1202	2H1	145-150	8.53	529	2.34	459	9.19	52.0	3.19	0.87	584	38.5	0.79
195	1202	2H2	145-150	10.03	500	0.45	439	9.15	49.4	3.47	0.88	682	36.9	0.61
195	1202	2H3	145-150	11.53	535	0.91	445	8.30	49.8	3.98	0.83	600	34.5	0.32
195	1202	2H4	145-150	13.03	494	0.53	448	10.1	50.6	3.28	0.91	637	34.4	0.43
195	1202	2H5	145-150	14.54	523	2.16	453	12.3	49.4	3.61	0.87	456	32.7	0.25
195	1202	2H6	145-150	16.04	517	0	439	9.24	49.9	3.30	0.85	254	35.5	0.80
195	1202	2H7	75-80	16.83	531	0	454	9.26	48.6	3.43	0.86	632	34.4	0.40
195	1202	3H1	145-150	18.05	506	0	434	8.53	48.7	3.40	0.86	614	35.5	0.52
195	1202	3H2	145-150	19.53	507	0.43	440	8.45	46.5	2.99	0.87	644	36.4	0.76
195	1202	3H3	145-150	21.04	520	0.65	424	8.20	46.9	3.23	0.82	869	36.0	0.84
195	1202	4H1	145-150	27.53	556	0	444	8.82	48.0	2.95	0.80	537	35.9	0.34
195	1202	4H6	145-150	34.63	542	1.07	451	12.4	45.3	2.87	0.83	567	33.6	0.22
195	1202	4H7	82-87	35.49	527	1.14	436	14.0	41.1	3.52	0.83	536	33.4	0.17
195	1202	5H1	145-150	37.03	555	0.35	433	10.1	47.0	4.88	0.78	425	35.6	0.18
195	1202	5H2	145-150	38.53	526	1.22	452	10.4	44.9	4.40	0.86	401	34.3	0.17
195	1202	5H3	145-150	40.03	530	1.17	437	11.3	39.6	3.91	0.82	418	34.7	0.17
195	1202	5H4	145-150	41.53	513	1.91	449	9.64	31.8	3.11	0.87	260	33.7	0.14
195	1202	6H3	145-150	49.53	546	0.78	424	7.08	41.9	4.97	0.78	489	36.1	0.47
195	1202	7H3	145-150	59.02	554	1.10	455	9.43	48.2	4.64	0.82	455	37.2	0.16
195	1202	8H3	145-150	68.54	564	0.40	451	8.70	42.1	3.65	0.80	437	38.4	0.14
195	1202	9H3	145-150	78.02	515	0	439	9.19	41.6	3.80	0.85	554	36.3	0.21
195	1202	10H3	145-150	87.45	531	0	443	7.82	47.9	4.41	0.83	565	37.0	0.28
195	1202	11H3	145-150	97.03	550	0.62	389	8.13	48.0	5.11	0.71	506	37.0	0.16
195	1202	12H3	145-150	106.52	561	0	446	9.43	46.1	4.37	0.79	448	35.8	0.17
195	1202	13H6	132-142	110.90	538	0	448	9.73	43.6	4.20	0.83	369	35.9	0.18
195	1202	14X3	140-150	118.89	544	2.77	436	8.63	45.6	4.29	0.80	438	37.4	0.19
195	1202	15X3	140-150	128.49	535	2.36	451	7.10	41.1	5.11	0.84	397	38.6	0.13
195	1202	16X3	140-150	138.17	544	3.90	451	8.74	41.2	6.04	0.83	379	37.8	0.19
195	1202	17X3	140-150	147.77	560	2.65	444	8.29	39.6	5.26	0.79	400	40.1	0.13
195	1202	20X3	140-150	176.66	539	3.51	445	9.29	42.0	6.07	0.83	585	39.9	0.15
195	1202	27X1	140-150	241.08	518	2.89	428	7.13	39.5	5.68	0.83	422	50.9	0.16
195	1202	30X1	140-150	269.87	522	7.43	448	12.0	43.2	7.49	0.86	440	40.9	0.25
195	1202	33X2	140-150	300.27	543	3.60	452	10.3	39.8	5.48	0.83	391	36.1	0.16
195	1202	36X2	140-150	329.08	554	3.10	433	9.19	39.7	5.98	0.78	451	37.2	0.18
195	1202	39X2	140-150	358.18	536	4.66	465	10.4	41.3	6.45	0.87	374	38.5	0.15
195	1202	42X2	140-150	387.10	518	4.17	430	9.96	39.2	5.83	0.83	484	39.1	0.15

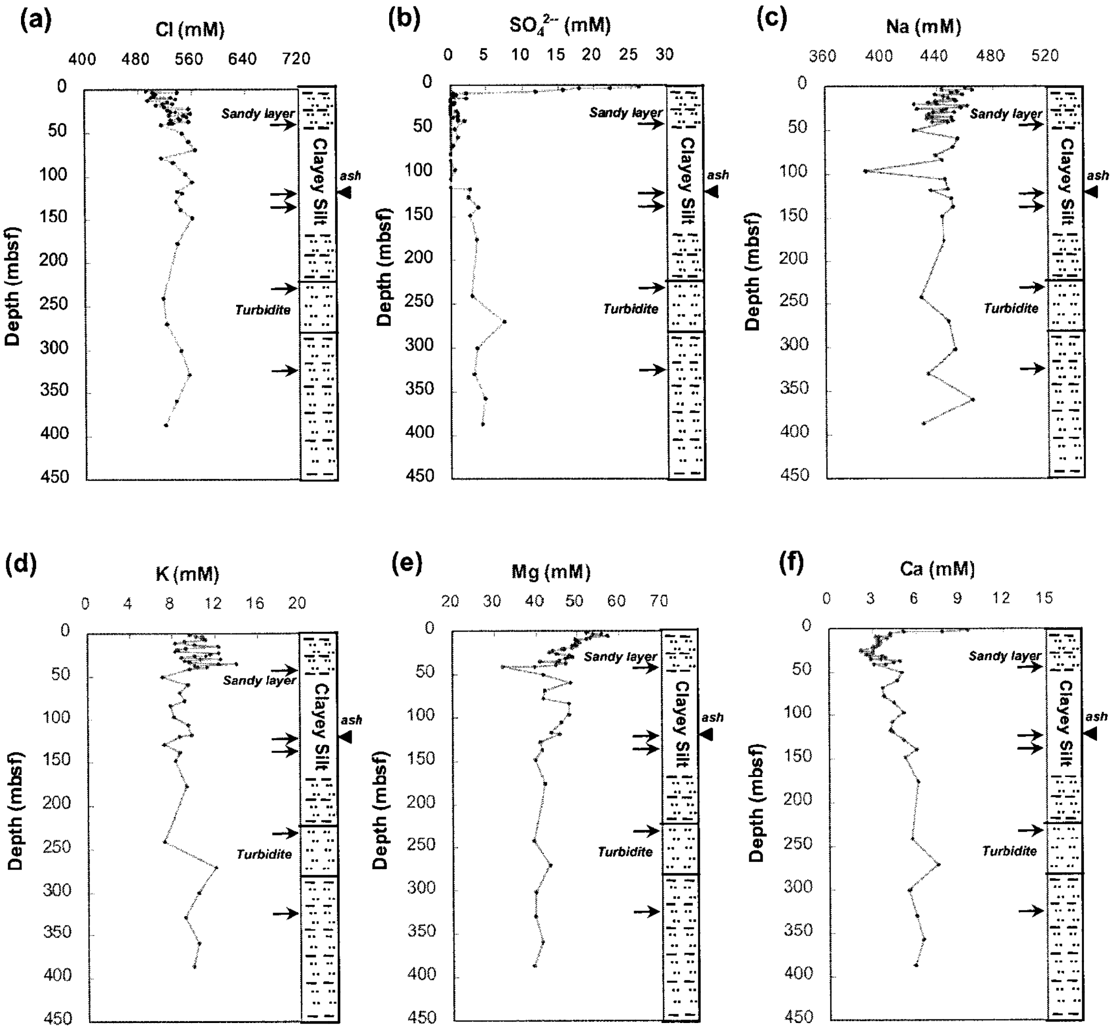


Fig. 2. Depth profiles of major constituents in pore fluids at Site 1202. (a) Chlorine; (b) Sulfate; (c) Sodium; (d) Potassium; (e) Magnesium; (f) Calcium. Also shows lithologic facies and the occurrences of sandy and ash layers (after Shipboard Scientific Party 2002).

dolomitization may release Ca and uptake Mg and K at greater depth. Other studies from rapidly deposited regions have shown similar Ca, Mg and K correlations (Gieskes 1975).

4.2 Boron Contents and B Isotopes

The B content in pore fluids at Site 1202 is, in general, slightly elevated relative to seawater (Fig. 4a). This phenomenon has been explained as a result of organic matter decomposition leading to release of B (You et al. 1993a, b). In the uppermost 40 mbsf, B varies largely ranging between 200 to 1200 μM. This partly is a result of fluid advection along the sandy horizons. Two distinct low B layers (50% seawater) are observed at 16.1 and 41.6 mbsf (see Fig. 4a), reflecting other sources and/or fresh water addition (Fig. 3e). Gas hydrate dissociation is a possible candidate for causing low B in pore waters (Kastner et al. 1995; Sample and Kopf 1995; Kopf et al. 2000). Other likely fresh water sources are clay dehydration water (e.g., smectite-illite transformation) and continental inputs. It is, however, difficult to distinguish these two mechanisms without further oxygen isotopic information (Fitts and Brown 1999). Further down-core, significant elevation of B (585 μM at 176 mbsf) was detected at 150 - 200 mbsf. At depths greater than 250 mbsf, B remains constant with average seawater concentration.

The B isotopes show an interesting correlation with that of dissolved B down-core (Fig. 4b). In general, the Site 1202 pore fluids are characterized by slightly lower δ^{11}B values than seawater. Similar to the dissolved B pattern, degradation of organic matter in the upper sedimentary column releases significant amounts of B enriched in ^{10}B (Brumsack and Zuleger 1992; You et al. 1993a; You et al. 1996). Between 40 and 120 mbsf, δ^{11}B remains low, possibly were affected by clay de-sorption (Spivack et al. 1987) and ash alteration (Brumsack and Zuleger 1992). Near the sandy horizons, δ^{11}B becomes more negative, suggesting mixing of fluids with low isotopic compositions. δ^{11}B increases gradually between 120 and 230 mbsf. At depths greater than 150 m, δ^{11}B becomes significantly heavier than seawater up to 50.9‰ (Fig. 4b). These enhanced B isotopic signatures coincide with the occurrence of sandy turbidites at 230 - 280 mbsf, however, no significant changes in dissolved B occurred. Below 280 mbsf, δ^{11}B decreases toward the seawater value.

4.3 Factors Controlling Chemical Distribution in Pore Waters

In the following discussion, we aim to evaluate fluid sources, flow pathways and possible mechanisms that influence major constituents in pore waters. In particular, we apply the characteristics of B and δ^{11}B to shed light on causes for compositional changes at various depth intervals.

The analytical results obtained for IAPSO seawater standard were added in the following discussion. The correlation plots of Ca vs. SO_4 and Mg vs. Ca are presented in Fig. 5. The Ca and SO_4 exhibit a linear relationship in the uppermost 40 mbsf, where intensive sulfate-reduction occurred (Fig. 5a). The Mg and Ca display a complicated relationship at different depth intervals (Fig 5b). At 40 - 100 mbsf, both dissolved Mg and Ca increase slightly with depth, possibly related to the occurrences of high-porosity sandy layers (Shipboard Scientific Party 2002). Between 100 - 150 mbsf intervals, Mg and Ca display negative correlation indicating possible dolomitization has occurred. Of special interest, at deeper section, is elevated Mg/Cl and Ca/Cl (Figs. 3c, d) being observed at the sandy turbidite zones.

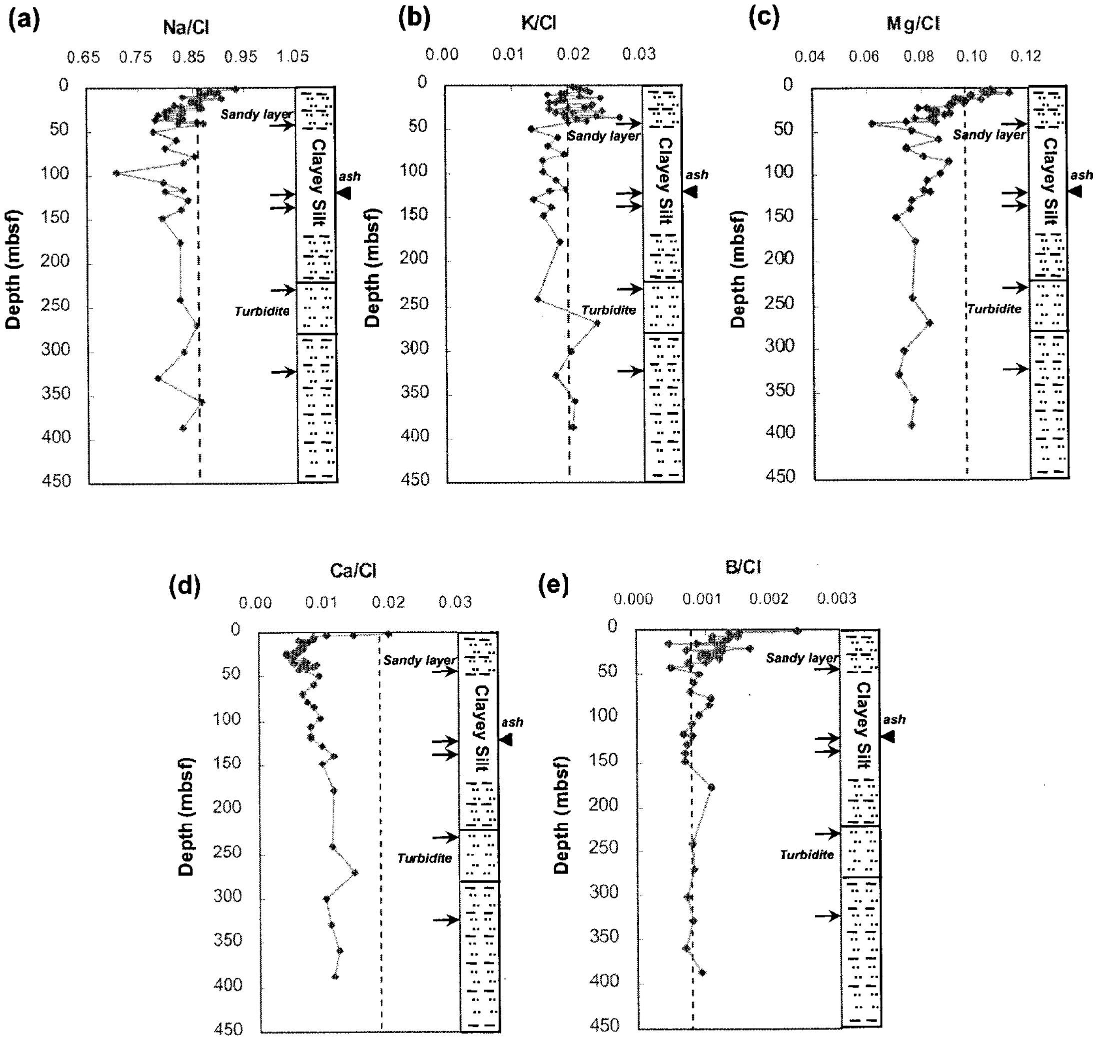


Fig. 3. Depth profiles of normalized major cations in pore fluids at Site 1202. (a) Na/Cl; (b) K/Cl; (c) Mg/Cl; (d) Ca/Cl; (e) B/Cl. The vertical line indicates an average seawater ratio. Also shows lithologic facies and the occurrences of sandy and ash layers (after Shipboard Scientific Party 2002).

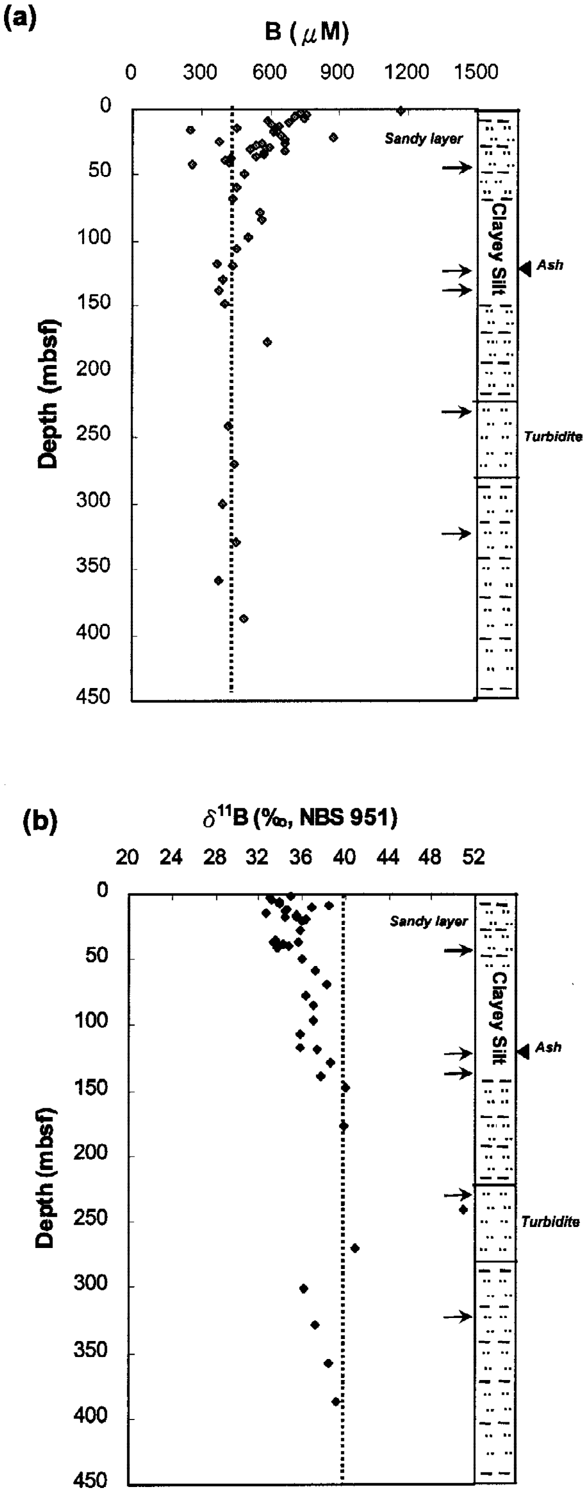
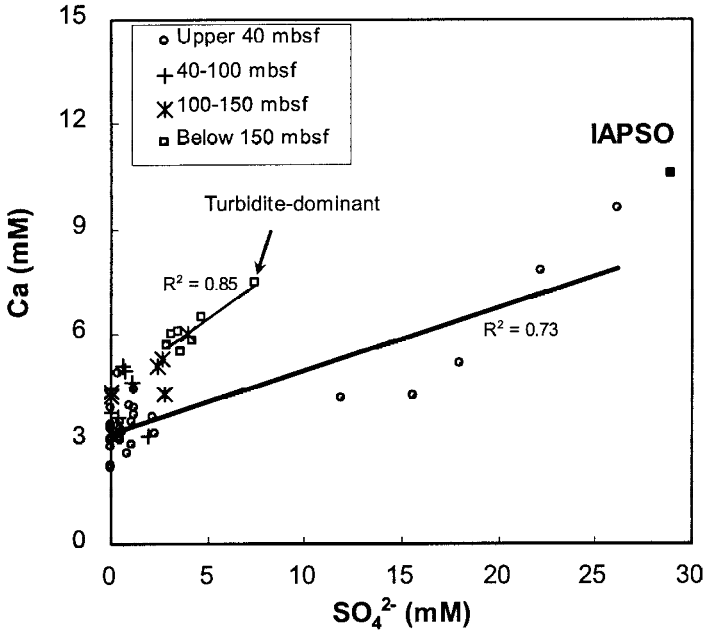


Fig. 4. Depth profiles of (a) B concentration and (b) $\delta^{11}B$ in pore fluids at Site 1202. The vertical dashed line represents seawater B content of 420 μM and $\delta^{11}B$ of 39.5‰. Also shows lithologic facies and the occurrences of sandy and ash layers (after Shipboard Scientific Party 2002).

(a)



(b)

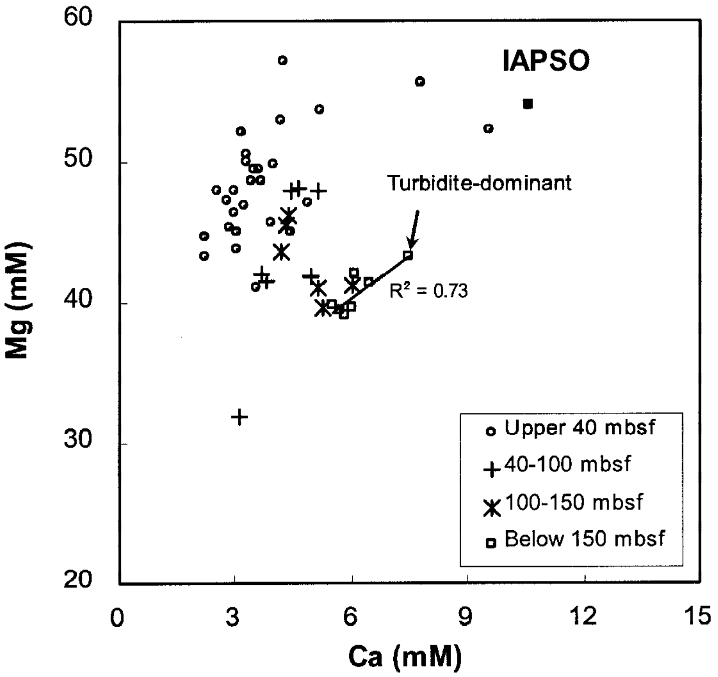


Fig. 5. Correlation plots of (a) Ca vs. SO_4 ; (b) Mg vs. Ca in pore fluids at Site 1202. Symbols: ■ = IAPSO standard seawater; ○ = Upper 40 mbsf; + = 40 - 100 mbsf; * = 100 - 150 mbsf; □ = Below 150 mbsf. The thick and thin line represents regression of data for the uppermost 40 mbsf and below 150 mbsf, respectively. Arrow indicates the location of turbidite-dominant sandy layer.

Boron and $\delta^{11}B$ are sensitive tracers for sedimentary diagenesis that might influence pore water geochemistry (Deyhle et al. 2001), as well as fluids processes at convergent margins (Brumsack and Zuleger 1992; You et al. 1993a; You et al. 1995; Kopf et al. 2000; Deyhle and Kopf 2001). Possible mechanisms that affect B and B isotope signatures in pore waters are briefly summarized as follow: (1) De-sorption of exchangeable B in clays, resulting in elevated B with low $\delta^{11}B$. In other words, adsorption of B will decrease B and cause heavier $\delta^{11}B$ in fluids (You et al. 1993a, b); (2) Mixing of fluids with different sources along high-porosity intervals affect B and $\delta^{11}B$ differently, depended on P-T conditions and local tectonic settings (Deyhle et al. 2004); (3) Involvement of deep generated fluids. The B and $\delta^{11}B$ in deep-seated fluids are rather variable and depend on lithology, regional fractures and shear zones. Elevated B and heavy B isotopes are reported in Naikai and Barbados Ridge Complex (You et al. 1993a, b; Deyhle et al. 2001). However, the $\delta^{11}B$ in pore waters is more negative (< 35‰) in fore-arc environments (e.g., Japan Trench, Deyhle and Kopf 2002); (4) Alteration of volcanic products shift $\delta^{11}B$ in fluids toward a positive direction (Palmer and Swihart 1996); (5) Carbonate precipitation leads to low B and high $\delta^{11}B$ due to preferential uptake of tetrahedral borate, $^{10}B(OH)_4^-$; (6) ^{10}B uptake into B-bearing minerals (e.g., tourmaline, borosilicate) decrease B and increase $\delta^{11}B$. The B and $\delta^{11}B$ in residual fluids depend on the original sources, metamorphic or magmatic (Palmer and Swihart 1996); (7) Opal-A to Opal-CT transition reduces B significantly (Brumsack and Zuleger 1992); (8) Illitization of smectite starts at ~60 - 70°C and reaches advanced levels at ~120 - 150°C, decrease B and elevate $\delta^{11}B$ in fluids (Weaver 1989; Williams et al. 2001).

These are no direct involvement of low B/Cl brine-type fluids as indicated in the B vs. B/Cl plot (Fig. 6). This is consistent with the previous notion that adsorption/de-sorption is the most important factor controlling B and $\delta^{11}B$ distribution at shallow depth. Previous experiments have demonstrated that when buried stress accumulates to an overburden of ~1.3 MPa clay minerals dehydration will occur (Fitts and Brown 1999). Under such pressure, some lattice waters in clays, as well as sedimentary exchangeable B were released simultaneously. The dehydration fluids are enriched in ^{10}B and subsequently were expelled and mixed with interstitial waters at shallow depth (Deyhle and Kopf 2002). The $\delta^{11}B$ and 1/B correlation plots are presented in Fig. 7. Two major B sources, seawater and clays derived exchangeable B, and possible mixing processes in the sedimentary column are indicated. Potential contribution from gas hydrate seems to be rather insignificant at Site 1202 (Fig. 7a). There are three samples deviated largely from the main trend, two in the uppermost section and one at 241.2 mbsf (Fig. 7b). The two low B samples coincide with high-porosity sandy layers at 16.1 and 41.6 mbsf. The sandy-turbidites sample shows high $\delta^{11}B$ with seawater concentration. Other causes for B and $\delta^{11}B$ variations in pore fluids will be discussed further below.

The most important reaction controlling the B and $\delta^{11}B$ distribution probably is the release of adsorbed B from clay minerals (Spivack et al. 1987; You et al. 1996; Deyhle and Kopf 2002). Observations of sedimentary B contribution in pore waters have been reported at numerous convergent margins (You et al. 1993a, b; Kopf et al. 2000), as well as in laboratory experiments (You et al. 1996). In high sedimentation regions, sufficient burial stresses may cause smectite-to-illite or opal-A-CT transformation to occur at shallow depths. These processes, however, are unlikely to be important at Site 1202 due to the low geothermal gradient and shallow drilling depth (Salisbury et al. 2002). Assuming diatomaceous ooze has B isotopic ratio of about -1.1‰ (Palmer and Swihart 1996), one would expect strong negative shift in δ^{11}B if opal alteration occurred. The most negative δ^{11}B at Site 1202, however, remains rather heavy approximately +32‰ (see Fig. 4b). Volcanic ash or tephra alteration may be important to both B and δ^{11}B (Gieskes and Lawrence 1981), however, no major tephra or ash layers were reported (Salisbury et al. 2002).

Based on major constituents and B isotopic characteristics in pore waters, Site 1202 were subdivided into four dominant zones. The uppermost zone, 0 - 40 mbsf, affects largely by water-sediment interaction and sulfate reduction. A transition zone situated between 40 and 100 mbsf is dominated by diffusion and advection of fluids along the high-porosity sandy horizons. Between 100 and 150 mbsf, the dominating process is fluid flows along sandy layers

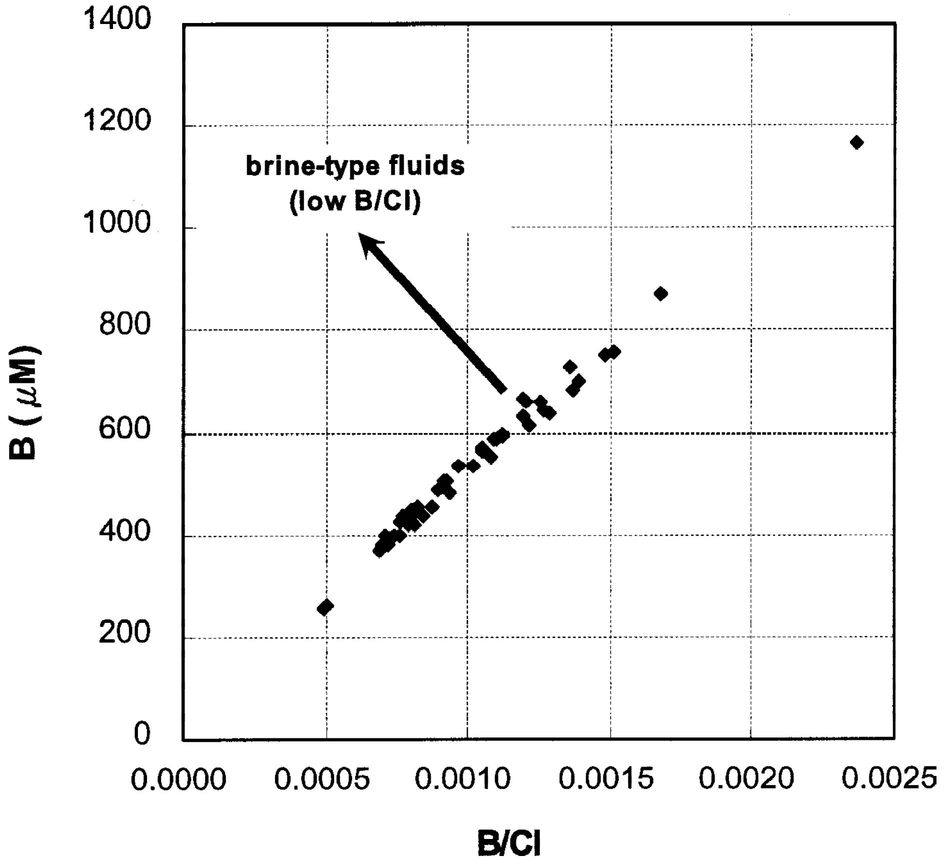


Fig. 6. Correlation plots of B vs. B/Cl in pore fluids at Site 1202. Arrow indicates the possible evolutional direction if brine-type fluids (low B/Cl) were added.

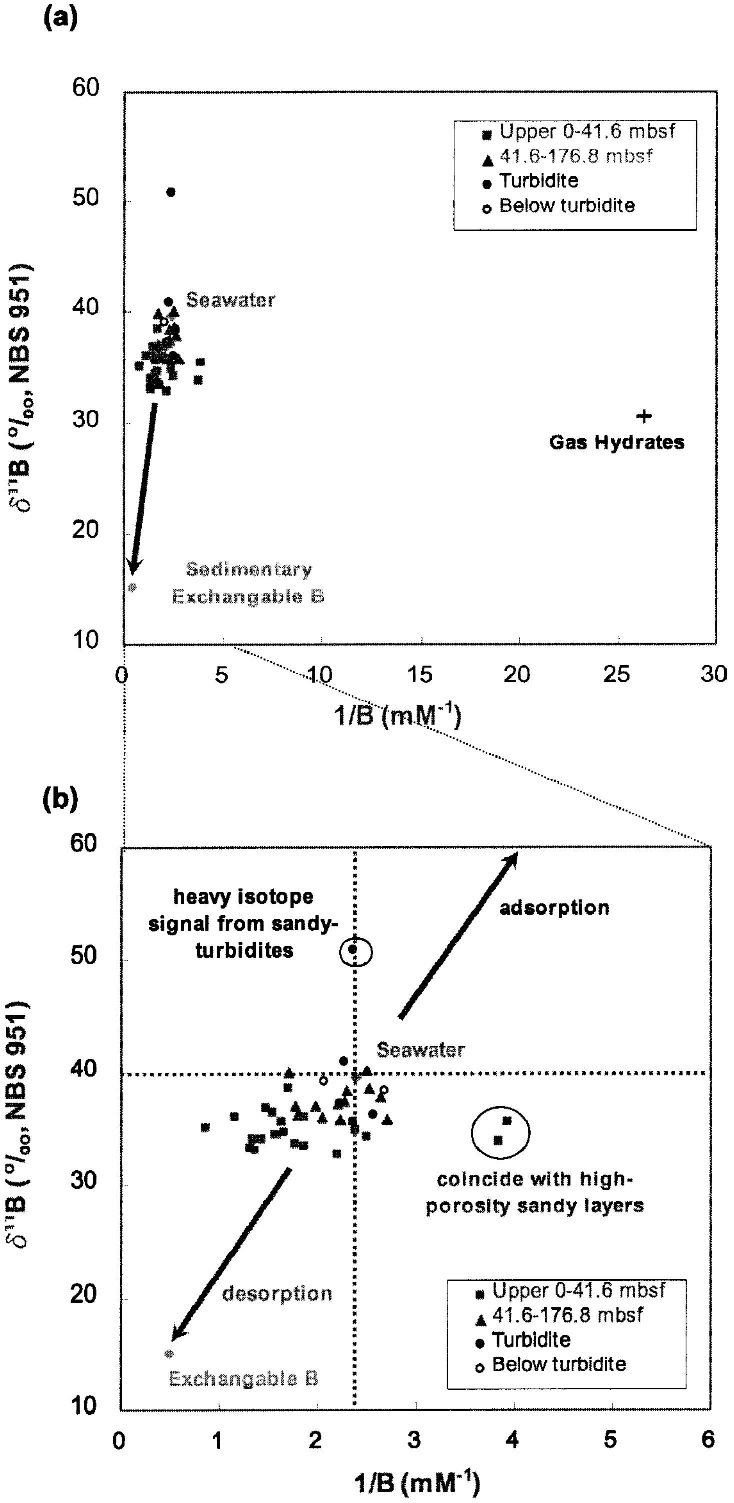


Fig. 7. Correlation plot of δ^{11}B vs. 1/B in pore fluids at Site 1202. The sketch illustrates three possible fluid sources: seawater ([B] = 420 μM and δ^{11}B = 39.5‰), exchangeable B ([B] = 2000 μM and δ^{11}B = 15‰, Kopf et al. 2000), and gas hydrates ([B]=38 μM and δ^{11}B = 30.6‰, Zuleger, unpublished data).

and minor dolomitization. The deepest zone is characterized by strong diagenetic reactions of terrigenous materials, in particular in the sandy turbidites.

4.4 Possible Causes for B and δ^{11}B Variations in Pore Waters

In the following discussion, we elaborate further geochemical processes at several depth intervals where B and δ^{11}B show complicated distribution profiles. The shifted δ^{11}B toward a low value is associated with low B at 0 - 50 mbsf. The slightly increased B content at 50 - 230 mbsf is accompanied with high δ^{11}B. Unusually high δ^{11}B occurred at 230 - 280 mbsf where no significant B changes occurred. The δ^{11}B increases gradually, but no B changes near the basement.

At a shallow depth, pore waters are characterized by low δ^{11}B with enhanced B concentrations. Similar observations have been reported due to organic matter degradation at low temperature (You et al. 1993a, b; You et al. 1995). The negative shifted δ^{11}B and B at 16.1 and 41.6 mbsf can be best interpreted in terms of fluid advection along the high-porosity sandy horizons (Salisbury et al. 2002). Dissociation of gas hydrates in the pore space cannot be completely ruled out.

Between 50 and 230 mbsf, most analyzed constituents show large fluctuations. Gradual increased δ^{11}B and slightly complicated B excursion at this interval, possibly due to sedimentary interactions and fluid advection through high-porosity sandy layers (Salisbury et al. 2002). Elevated B and low δ^{11}B occur also at 70 - 90 mbsf where carbonate increased abruptly (H. L. Lin, unpublished data).

The most peculiar B distribution is located at 230 - 280 mbsf, where sediment is characterized by sandy turbidites consisting of large amounts of terrigenous materials, detrital carbonate, mica, low-grade metamorphic schists and marls, and heavy minerals (green bornblede, tourmaline, epidote, and zircon) (Salisbury et al. 2002). An extremely heavy value of δ^{11}B (50.9‰) with seawater-like B in fluids is detected at ~241 mbsf. This is possibly linked with preferential uptake of ^{10}B into borosilicate lattices. Formation of B-bearing minerals (e.g., tourmaline) has been proposed under high pressures. In general, the δ^{11}B in sedimentary tourmalines are 8 - 10‰ lighter than the fluid reservoirs (Palmer and Swihart 1996). The P-T condition does not favor in situ tourmaline formation at Site 1202, however, alteration of detrital sources cannot be ruled out. Fluids migration along permeable conduits has been reported enriched in ^{11}B (Deyhle and Kopf 2002). Re-adsorption of B at shallow depths is an alternative for the observed high δ^{11}B (Deyhle et al. 2004). Formation of a secondary mineral may show similar results (Kopf et al. 2000). The systematics of B and δ^{11}B in deep-generated fluids, however, highly depend on local lithology and the regional tectonic framework.

Below the turbidite-dominant layers, the δ^{11}B shows a gradually increasing trend, but no systematic changes in B. Mixing of deep-seated fluids from shear zones, décollement or fracture zones of basaltic basement affect pore water chemistry significantly (Spivack et al. 1987; You et al. 1993a 1995; Kopf et al. 2000; Deyhle and Kopf 2002). For instance, fluids derived from the décollement zone at the Barbados Ridge accretionary prism (You et al. 1995) and the Nankai accretionary complex (You et al. 1993a) contains 2000 μM and 3000 μM of B respectively.

5. CONCLUSIONS

From the study of major ions, B and δ^{11}B distribution in forty-one pore fluids separated from ODP Leg 195 Site 1202, Okinawa Trough, the following conclusions can be drawn:

1. Major constituents and boron do not behave conservatively in pore fluids, and are strongly affected by sedimentary diagenetic processes, such as sulfate reduction, dissolution - re-crystallization of biogenic carbonate or silica, dolomitization, ash alteration and organic matter degradation.
2. B and δ^{11}B show a wide range of down-core distribution at Site 1202. B contents fall in a range between 250 and 1200 μM and δ^{11}B varies from ~32.7 to 50.9‰.
3. High B concentration with low δ^{11}B is observed in the uppermost intervals, most likely due to organic alteration. At intermediate depths, the B and δ^{11}B show more scatter, possibly due to mixing of fluids along the high porosity sandy horizons. The distribution of B and δ^{11}B provide useful information for assessing the origin and pathway of these sedimentary fluids.
4. The δ^{11}B and 1/B plot suggests that de-sorption of clay-rich sediments is the main source of B in pore waters, resulting in elevated B with low δ^{11}B. Other mechanisms including precipitation of carbonate, interaction with terrigenous sediments, and low temperature ash alteration may also affect the B and δ^{11}B distribution in pore fluids at Site 1202.

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