

5. IODINE AND BORON IN MARIANA SERPENTINITE MUD VOLCANOES (ODP LEGS 125 AND 195): IMPLICATIONS FOR FOREARC PROCESSES AND SUBDUCTION RECYCLING¹

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ABSTRACT

Iodine and boron were analyzed in pore fluids, serpentized ultramafic clasts, and the serpentized mud matrix of the South Chamorro Seamount mud volcano (Ocean Drilling Program Leg 195 Site 1200) to determine the distribution of these elements in deep forearc settings. Similar analyses of clasts and muds from the Conical Seamount mud volcano (Leg 125 Site 779) were also carried out. Interstitial pore fluids are enriched in boron and iodine without appreciable change in chloride concentration relative to seawater. Both the ultramafic clasts and the associated serpentized mud present the highest documented iodine concentrations for all types of nonsedimentary rocks (6.3–101.7 $\mu\text{mol/kg}$). Such high iodine concentrations, if commonplace in marine forearc settings, may constitute a significant, previously unknown reservoir of iodine. This serpentized forearc mantle reservoir may potentially contribute to the total crustal iodine budget and provide a mechanism for its recycling at convergent plate margins. Both clasts and mud show concurrent enrichments in boron and iodine, and the similarity in pore fluid profiles also suggests that these two incompatible, fluid-mobile elements behave similarly at convergent plate margins.

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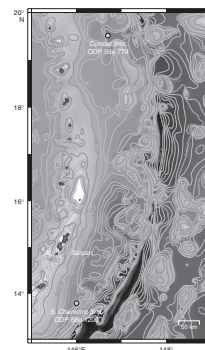
INTRODUCTION

Subduction recycling of sediments and altered oceanic crust in marine systems is intimately linked to the systematics of both fluid-mobile and volatile elements, including iodine and boron. The relative abundance and isotopic signature of these two elements in marine sediments are distinct from those of igneous rocks, and each has been used as a tracer of the dehydration processes in the forearc (e.g., You et al., 1993; Deyhle and Kopf, 2002; Kopf et al., 2000; Deyhle et al., 2001; Muramatsu et al., 2001) and of subduction recycling (e.g., Leeman and Carr, 1995; Ryan et al., 1996; Noll et al., 1996; Snyder et al., 2003, 2002; Snyder and Fehn, 2002). Until recently, forearc studies have focused mostly on fluid chemistry along the accretionary portions of forearcs, where dewatering and early diagenetic releases of iodine and boron have been confined to relatively low temperatures along the décollement. Active fluid-rock interactions at greater depths have largely eluded researchers, even though they are important in determining the budget of fluid-mobile elements that are transported to subarc depths.

We present recent data comparing the relative mobility of iodine and boron in submarine mud volcanoes recovered from the Mariana forearc region during Ocean Drilling Program (ODP) Legs 125 and 195 (Fig. F1). Serpentinized peridotites, serpentinite muds, and pore fluids recovered from these mud volcanoes provide a unique window into the processes occurring at depths of ~30 km at the top of the subducted Pacific plate (Benton et al., 2001; Mottl et al., 2003) and, therefore, can bridge the spatial gap between early forearc processes and island arc devolatilization. Earlier investigations on the production of metamorphic fluids associated with serpentinization in the western United States noted that the waters were alkaline and contained significant concentrations of boron (as high as 28,000 μM) (Barnes and O'Neil, 1969; Barnes et al., 1972). In the Mariana marine environment, Benton et al. (2001) determined $\delta^{11}\text{B}$ values in mud and clasts from Conical Seamount and found them to be roughly 30‰ lighter than seawater and 5‰ heavier than most arc volcanics. They hypothesized that a progressive release of fluids enriched in ^{11}B as sediments and altered oceanic crust is transported to depth. The work of Wei et al. (this volume) as well as Savov et al. (2004) confirms these trends by looking at the $\delta^{11}\text{B}$ of pore fluids, clasts, and mud from both the Conical and South Chamorro seamounts.

Despite a growing body of evidence regarding how boron behaves during its migration from trench to forearc to arc, relatively little is known regarding how the boron system is coupled with other elemental systems. In this investigation, we focus on the relationship between iodine, which is concentrated in marine organic matter, and the presence of boron in both mineral and fluid phases. Recent investigations of iodine in the same boron-rich springs hosted in serpentinites that were studied by Barnes et al. (1972) suggest a general correlation between the two elements (Hurwitz et al., 2004). High iodine concentrations are also accompanied by high boron concentrations in a variety of springs and fumaroles (Goff and McMurtry, 2000), suggesting that both elements are a significant component of island arc volatiles. By measuring iodine and bromine concentrations in both the fluid and the solid phases of the Mariana mud volcanoes we can infer how dehydration reactions influence the distribution of these elements in the early stages of subduction, before they are introduced into the subarc mantle.

F1. Map of South Chamorro and Conical seamounts, p. 13.



The large ionic radius of iodine makes it highly incompatible in most igneous mineral phases (McDonough and Sun, 1995; Déruelle et al., 1992; Muramatsu and Wedepohl, 1998). Because it is biophilic (Elderfield and Truesdale, 1980), iodine is an important tracer of the fate of organic matter at convergent plate margins. Bulk iodine determinations for a broad variety of rock types by Muramatsu and Wedepohl (1998), yielded fairly uniform concentrations of 0.05–0.07 $\mu\text{mol/kg}$ for igneous rocks, consistently less than the average concentration for sedimentary rocks of 11 $\mu\text{mol/kg}$. An earlier investigation (Becker et al., 1968) yielded similar results for a variety of ultramafic rocks (0.07–5 $\mu\text{mol/kg}$) but also suggested that carbonatites in the lower crust may be slightly enriched in iodine (3.5–7.8 $\mu\text{mol/kg}$). Similar work by Déruelle et al. (1992) concluded that because iodine is enriched in the crust and depleted in the mantle, then the overall iodine cycle must be similar to that of the noble gases, inasmuch as these elements are released before they can be introduced into the upper mantle (Staudacher and Allégre, 1988). Despite this, it has been hypothesized that subducted organics contribute significantly to the volatile budget of carbon and nitrogen in island arc systems (e.g., Sano and Marty, 1995; Sano et al., 1998; Fischer et al., 2002) and studies of forearc metasedimentary rocks suggest that at least a portion of the subducted volatile elements are delivered to the subarc mantle (Bebout, 1995). Thus, it is likely that a portion of the marine iodine reservoir is also subducted along with the other volatile components. Subsequent studies have demonstrated that the marine-cosmogenic signature of subducted ^{129}I is preserved in island arc fumaroles and geothermal systems (Snyder et al., 2002; Snyder and Fehn, 2002; Fehn and Snyder, 2003). The mineral phases that might enhance the transfer of iodine to depths beneath the mantle wedge are unknown; however, previous work has focused on quantifying both the marine input (Muramatsu and Wedepohl, 1998) and the volcanic output (Snyder and Fehn, 2002) without specifying a mechanism for iodine transfer.

SAMPLES AND METHODS

The pore fluid samples analyzed in this research are either splits from the samples analyzed on board and reported in Salisbury, Shinohara, Richter, et al. (2002) and Mottl et al. (2003) or residues from the on-board hydraulic conductivity tests of Hart and Hammon (2002). The former were collected from 3-cm-long sample splits from whole-round serpentinite mud-containing cores. The experiments were conducted using the same apparatus and techniques as the routine onboard pore fluid sample collection. The analyzed rock samples are serpentinitized peridotite clasts and muds collected aboard the *JOIDES Resolution* during ODP Legs 125 (Site 779: Conical Seamount) and 195 (Site 1200A: South Chamorro Seamount). For detailed descriptions of the clasts and muds see Salisbury, Shinohara, Richter, et al. (2002), [Fryer and Salisbury](#) (this volume), [Savov et al.](#) (this volume), and Savov (2004).

Iodine and bromide concentrations in mud, ultramafic clasts, and pore fluids were determined using inductively coupled plasma–mass spectrometry (ICP-MS) at the Japanese Institute for Nuclear and Radiological Sciences. Prior to analysis, the mud and clast samples were washed and the halides were extracted using hydrolysis and collected in a solution of 2% tetramethylammonium hydroxide (Schnetger and Muramatsu, 1996). Extractions were carried out three times in or-

der to assure reproducibility, and both Cs and Rh were added as primary and secondary internal standards.

The boron abundances of the serpentinized peridotite clasts and muds were measured by direct-current plasma emission spectrometry (DCP-ES) at the University of South Florida (Tampa, Florida, USA) after Na_2CO_3 flux fusion in Pt crucibles and followed by standard additions (Ryan and Langmuir, 1993). Uncertainties strongly depend on the concentrations but are $\pm 5\%$ for the majority of the samples. Boron measurements were always reproducible, based on monitoring by replicates of the certified U.S. Geological Survey (USGS) and Geological Survey of Japan (GSJ) standards DTS-1, BIR-1, BHVO-1, JP-1, and JB-3. Pore fluid boron concentrations were measured using a JY2000 inductively coupled plasma-atomic emission spectrometer (ICP-AES) aboard the *JOIDES Resolution* following procedures described in Mottl (1992) and Mottl et al. (2003).

RESULTS

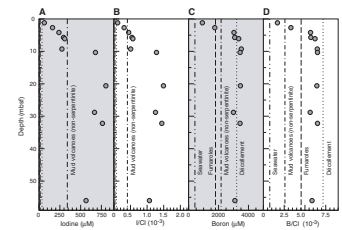
Pore fluid concentrations of iodine and boron are presented in Table T1. In addition, the iodine and boron pore water content is also presented in millimoles per cubic meter of wet sediment, based on measured concentrations and shipboard determinations of sediment porosity. Depth profiles of iodine (Fig. F2B) show shallow concentrations starting at seawater values and reaching a maximum ($\sim 800 \mu\text{M}$) at just over 20 meters below seafloor (mbsf). The deep iodine concentrations far exceed seawater ($0.44 \mu\text{M}$) and therefore must be derived from either mineral dewatering reactions or diagenesis of locally deposited marine organic material. Concentrations of iodine are also well above the typical value for high-temperature island arc fumaroles ($13.06 \mu\text{M}$) (Snyder et al., 2002; Tedesco and Toutain, 1991) as well as that of pore water samples recovered from the relatively shallow décollement of the Nankai accretionary prism ($35 \mu\text{M}$) (You et al., 1993). They are also above those of waters derived from seafloor mud volcanoes not associated with serpentinization (Aloisi et al., 2004). Because the chloride concentrations of the pore fluids do not vary appreciably with depth, normalizing iodine concentrations to chloride concentrations (Fig. F2B) produced a similar pattern.

The boron contents of the pore fluids show a dramatic increase with increasing core depth, after which they stabilize at $\sim 3500 \mu\text{mol/kg}$ (Fig. F2C) at a depth of ~ 10 mbsf. This is consistent with results from previous investigations of the Conical Seamount (Mottl et al., 2003; Mottl, 1992). As with iodine, boron concentrations in the deep fluids exceed those of both seawater ($420 \mu\text{M}$) (Spivack and Edmond, 1987) and high-temperature fumarolic condensates ($1795 \mu\text{M}$) (Goff and McMurtry; 2000). Unlike iodine, the boron abundances of the deep fluids from the South Chamorro Seamount are indistinguishable from décollement fluids of the Nankai Trough ($3210 \mu\text{M}$) (You et al., 1993, 1995). The similarity is also true with respect to B/Cl ratios (Fig. F2D), despite the fact that the Nankai is a shallow accretionary system and the Marianas system is a nonaccretionary system where the fluids are derived from much greater depths.

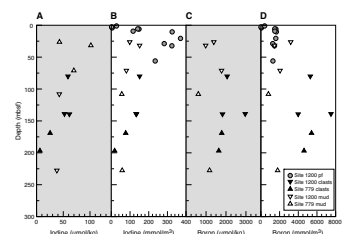
The maximum concentration of iodine in serpentinized clasts ($61 \mu\text{mol/kg}$; 139 mbsf) is, to the author's knowledge, the highest concentration measured in nonsedimentary rock types (Fig. F3A). Maximum iodine concentrations in the muds are even greater than the clasts (102

T1. Interstitial water halogen and boron data, Site 1200, p. 17.

F2. Depth profiles for pore fluids, Site 1200, p. 14.



F3. Depth profiles for clasts and mud, Sites 1200 and 779, p. 15.



$\mu\text{mol/kg}$; 32 mbsf). The iodine concentrations for both are an order of magnitude lower than the average values for marine sediment ($332 \mu\text{mol/kg}$) (Martin et al., 1993) and yet more than three orders of magnitude greater than accepted values for the depleted upper mantle ($0.003 \mu\text{mol/kg}$) (Burgess et al., 2002) and more than two orders of magnitude greater than those measured in rocks associated with island arc volcanism ($0.079 \mu\text{mol/kg}$) (Muramatsu and Wedepohl, 1998). No appreciable difference was observed between the samples obtained from the Conical Seamount and those obtained from the South Chamorro Seamount. Although the total number of samples was limited and the depth resolution was low, iodine concentrations decrease somewhat with depth, perhaps because of diagenetic loss as both mud and clasts are buried by fresher deposits. Iodine concentrations in the clasts and muds were normalized to the bulk wet sediment volume (and expressed in millimoles per cubic meter) using onboard porosity and grain density determinations (Salisbury, Shinohara, Richter, et al., 2002; Fryer, Pearce, Stokking, et al., 1990). Although pore fluid samples were only available for the upper 60 m, they clearly show that the amount of iodine residing in the pore fluids is greater than that residing in the sediments, except at depths <26 mbsf (Fig. F3B).

The boron concentrations in the serpentinitized peridotites and serpentinite muds from the South Chamorro Seamount (Savov et al., this volume, 2002) and Conical Seamount (Benton, 1997; Savov et al., 2000) do not change appreciably with depth (Fig. F3C). The average boron concentration of the clasts is $2050 \mu\text{mol/kg}$, whereas that of the muds is $1190 \mu\text{mol/kg}$. This difference becomes even more apparent if the concentrations are normalized to the volume of wet sediment because the intervals with clasts have lower porosity and greater grain density (Fig. F3D). The concentrations in serpentinites from both seamounts are an order of magnitude lower than concentrations generally found in marine sediments (Ishikawa and Nakamura, 1993; Leeman, 1996) and are two orders of magnitude greater than values associated with fresh mid-ocean-ridge basalt glasses, representing depleted upper mantle values ($23 \mu\text{mol/kg}$) (Ryan and Langmuir, 1993). Boron concentrations in the serpentinitized ultramafics and muds are also very similar to those of the Izu-Bonin-Mariana island arc products (Straub and Layne, 2002), as well as island arc lavas globally (Ryan and Langmuir 1993; Leeman, 1996). Unlike iodine, the pore fluids contribute less to the bulk boron content than do the mud and clasts. Although the pore fluids achieve higher concentrations of boron than iodine with depth (Fig. F2), the relative proportion of residual boron in the fluid phase is less.

DISCUSSION

The pore fluids and serpentinitized materials from the South Chamorro and Conical seamounts are unique in several respects. Values of $\delta^{11}\text{B}$ in the fluids (Wei et al., this volume; Savov et al., 2004) indicate slab sources derived from depth rather than a shallow-marine sediment source. In addition, the low δD and high $\delta^{18}\text{O}$ of the Conical Seamount pore waters are clearly different from seawater (Benton, 1997) and point to mineral dehydration/metamorphic reactions as a water source. Moreover, the pore fluid concentrations of boron in the South Chamorro Seamount (Mottl et al., 2003) are also similar to those along the décollement of the Nankai Trough (You et al., 1993), indicating that perhaps

the fluids encountered in the décollement of the Nankai Trough are also sourced from greater depths.

Whereas local productivity in the Mariana region could potentially produce an iodine-rich sediment component, the organic content of the sediments around the South Chamorro Seamount is <0.5% in the upper meter and generally <0.2% in deeper sediments (Salisbury, Shinohara, Richter, et al., 2002) and generally <0.3% throughout the core sections of the Conical Seamount (Fryer, Pearce, Stokking, et al., 1990). Depth profiles for pore fluid iodine (Fig. F2) are similar to those found in sediments along other margins with high productivity (Martin et al., 1993; Mahn and Gieskes, 2001; Egeberg and Dickens, 1999; Fehn and Snyder, 2003; Fehn et al., 2003). In these cases, however, the increase in iodine concentration with depth tends to be paralleled by an increase in bromine concentration. The Mariana serpentinite mud volcanoes, however, have bromine concentrations in the pore fluids that actually decrease slightly with depth (Wei et al., this volume). Given that seawater is depleted in iodine and local productivity is also an unlikely source, the pore fluid iodine most likely originates from deeply derived slab fluids.

Another unique aspect of this study is that both the serpentinite muds and clasts from the South Chamorro and Conical seamounts have the highest iodine concentrations ever recorded for nonsedimentary rocks (6–102 $\mu\text{mol/kg}$). Muramatsu and Wedepohl (1998) note that hydrothermal iodine enrichment occurs only modestly in altered granites (1.3 $\mu\text{mol/kg}$) and show that even metamorphic rocks do not have iodine concentrations >0.4 $\mu\text{mol/kg}$. The possibility that a significant and previously undocumented iodine reservoir exists in low-temperature altered ultramafic forearc materials has several important implications. First, it provides a mechanism for transport of iodine to subarc depths. This explains, in part, both the widespread presence of iodine in island arc volatiles and the presence of subducted ^{129}I signatures in fumaroles and crater lakes (Fehn and Snyder, 2003; Snyder and Fehn, 2002; Fehn et al., 2002). A similar mechanism of the involvement of heavy $\delta^{11}\text{B}$ mantle wedge serpentinites in the arc magma sources was recently proposed by Straub and Layne (2002) to explain the very heavy $\delta^{11}\text{B}$ of tephra glasses from the Izu island arc.

Second, the presence of a significant iodine reservoir in the forearc, and possibly in subarc conditions, can have significant implications in our understanding of the chronology of the Earth's accretion and differentiation. One measure of the time involved in planetary accretion is by comparing the ratio of $^{129}\text{Xe}_{\text{excess}}/^{127}\text{I}$ of the bulk silicate earth (BSE) to that of primitive meteorites (e.g., Allègre et al., 1995; Zhang, 1998, 2002). These time estimates depend on a reliable estimate of the fraction of Xe presently degassed from the whole mantle, as well as the amount of iodine presently residing in the BSE. In addition, there are cases where excess ^{129}Xe (the daughter product of the decay of ^{129}I) has been observed, presumably migrating from beneath continental crust. The transfer of iodine-bearing serpentinitized peridotites to great depths may be a mechanism for initiating heterogeneities in the iodine reservoir of the upper mantle and lower crust, although it does not explain the concurrent abundance of the lighter xenon isotopes where excess ^{129}Xe is observed (Caffee et al., 1999).

Finally, the release of iodine in forearc regions may have a significant impact on the marine iodine cycle. A recent study of the iodine flux from a nonserpentinite mud volcano in the Black Sea (Aloisi et al.,

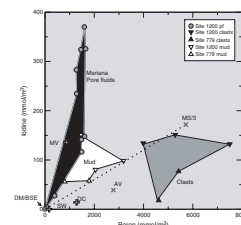
2004), when extrapolated to a global scale, suggests that the input of iodine into the oceans from mud volcanoes is on the same order of magnitude as the total riverine input (Muramatsu and Wedepohl, 1998). Given the even higher iodine concentrations present in the South Chamorro Seamount (Fig. F2A), it is possible that the flux is even greater.

A comparison of iodine and boron concentrations in muds, clasts, and pore fluids (Fig. F4) offers some insight into the degree to which these systems are coupled. In order to compare the solid and fluid components, both were normalized to the sediment volume. The end-members suggested in Tables T1 and T2 were also normalized to the volume. With only one exception, the mud samples fell along a mixing trend between depleted mantle (DM) values and marine sediment (MS) values. The concentration of boron in the clast samples exceeds that of the mud and is roughly a third that of the MS end-member. Despite the boron enrichment, the clasts are not more enriched in iodine than the muds. The clasts plot below the mixing line between DM and MS, whereas the muds plot above the mixing line. The clast data is consistent with the recycling of a serpentinized source in island arc systems because volcanic rocks also have a similar ratio of iodine to boron. Pore fluid boron concentrations in the Mariana serpentinite mud volcanoes have pore fluid boron concentrations that all fall along a restricted range of 1000–2000 mmol/m³, despite large variations in iodine concentration. This trend is distinct when compared with the average for the relatively shallow décollement fluids of the Nankai. From these data, we can conclude that significant amounts of iodine are incorporated into the serpentinized clasts, although less readily than boron, and that at greater depths, iodine is released into the pore fluids, which are released in the Mariana mud volcanoes. Nonserpentinite mud volcanoes may also show similar enrichments in iodine (Aloisi et al., 2004).

BSE values for halogens are generally calculated from crust and mantle values (Déruelle et al., 1992; Muramatsu and Wedepohl, 1998) and by comparison to the relative ratios of volatile to nonvolatile elements in meteorites; however, it has been noted that adsorption and entrainment may complicate matters (Allègre et al., 2001). Although the marine sedimentary pile has been considered the major reservoir, our data also suggest that the failure to account for adsorption to serpentinized ultramafic materials may also produce an underestimate of the crustal iodine reservoir. Likewise, large uncertainties exist in the estimation of BSE values for boron (McDonough and Sun, 1995; Allègre et al., 2001). Because BSE values generally plot between mantle and sediment values, a large altered ultramafic reservoir would shift the BSE for these two elements away from the DM and toward the MS/3 end-member.

Marine sediments make up a scant 4.9% of the oceanic crust by mass, yet they compose 68% of the total iodine inventory in crustal and lower crustal rocks (Muramatsu and Wedepohl, 1998). When combined with sedimentary rocks on the continental crust, >90% of the crustal inventory is presumably accounted for (Déruelle et al., 1992; Muramatsu and Wedepohl, 1998). The overall iodine budget may be subject to some scrutiny, however, because it does not consider the enrichment of ultramafics through hydrothermal alteration. Enrichment of boron in oceanic crust is well documented (e.g., Seyfried et al., 1984; Spivack and Edmond, 1987), although supporting data to confirm or refute iodine enrichment in the altered oceanic crust are conspicuously lacking. Because iodine concentrations in sediments and associated pore waters

F4. Bulk concentrations of pore fluid, mud, and clasts, p. 16.



T2. Clast/mud halogen and boron data, Sites 779 and 1200, p. 18.

are a function of both marine productivity and deposition rates (Kennedy and Elderfield, 1987; Mahn and Gieskes, 2001), fluids associated with hydrothermal circulation in the open ocean may not have high concentrations of iodine available to alter the oceanic crust in areas of low productivity. Where iodine is available in formation waters, a modest increase in the I/Cl ratios of mineralizing fluids associated with the quartz veins of Cu porphyry deposits has been observed (Kendrick et al., 2001); perhaps this process may be analogous to the process of iodine enrichment in the oceanic crust as well as in ultramafic material. Thus, the phenomenon of iodine enrichment in ultramafic materials is possibly limited to forearc serpentinization along active convergent margins

The South Chamorro and Conical seamounts provide a unique window to determine the presence of iodine in the deep forearc. The similarity between boron and iodine profiles in both the fluids and serpentinized material suggests that these two elements behave somewhat similarly in forearc settings, although boron may be preferentially preserved during deep serpentinization. Despite this, both the ultramafic clasts and the serpentinized muds point to a previously undocumented reservoir that may contribute significantly to the overall crustal iodine budget. Although our data are limited in quantity and distribution, they point to an area that merits future research. Further investigations should combine halogen, stable isotope, and ^{129}I determinations to ascertain the source and residence time of the halogens within these unusual fluids and the serpentinized material.

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Figure F1. Locality map of the South Chamorro Seamount (Smt.) (Leg 195 Site 1200) and the Conical Seamount (Leg 125 Site 779) mud volcanoes.

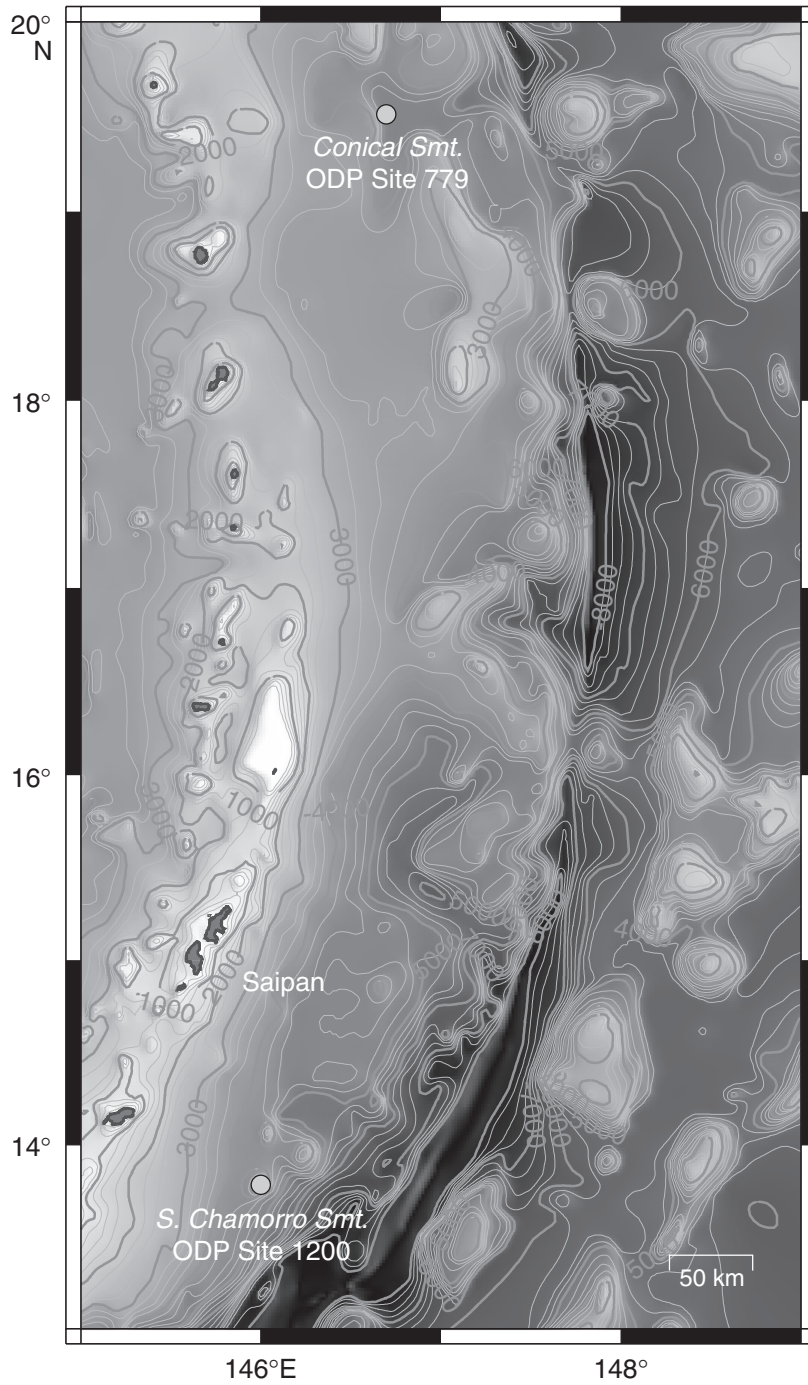


Figure F2. Depth profiles for pore fluids in the South Chamorro Seamount (Site 1200). Representative concentrations for mud volcanoes, seawater, fumaroles, and so on are shown for reference (see Table T1, p. 17). **A.** Iodine concentrations are much greater than seawater and other common reservoirs and are generally more than twice that of fluids in nonserpentinite mud volcanoes. **B.** Values of I/Cl show a similar trend when compared with iodine concentrations. **C.** Boron concentrations from Site 1200 are similar to average values for shallow décollement fluids in the Nankai Trough. Shallow concentrations approach the seawater boron concentration. **D.** Ratios of B/Cl also approach those of the Nankai Trough décollement fluids.

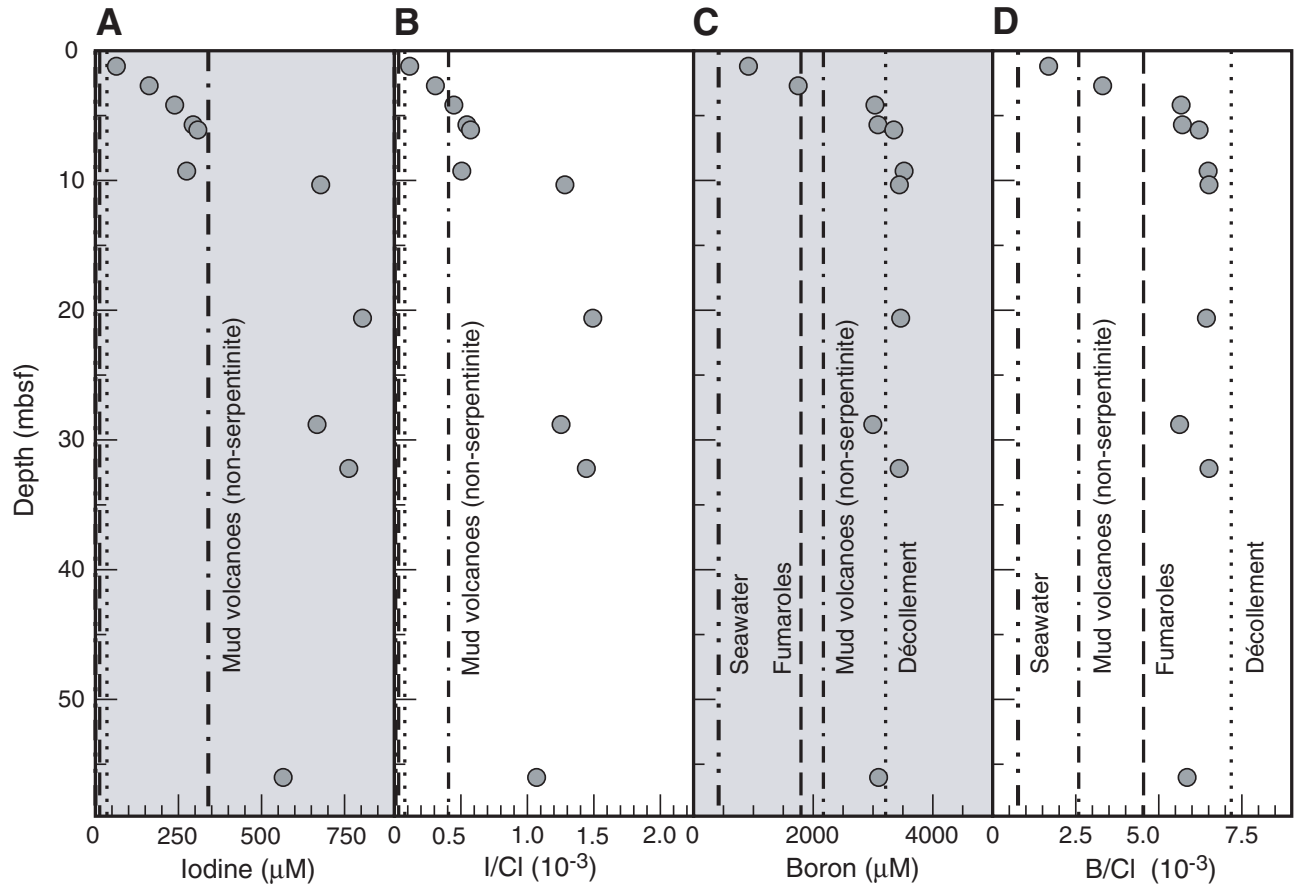


Figure F3. Depth profiles for clasts and mud from the South Chamorro Seamount (Site 1200) and the Conical Seamount (Site 779). **A.** Shallow mud samples have the highest iodine concentration. Concentrations decrease slightly with depth. **B.** Pore fluid (pf), clast, and mud concentrations normalized to cubic meters of wet sediment. From 25 to 50 mbsf, more iodine resides in the pore fluids than in the solid phases. **C.** Depth profiles for boron concentrations in clasts and muds. **D.** Depth profiles for boron in pore fluid samples, clasts, and mud normalized to cubic meters of wet sediment. Concentrations are greater for clasts than muds because of lower porosity.

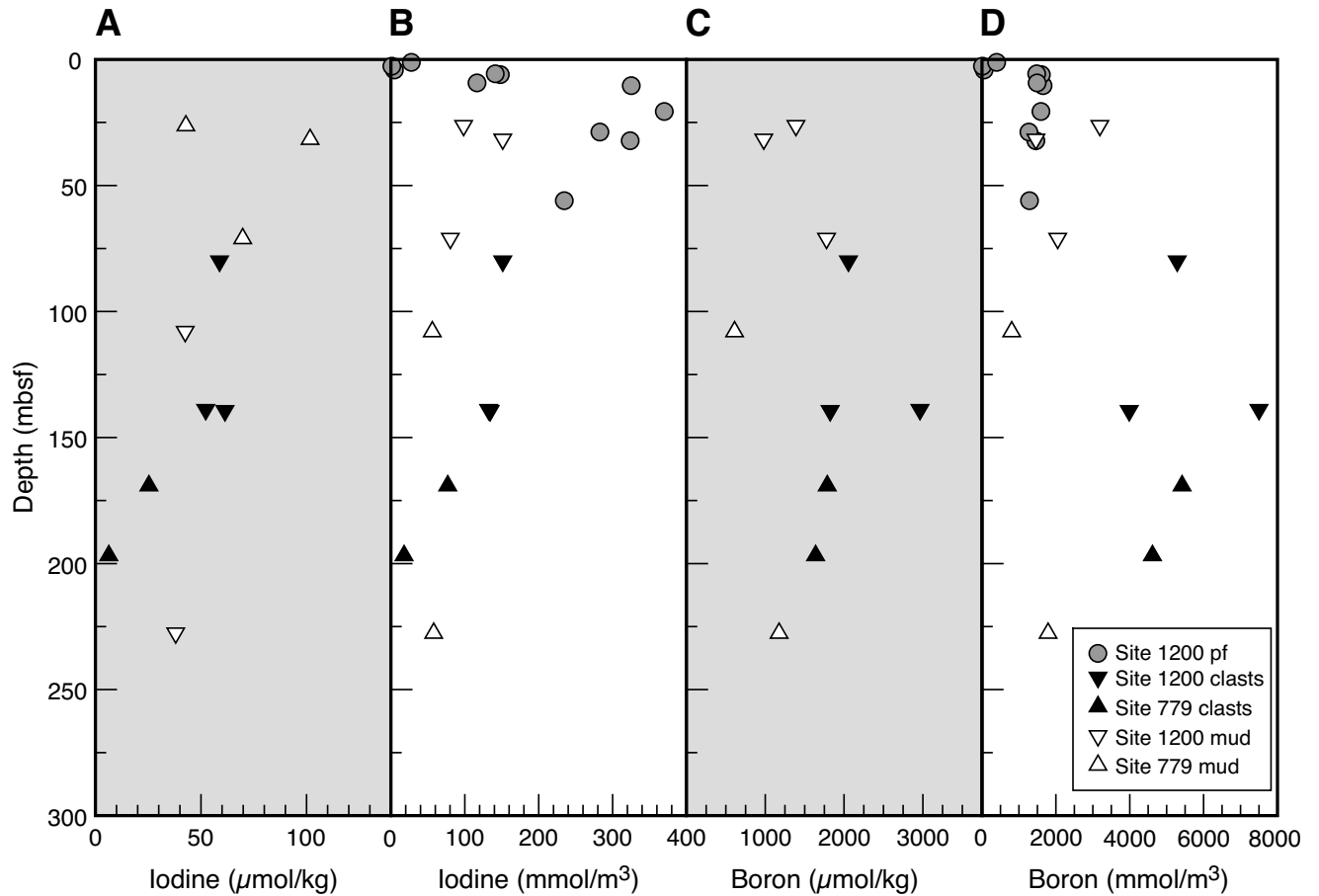


Figure F4. Bulk concentrations of pore fluid (pf), mud, and clasts. Representative concentrations: white crosses = fluids in marine sediment (assuming porosity = 40%). SW = seawater in sediment, MV = mud volcano, DC = shallow décollement fluids. Black X = solid end-members. MS/3 = one-third marine sediment concentration (porosity = 40%, density = 2.6 g/cm³), AV = arc volcanics, DM = depleted mantle, BSE = bulk silicate earth (assumed porosity for rocks = 0.1%, density = 3 g/cm³). Dotted line shows mixing between DM and MS.

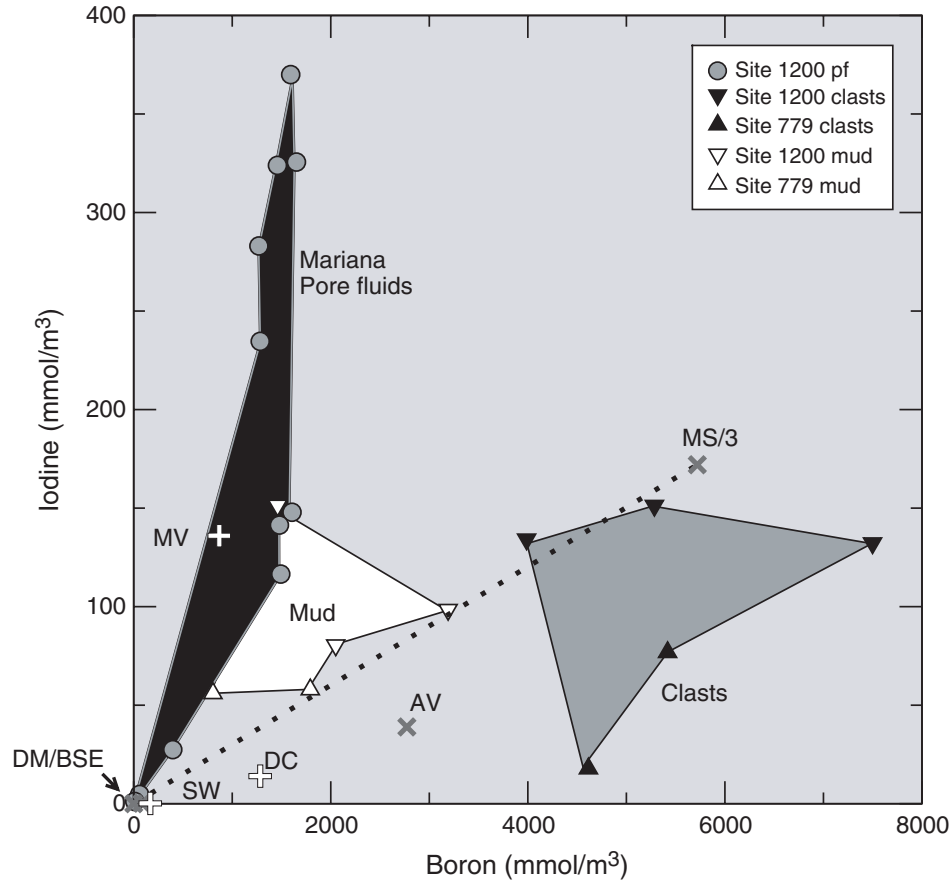


Table T1. Interstitial water halogen and boron data, Site 1200, and some representative concentrations.

Core, section, interval (cm)	Depth (mbsf)	I (μM)	B (μM)	Cl (mM)	I* (mmol/m ³)	B* (mmol/m ³)
195-1200D-						
1H-1, 120–130	1.20	63.0	914.0	543.4	27.4	398
1H-2, 120–130	2.70	162.0	1745.8	527.6	1.1	12
1H-3, 120–130	4.20	238.2	3031.4	535.0	4.8	61
1H-4, 120–130	5.70	294.6	3081.9	540.1	141.4	1479
1H-5, 10–20	6.10	308.2	3346.1	538.5	147.9	1606
2H-2, 88–98	9.28	274.7	3519.0	542.4	116.8	1492
9H-1, 80–90	28.80	667.4	2997.7	532.7	283.0	1271
195-1200E-						
2H-3, 123–133	10.33	678.2	3442.6	528.9	325.5	1652
5H-3, 51–61	20.62	804.2	3465.5	539.1	369.9	1594
7H-5, 30–40	32.20	762.2	3437.7	527.9	323.9	1461
10H-3, 62–72	56.02	565.3	3093.9	529.1	234.6	1284
Representative concentrations						
Seawater:		0.44	420	550		
Mud volcanoes:		340	2170	835		
Décollement fluids:		35	3210	447		
Arc fumaroles:		13	1795	395		

Notes: Chloride concentrations from nearest corresponding pore fluid splits analyzed onboard (Salisbury, Shinohara, Richter, et al., 2002). * = calculated from measured concentrations (this study) and sediment porosity (Salisbury, Shinohara, Richter, et al., 2002). Seawater concentrations are from Broecker and Peng (1982). Nonserpentinite mud volcano fluids are from Aloisi et al. (2004). Décollement fluids are from the Nankai Trough (You et al., 1993; Kastner et al., 1993). High-temperature fumarolic condensate (885°C) is from Satsuma-Iwojima (Snyder et al., 2002; Goff and McMurtry, 2000).

Table T2. Serpentinized ultramafic clasts and interstitial serpentinite mud from Sites 779 and 1200 and global reservoir values.

Core, section, interval (cm)	Sample type	Depth (mbsf)	I ($\mu\text{mol/kg}$)	B ($\mu\text{mol/kg}$)	I* (mmol/m^3)	B* (mmol/m^3)
125-779A-						
13R-1, 138–140	Mud	107.98	42.6	611.1	56.0	804.0
20R-1	Clast	169.10	25.4	1,787.0	76.9	5,418.0
25R-1	Clast	196.80	6.3	1,638.9	17.8	4,615.0
28R-2, 112–114	Mud	227.59	38.0	1,175.9	57.9	1,791.0
195-1200A-						
9R-1, 63–65	Mud	71.03	69.7	1,777.8	80.4	2,050.0
10R-1, 13–15	Clast	80.03	58.8	2,055.6	151.2	5,285.0
16R-1, 133–135	Clast	138.93	52.3	2,963.0	132.2	7,499.0
16R-2, 48–50	Clast	139.38	61.4	1,824.1	134.2	3,987.0
195-1200D-						
8H-1, 127–129	Mud	26.27	42.8	1,388.9	98.4	3,191.0
195-1200E-						
7H-4, 127–129	Mud	31.67	101.7	981.4	151.3	1,461.0
Representative concentrations						
Marine sediments:			330	11,000		
Depleted mantle:			0.0031	23		
Bulk silicate earth:			0.079	28		
Arc volcanics:			0.079	925		

Notes: * = calculated from measured concentrations (this study), grain density, and porosity (Salisbury, Shinohara, Richter, et al., 2002; Fryer, Pearce, Stokking, et al., 1990). Marine sediment values for halogens from the Peru margin (Martin et al., 1993) and boron values from Leeman (1996). Depleted mantle values for halogens based on Siberian coated diamonds (Burgess et al., 2002) and boron value from mid-ocean-ridge basalt glass (Ryan and Langmuir, 1993). Bulk silicate earth values from McDonough and Sun (1995). Arc volcanic concentration for iodine from Muramatsu and Wedepohl (1998), bromine from Yoshida et al. (1971), and boron from Leeman (1996).