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# Deep-slab fluids fuel extremophilic *Archaea* on a Mariana forearc serpentinite mud volcano: Ocean Drilling Program Leg 195

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[1] As the Pacific plate subducts beneath the Mariana forearc it releases water that hydrates the overlying mantle wedge, converting it to serpentinite that protrudes to form mud volcanoes at the seafloor. Excess H<sub>2</sub>O ascends through these mud volcanoes and exits as cold springs at their summits. The composition of this deep-slab derived water has been determined by drilling on two of these seamounts. It has a pH of 12.5 and, relative to seawater, is enriched in sulfate, alkalinity, Na/Cl, K, Rb, B, light hydrocarbons, ammonia, <sup>18</sup>O, and deuterium, and depleted in chloride, Mg, Ca, Sr, Li, Si, phosphate, and <sup>87</sup>Sr. Within the upper 20 m below seafloor at South Chamorro Seamount a microbial community operating at pH 12.5, made up overwhelmingly of *Archaea*, is oxidizing methane from the ascending fluid to carbonate ion and organic carbon, while reducing sulfate to bisulfide and probably dissolved nitrogen to ammonia.

**Components:** 5892 words, 9 figures, 1 table.

**Keywords:** Subduction factory; pore water; serpentinite; forearc; mud volcano; Ocean Drilling Program.

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**Theme:** Trench to Subarc: Diagenetic and Metamorphic Mass Flux in Subduction Zones

**Guest Editors:** Gary Bebout and Tim Elliot

## 1. Introduction

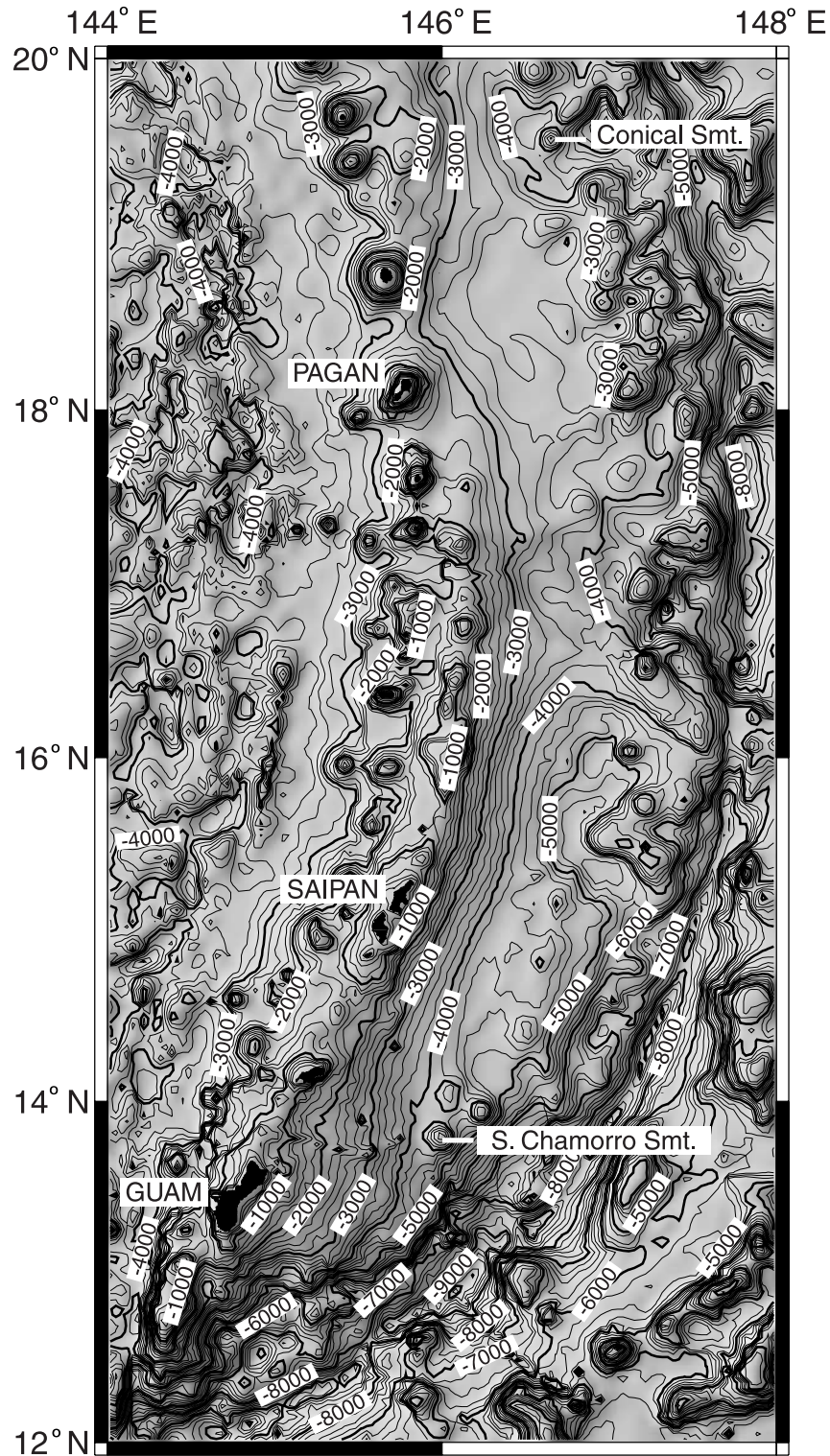
[2] The Mariana subduction complex is formed between the northwestward subducting Pacific plate and the overriding Philippine plate. Volatiles released from the downgoing Pacific plate hydrate the overlying mantle wedge of the Philippine plate and convert depleted harzburgite to low-density serpentinite. The resulting serpentinite mud, containing variably serpentinitized harzburgite clasts, ascends buoyantly along fractures and extrudes at the seafloor, where it forms large (50 km diameter, 2 km high) mud volcanoes along the outer Mariana forearc, in a band that extends from 30 to 120 km behind the trench axis [Fryer *et al.*, 1985, 1995, 2000]. These mud volcanoes are built from flows of poorly consolidated sedimentary serpentinite fed through a central conduit. Cold ( $\sim 2^{\circ}\text{C}$ ) spring waters fresher than seawater have been sampled on several of these mud volcanoes, by manned submersibles [Fryer *et al.*, 1990; Fryer and Mottl, 1997], deep drilling [Mottl, 1992], and piston and gravity coring [Fryer *et al.*, 1999]. We report here the most comprehensive sampling of such waters to date, on Ocean Drilling Program (ODP) Leg 195 in 2001, and the discovery that they support a community of extremophilic microbes, mainly *Archaea*, within serpentinite mud 0–20 m below seafloor (mbsf). This community operates at pH 12.5.

[3] The first serpentinite mud volcano drilled in the Mariana forearc, on ODP Leg 125, was Conical Seamount, 90 km arcward (west) of the trench near  $19.5^{\circ}\text{N}$  (Figure 1 and Table 1) [Fryer *et al.*, 1992]. In 1987 divers in the submersible *Alvin* discovered chimneys up to 3.5 m tall at the summit, composed of aragonite, calcite, and amorphous Mg-silicate; when one chimney was disturbed it began to emit a slow flow of cold ( $\sim 1.5^{\circ}\text{C}$ ) water with pH 9.3 and elevated dissolved carbonate, methane, sulfate, and reduced sulfur relative to the surrounding seawater [Fryer *et al.*, 1990]. Bacterial mats and small limpets and gastropods were collected from the chimneys. Although none of these chimneys could be located during Leg 125, drilling at the summit recovered unusual pore water that had less than half the chloride and bromide of seawater, pH of 12.6, and was highly enriched in dissolved carbonate,

light hydrocarbons, sulfate, bisulfide, Na/Cl, K, Rb, and B (Table 1). Near-surface gradients in chloride indicate that this water was upwelling at 1–10 cm/yr [Mottl, 1992]. Also drilled during Leg 125 was Torishima Forearc Seamount, an inactive serpentinite mud volcano in the Izu-Bonin forearc near  $31^{\circ}\text{N}$ . Pore water recovered from serpentinite on this seamount reflects reaction of cool ( $4\text{--}11^{\circ}\text{C}$ ) seawater with harzburgite and contrasts greatly with that from the active Conical Seamount (Table 1). The distinctive composition of water upwelling at Conical Seamount implies that it originates by dehydration of the subducting Pacific plate,  $\sim 29$  km below the seafloor based on earthquake depths [Hussong and Fryer, 1981; Seno and Maruyama, 1984]. The upwelling  $\text{H}_2\text{O}$  is in excess of that which, during its ascent, hydrates the overlying mantle wedge, and represents one of the earliest returns of subducted volatiles to the oceans. Unlike deeply sourced water sampled from other subduction zones, this water has not interacted with an accretionary sedimentary prism, as the Mariana subduction zone is non-accretionary; the origin of this water is thus easier to infer because it has reacted mainly with a relatively simple matrix of harzburgite during its ascent.

## 2. Results

[4] ODP Site 1200 was drilled on the summit of South Chamorro Seamount, 85 km arcward of the trench near  $14^{\circ}\text{N}$  (Figure 1 and Table 1) and  $\sim 27$  km above the top of the subducting Pacific plate. Dives in 1996 discovered and sampled three cold springs with carbonate crusts and chimneys and an abundant biota of mussels, small tube-worms, whelks, and galatheid crabs [Fryer and Mottl, 1997]. Pore water from Site 1200 was recovered by squeezing serpentinite mud from four holes that form a transect from one of the springs. Holes 1200A and 1200E are located within a few meters of the spring and Holes 1200F and 1200D are 20 m north and 80 m northwest of the spring, respectively (Figure 2). Temperature gradients were low such that none of the pore water exceeded  $3.0^{\circ}\text{C}$  at the sampling depth, compared with a bottom water temperature of  $1.67^{\circ}\text{C}$  [Shipboard Scientific Party, 2002].



**Figure 1.** Location of Conical and South Chamorro Seamounts, two active serpentinite mud volcanoes in the Mariana forearc that have been drilled.

**Table 1.** Composition of Pore Water From Three Serpentinite Seamounts Versus Seawater

Seamount	Conical <sup>a</sup>	South Chamorro <sup>a</sup>	Torishima Forearc <sup>b</sup>	Seawater <sup>c</sup>
ODP Site	780	1200	783, 784	
Latitude	19°32.5'N	13°47.0'N	30°57.86, 54.49'N	
Longitude	146°39.2'E	146°0.2'E	141°47.27, 44.27'E	
Deepest sample (mbsf)	130	71	400	
Chloride (mmol/kg)	260 ± 25	510 ± 5	550 ± 5	542
Sulfate (mmol/kg)	46 ± 1	28 ± 1	9 ± 3	28.0
Alkalinity (meq/kg)	52 ± 13	62 ± 8	1.3 ± 0.4	2.3
Carbonate Alkalinity <sup>d</sup>	35 ± 15	45 ± 7 <sup>e</sup>	1.1 ± 0.4	1.9
pH at 25°C	12.5 ± 0.1	12.5 ± 0.1	9.6 ± 0.4	8.1
Na (mmol/kg)	390 ± 10	610 ± 10	460 ± 20	466
Na/Cl (molar)	1.5 ± 0.1	1.2 ± 0.02	0.84 ± 0.02	0.860
K (mmol/kg)	15 ± 1	19 ± 1	5 ± 1	10.1
Mg (mmol/kg)	0.003 ± 0.002	<0.01	1 ± 1	52.4
Ca (mmol/kg)	1 ± 0.5	0.3 ± 0.1	55 ± 5	10.2
Charge Balance (calc.)	3.0 ± 25	1.6 ± 10	7.7 ± 20	0.9
CH <sub>4</sub> (μmol/kg)	2000 ± 1000	2000 ± 1000 <sup>e</sup>	2 ± 1	0.0004
Li (μmol/kg)	1.6 ± 0.5	0.4 ± 0.1	16 ± 5	26
Rb (μmol/kg)	7.8 ± 0.6	11 ± 2	1 ± 0.2	1.37
Sr (μmol/kg)	20 ± 10	10 ± 2	200 ± 50	90
Ba (μmol/kg)	0.1 ± 0.05	0.4?	1.6 ± 0.7	0.14
B (μmol/kg)	3900 ± 100	3200 ± 200	180 ± 80	410
Si (μmol/kg)	60 ± 30	70 ± 20	10 ± 8	190
F (μmol/kg)	not determined	47 ± 3	not determined	67
Mn (μmol/kg)	<0.01	0.01	0.4 ± 0.2	0
Fe (μmol/kg)	2 ± 1	2 ± 0.5	1 ± 0.9	0
Phosphate (μmol/kg)	0.4 ± 0.3	0.2	not determined	2.8
NH <sub>3</sub> (μmol/kg)	265 ± 5	220 ± 10	140 ± 20	0
Reduced S (μmol/kg)	<250	<250	0	0
C <sub>2</sub> H <sub>6</sub> (μmol/kg)	7	2	0	0
C <sub>1</sub> /C <sub>2</sub> (molar)	290 ± 15	780 ± 10		
<sup>87</sup> Sr/ <sup>86</sup> Sr	<0.7062	0.70535 ± 0.0001 <sup>f</sup>	<0.7070	0.7091
δ <sup>34</sup> SO <sub>4</sub> (‰ CDT)	13.7 ± 0.3	not determined	31.2 ± 0.4	20.5
δ <sup>18</sup> O (‰ SMOW)	4.0 ± 0.5	2.5 ± 0.5	-0.4 ± 0.2	0.0
δD (‰ SMOW)	3 ± 2	12 ± 2	-2 ± 2	0.0

<sup>a</sup> Asymptotic composition of deep upwelling fluid from active mud volcano. Conical data are from Mottl [1992], Mottl and Alt [1992], Haggerty and Chaudhuri [1992], and Benton [1997].

<sup>b</sup> Product of harzburgite-seawater reaction within inactive mud volcano in the Izu-Bonin forearc [Mottl, 1992].

<sup>c</sup> Estimated composition of local bottom water.

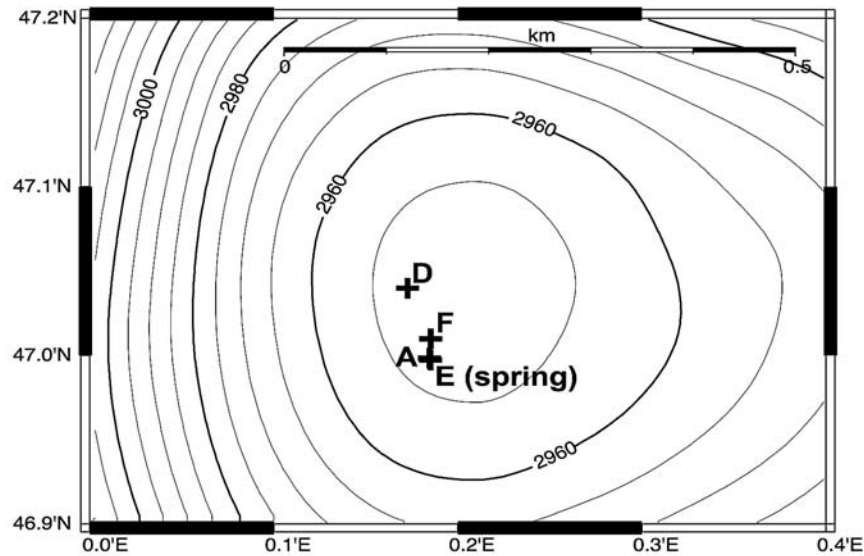
<sup>d</sup> meq/kg, calc'd from PHREEQC [Parkhurst and Appelo, 1999].

<sup>e</sup> δ<sup>13</sup>CH<sub>4</sub> = -11 ± 5‰ VPDB in deep fluid; δ<sup>13</sup>C-DIC = -16‰ VPDB at 15 mbsf, still within microbial zone.

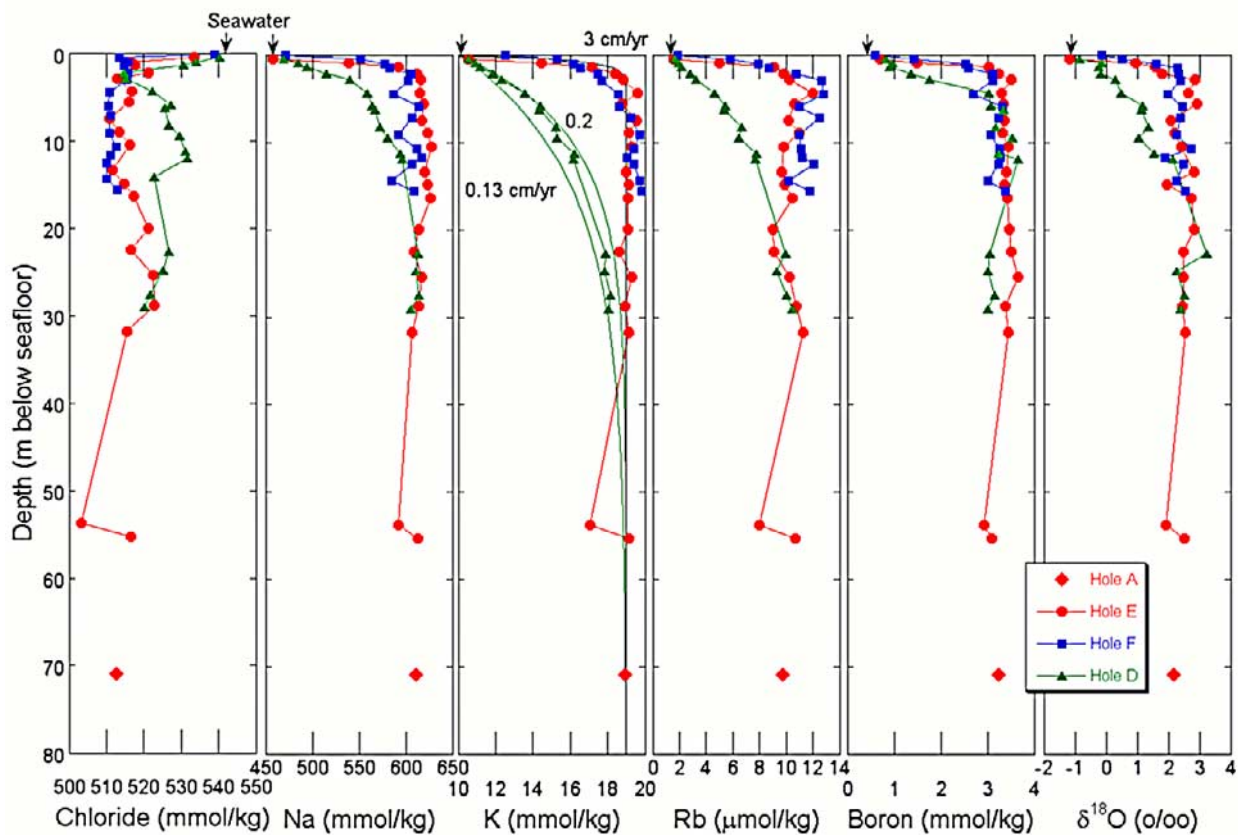
<sup>f</sup> Bickford and Siegel (personal communication, 2002).

[5] Depth profiles of pore water composition (Figures 3 and 4) show the typical convex-upward shape and steep near-surface gradient indicative of upwelling at several cm/yr of a fluid compositionally different from seawater. Chloride profiles also show irregularities down to 30 mbsf, especially in Hole 1200D (Figure 3). These probably result from leaching of chloride from iowaite, a Mg-Fe hydroxy-chloride hydrate mineral thought to form at shallow depth by interaction of seawater with brucite [Heling and Schwarcz, 1992; Fryer and Mottl, 1992]. Profiles of Na, Na/Cl, K, Rb, B, δ<sup>18</sup>O (Figure 3), <sup>87</sup>Sr/<sup>86</sup>Sr (not shown), and pH

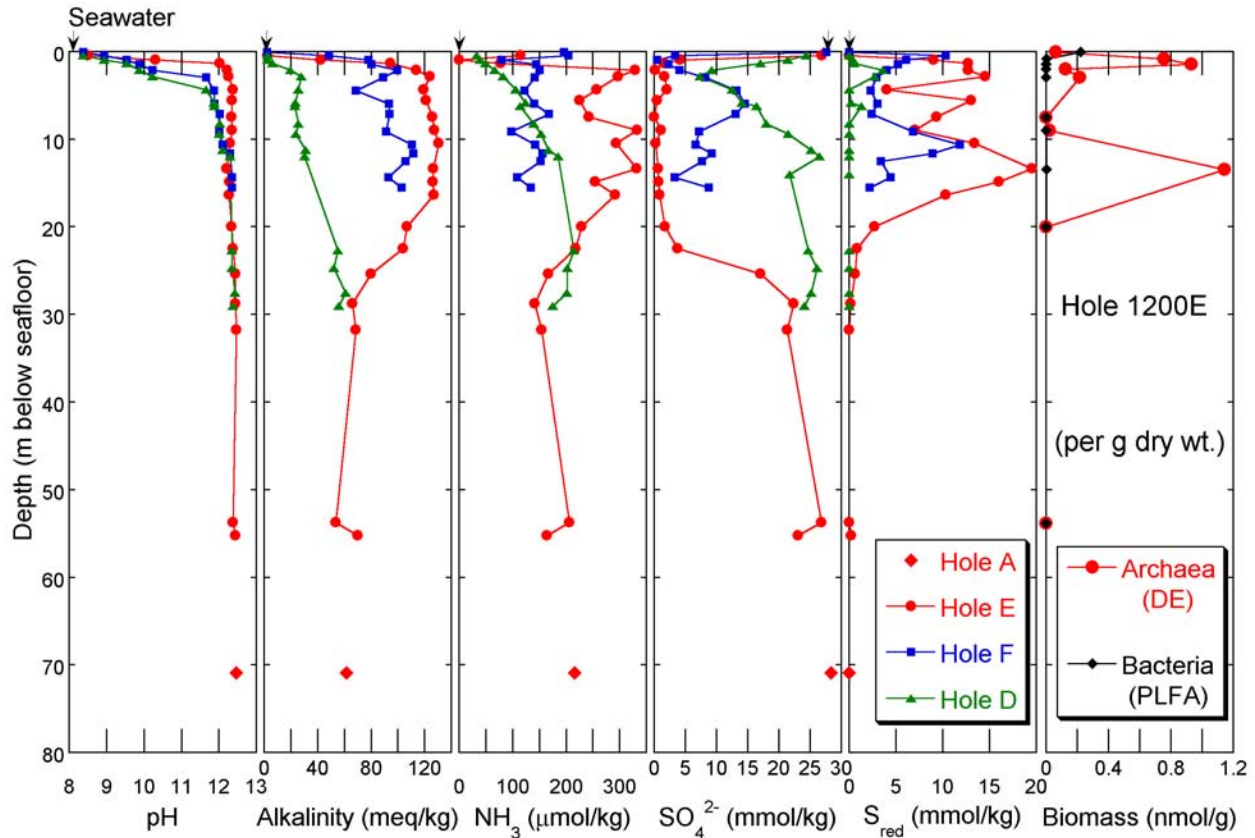
(Figure 4) approach asymptotic values within 3–4 mbsf in Hole 1200E at the spring. Gradients become progressively less steep at Holes 1200F and 1200D to the north, implying that upwelling slows away from the spring, from about 3 cm/yr at Hole 1200E to 0.2 cm/yr at Hole 1200D, based on the K profile. However, the profiles approach the same asymptotic value with depth, thereby defining a single deep composition at all three locations, reported in Table 1. Profiles for these chemical species reflect mainly vertical upwelling and chemical diffusion because these species are relatively unreactive over the sampled depth. Alone among the



**Figure 2.** Location of ODP Site 1200 drillholes on the summit of South Chamorro Seamount. Holes 1200A and 1200E are within a few meters of an active cold spring. Minutes shown on the axes of this map are for 13°N and 146°E.



**Figure 3.** Composition of pore water from ODP Site 1200 on the summit of South Chamorro Seamount versus depth. Convex-upward profiles result from upwelling of deep fluid at seepage velocities ranging from 3 cm/yr at Hole 1200E near the spring to 0.2 cm/yr at Hole 1200D 80 m NNW of the spring, as estimated from the K profiles at 2°C, porosity 0.51, formation factor 3.7,  $D_w$  for K 0.0334, and  $D_{sed}$  0.0177 m<sup>2</sup>/yr.



**Figure 4.** Composition of pore water from ODP Site 1200, South Chamorro summit, compared with microbial (archaeal and bacterial) biomass, versus depth. Sulfate reduction by *Archaea* at 1 to 3 and 13 mbsf produces alkalinity, dissolved reduced sulfur (virtually all bisulfide at this high pH), and ammonia.

chemical species measured, K, Rb, and  $\delta^{18}\text{O}$  plot linearly against one another for all three holes (Figure 5) and thus define a mixing line between the end-member ascending fluid and bottom seawater. As alkali elements of intermediate atomic weight, K and Rb can be expected to react similarly to one another, but not to oxygen isotopes. The mutual linear relationships thus imply that these three species are the least reactive. These are followed by B and Na, which are linear with K only for Holes 1200E and 1200F (Figure 5). At Hole 1200D farthest from the spring, where slower upwelling would allow the effects of reaction to become obvious, some points plot above the mixing line, implying that B and Na are leached from the solids over part of the sampled depth. Except for chloride, which is depleted by 6% relative to bottom seawater, all of these species are highly enriched in the deep ascending fluid. Similar but mirror-image profiles

are shown by Mg, Ca, Sr, Mn, and Li, all of which decrease sharply with depth and are thus highly depleted in the deep fluid (Figure 6). Plots of these elements against the conservative element K (not shown) indicate that all five are taken up by serpentine over the sampled depth, and all are more rapidly reactive than the elements that are mobilized, in the order  $(\text{Si}^>)\text{Ca} = \text{Sr} > \text{Mg} > \text{Li}$ . Mn is further complicated by a sharp maximum within one meter of the seafloor that results from mobilization under reducing conditions.

[6] Depth profiles of other chemical species, including alkalinity, ammonia, sulfate, bisulfide (Figure 4), Fe, Si, phosphate, and F (Figure 7), again imply a single deep fluid composition, but these species are greatly affected by a different set of reactions within the upper 20 mbsf. The first five species are those typically affected by microbial oxidation of organic

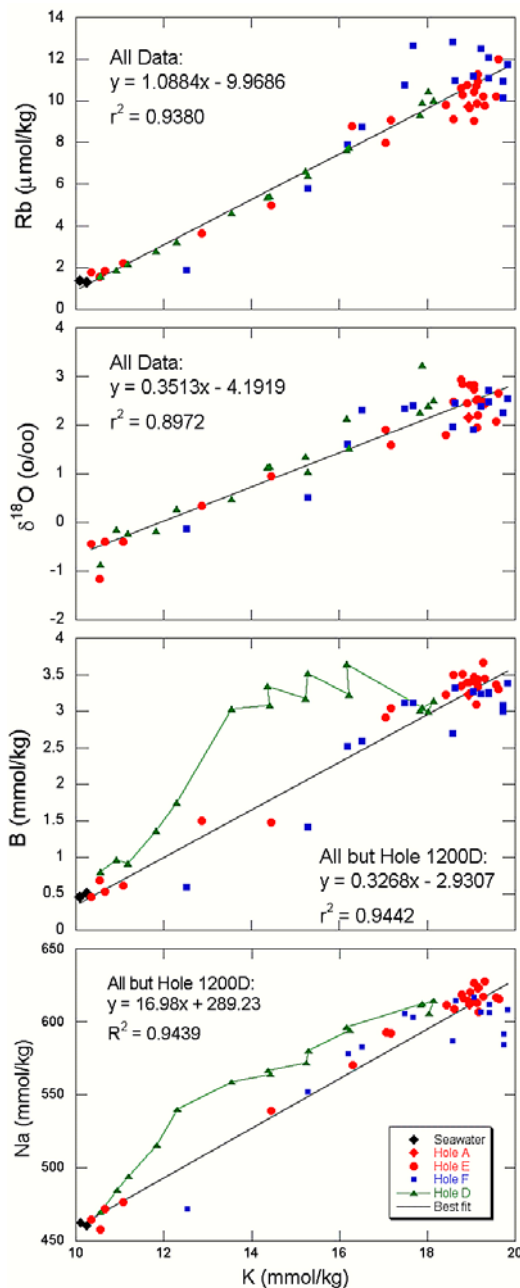
matter in marine sediment and the accompanying reduction of seawater sulfate and precipitation of Fe-sulfide minerals. Sulfate approaches zero between 2 and 20 mbsf in Hole 1200E at the spring, but shows two minima in Holes 1200F and 1200D, at 1–3 and 13 mbsf, indicating that sulfate is being reduced at these two depths, supplied from the overlying seawater at the shallower depth and from the deep upwelling water at the greater depth. Bisulfide (virtually the only form of dissolved reduced sulfur at pH 12.5) and ammonia show

maxima at about the same depths as the two sulfate minima, as does alkalinity in Hole 1200F, whereas Fe shows minima at these depths reflecting precipitation of Fe-sulfide. Sulfur content of the serpentine mud is <0.01 wt.% except for a near-surface enrichment by Fe-sulfide precipitation (Figure 8).

### 3. Discussion

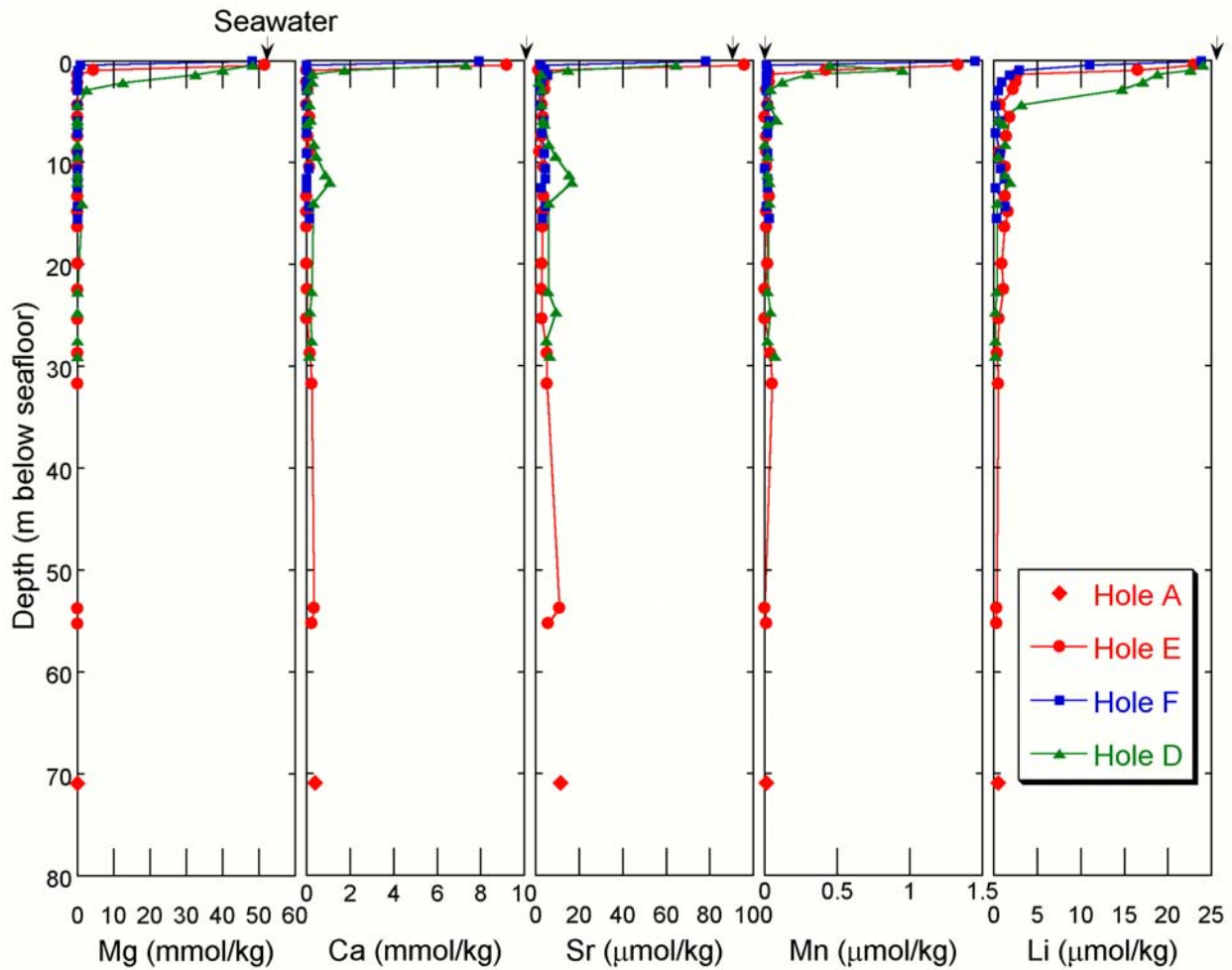
#### 3.1. Origin of the Ascending Fluid

[7] The deep upwelling fluid within the two active mud volcanoes is generally similar, except for much lower chloride and Na and higher sulfate at Conical Seamount (Table 1). Relative to seawater, both fluids have higher to much higher sulfate, alkalinity, pH, Na/Cl, K, Rb, B, light hydrocarbons, ammonia,  $\delta^{18}\text{O}$ , and  $\delta\text{D}$ ; and lower to much lower chloride, Mg, Ca, Sr, Li, Si, phosphate, and Sr isotopic ratio. Ba, Mn, Fe, and bisulfide are low in both deep fluids. By contrast, pore water from Torishima Forearc Seamount, produced by reaction of cool seawater with harzburgite, shows the opposite direction of change for chloride, sulfate, alkalinity, K, Rb, Ca, Sr, B,  $\delta^{18}\text{O}$ , and  $\delta\text{D}$ . Na/Cl is unchanged; pH, methane, Si, and ammonia are not nearly as high; and Ba, Li, and Mn are much higher. The deeply sourced water upwelling within the two active mud volcanoes clearly cannot have originated by simple reaction of seawater with peridotite. Considering that depleted harzburgite contains essentially no alkali elements, the source of the fresh water is almost certainly dehydration of sediment and altered basalt at the top of the



**Figure 5.** (opposite) K versus Rb,  $\delta^{18}\text{O}$ , B, and Na in pore waters from ODP Site 1200 on the summit of South Chamorro Seamount. Correlations are linear for K versus Rb and  $\delta^{18}\text{O}$  for all the holes, implying that K, Rb, and  $\delta^{18}\text{O}$  are relatively non-reactive over the sampled depth interval. By contrast, B and Na deviate from linearity, but only at Hole 1200D farthest from the spring where the upwelling speed is slowest. This deviation presumably results from leaching of B and Na from the serpentinite mud in Hole 1200D, over depth intervals from 3 to 12 mbsf for B and from 3 mbsf to greater than the maximum depth sampled of 29 mbsf for Na. These reactions presumably take place in Holes 1200E and 1200F as well, but faster upwelling at these holes overwhelms the effects of these reactions on the composition of the pore waters.



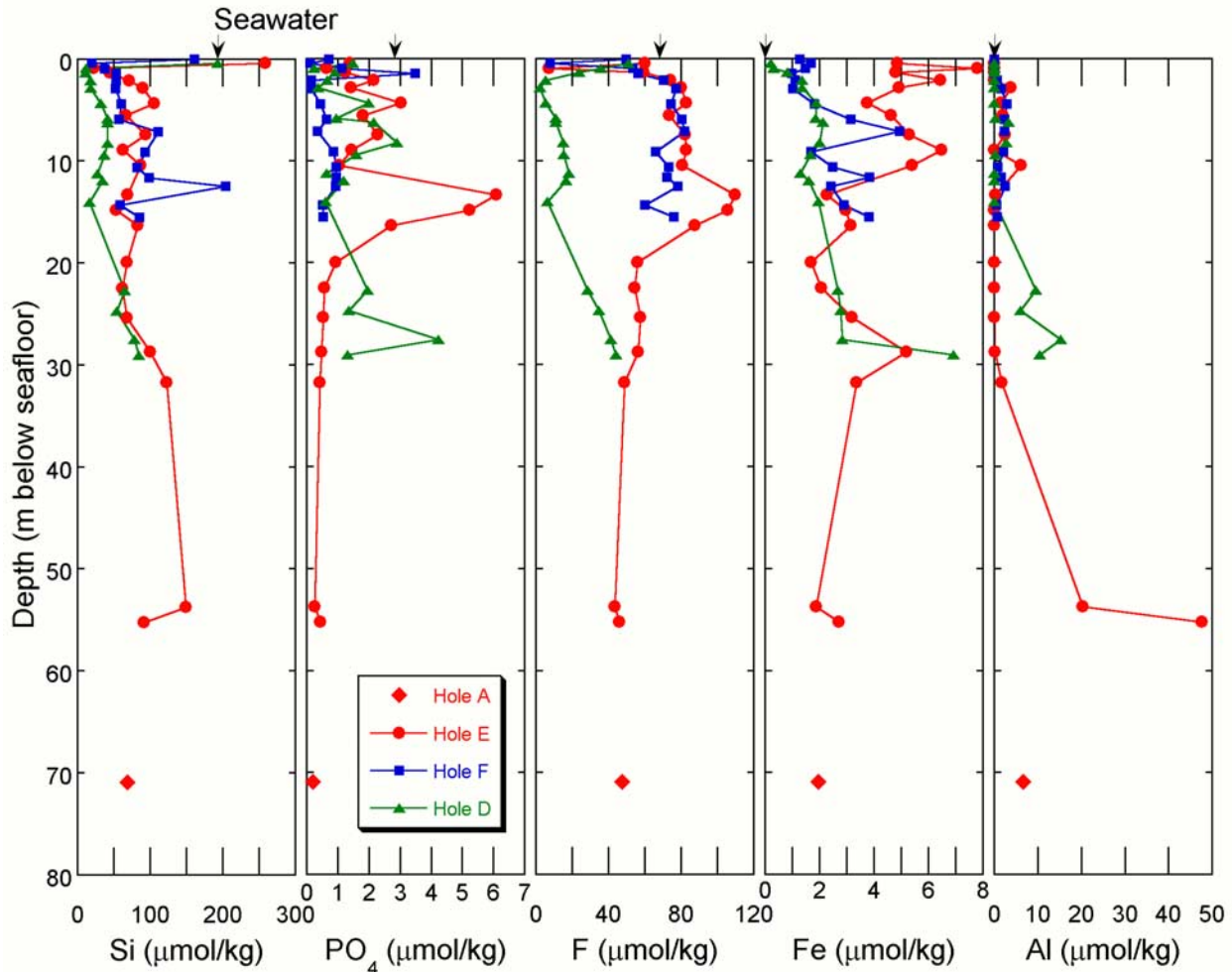


**Figure 6.** Composition of pore water from ODP Site 1200 on the summit of South Chamorro Seamount versus depth. These elements are all present at low concentrations in the deep upwelling water relative to seawater, except for Mn, which displays a large maximum just below the seafloor caused by the onset of reducing conditions. The slight recovery of Ca and Sr below 20 mbsf in Hole 1200E results from the decrease in alkalinity over this depth range and implies that the solutions are saturated with  $\text{CaCO}_3$ .

subducting Pacific plate. The high carbonate alkalinity, and its absence in pore waters from mud volcanoes closer to the trench, imply that beneath South Chamorro and Conical Seamounts dehydration is accompanied by decarbonation or carbonate dissolution [Fryer *et al.*, 1999].

[8] These are probably the most pristine slab-derived fluids recovered to date from a subduction zone, given the simplicity of their harzburgitic matrix. Because the depth of origin and the physical conditions there are poorly known, specific sources of fluid components and the processes that generate them are obscure. For subduction param-

eters characteristic of the Mariana arc, steady state thermal models suggest temperatures of 150–250°C at 0.8 GPa and 27 km depth [Peacock, 1996; Kincaid and Sacks, 1997]. This range is consistent with mineral assemblages of blueschist facies metabasites recovered from Conical Seamount (150–250°C and 0.5–0.65 GPa) [Maekawa *et al.*, 1993] and from South Chamorro Seamount (<350°C for  $P < 0.8$  GPa) [Fryer *et al.*, 2000], as well as with a serpentine assemblage dominated by lizardite at South Chamorro Seamount summit [Shipboard Scientific Party, 2002] and by chrysotile at Conical Seamount summit [Heling and Schwarcz, 1992; Fryer and Mottl, 1992]. It is also

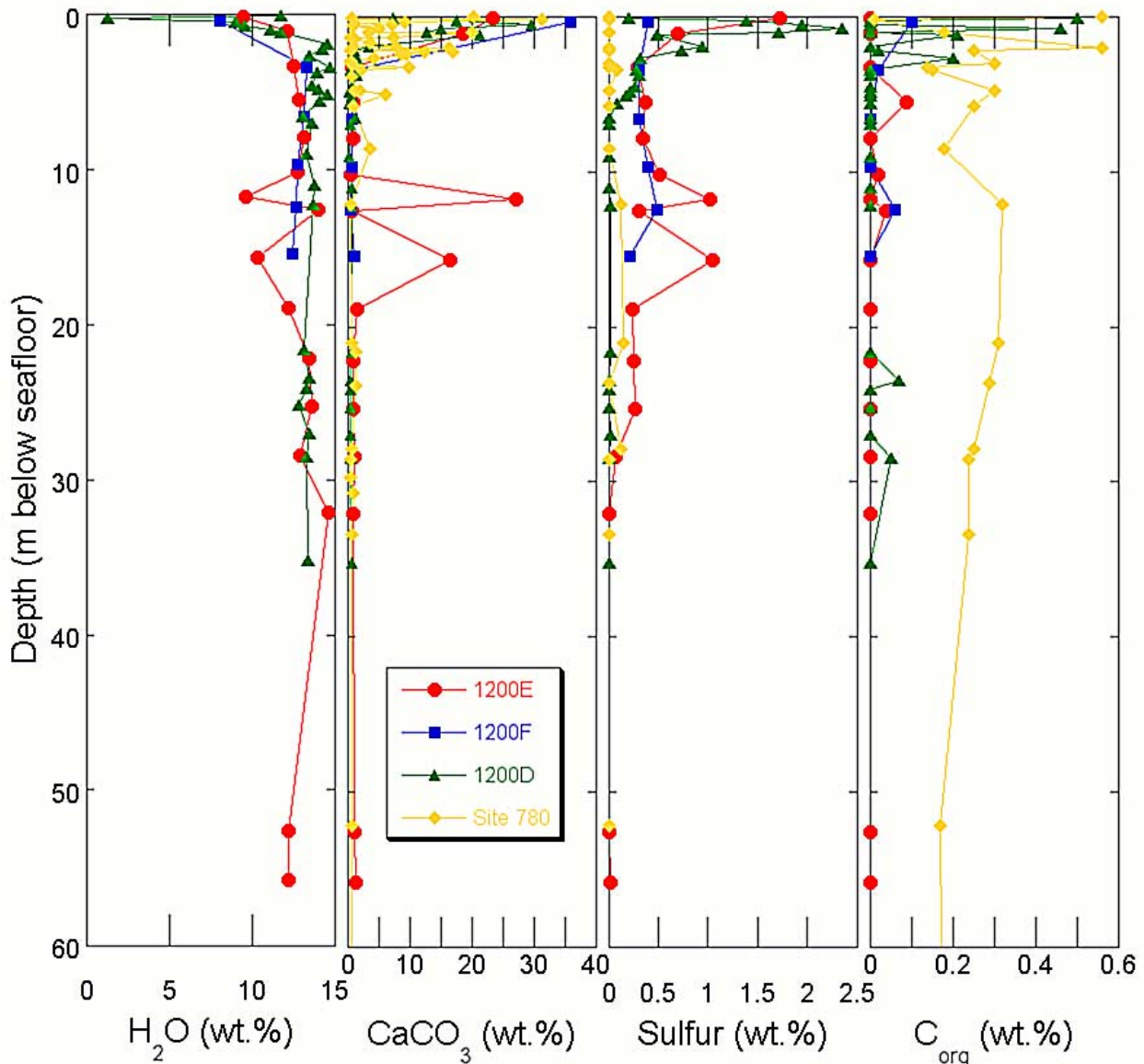


**Figure 7.** Composition of pore water from ODP Site 1200 on the summit of South Chamorro Seamount versus depth. These species show multiple maxima and minima, indicating that they are highly reactive over the sampled depth interval.

consistent with high K and Rb in solution, as these elements typically are leached from oceanic crustal rocks only above  $\sim 150^\circ\text{C}$ ; at lower temperatures they are taken up into alteration minerals [Seyfried and Bischoff, 1979; Magenheimer et al., 1995]. As for the source of the solutions, compactive dewatering can take place at any temperature, but the chemical dehydration that produces freshened fluids requires elevated temperatures, over the range 1)  $30\text{--}80^\circ\text{C}$  for expulsion of interlayer water and conversion of opal-A to opal-CT, 2)  $50\text{--}150^\circ\text{C}$  for expulsion of interlayer water and conversion of smectite to illite, 3)  $>250^\circ\text{C}$  for dehydration of sedimentary minerals, mainly clays and zeolites, and 4)  $>450^\circ\text{C}$  for dehydration of hydrous alteration phases in the basaltic oceanic crust [Peacock, 1990]. These

dehydration reactions are accompanied by breakdown of heavier hydrocarbons to methane in subducted sediment at  $60\text{--}150^\circ\text{C}$  [Peacock, 1990] and decarbonation of sedimentary and vein carbonates at  $>400^\circ$  to  $>540^\circ\text{C}$  at 0.8 GPa [Kerrick and Connolly, 2001a, 2001b].

[9] Sediment and altered oceanic crust at the top of the subducting slab beneath Conical and South Chamorro Seamounts are therefore hot enough to supply  $\text{H}_2\text{O}$  and light hydrocarbons to the ascending fluids but not  $\text{CO}_2$ , which must be supplied by dissolution of carbonate minerals at the source rather than by decarbonation. An alternative to thermogenic production of light hydrocarbons from organic matter is reduction of dissolved carbonate



**Figure 8.** Partial composition of serpentinite mud cored at ODP Site 1200 on the summit of South Chamorro Seamount and at Site 780 on the summit of Conical Seamount versus depth. Water content is typical of that for serpentinite; smaller concentrations near the seafloor result from dilution of serpentinite by  $\text{CaCO}_3$  (typically aragonite needles) that precipitates at a reaction front between the upwelling water, rich in carbonate alkalinity and poor in Ca, and downward-diffusing bottom seawater that is relatively rich in Ca and poor in alkalinity. Hole 1200E contains pyritized foraminifera at 12 and 16 mbsf, where  $\text{CaCO}_3$  is enriched, indicating that serpentinite mud at these depths was exposed at the seafloor for extended periods prior to burial by more serpentinite mud; some of this enrichment also results from  $\text{CaCO}_3$  precipitation at a similar reaction front when mud at these depths was at the seafloor. The sulfur enrichment near the seafloor at Site 1200 results from Fe-sulfide minerals that precipitate as a result of microbial (archaeal) sulfate reduction (Figure 4). These sulfides typically blacken the core. The zone of sulfur enrichment extends to 25 mbsf in Hole 1200E at the spring, to at least 15 mbsf in Hole 1200F 20 m away, and to only 5 mbsf in Hole 1200D 80 m from the spring. It is essentially absent at Site 780 on the summit of Conical Seamount, which also lacks a macrofauna even though it has a much higher content of organic carbon in the serpentinite mud than is present at Site 1200. The enrichment of organic carbon at 0–3 mbsf in Hole 1200D farthest from the spring correlates with a high concentration of foraminifera [Shipboard Scientific Party, 2002]. Except for this enrichment, organic carbon is extremely low in the serpentinite mud at Site 1200.

by H<sub>2</sub>, produced during serpentinization by oxidation of ferrous iron in peridotite. Such an abiogenic origin is implied by the unusually heavy δ<sup>13</sup>C of methane and the high ratio of methane to ethane (Table 1), both of which resemble those in gases emitted from ultramafic rocks in the Zambales ophiolite in the Philippines, for which *Abrajano et al.* [1988] hypothesized an abiogenic origin.

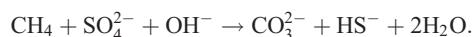
[10] Other species that are presumably dissolved from the subducting Pacific crust include Na, K, Rb, B, sulfate, and ammonia. Chloride could be similarly leached, or originate from pore water or from incursion of seawater into the seamounts, but whatever its source, its concentration would increase steadily as the fluid ascended and H<sub>2</sub>O was lost to serpentinization along the flow path. The lower chloride in the ascending fluid at Conical vs. South Chamorro Seamount could result from either lesser supply of chloride or less serpentinization beneath Conical Seamount, possibly because the flow system there is more mature and the flow channels already heavily serpentinized. That serpentinization is ongoing is demonstrated by the presence of olivine, orthopyroxene, and clinopyroxene in clasts suspended in the serpentinite mud [*Shipboard Scientific Party*, 2002] and by the extraordinarily high pH (W.E. Seyfried, Jr., personal communication, 2002), the highest ever recorded in a deep-sea setting. Serpentinization keeps concentrations of Mg, Si, and Li (which substitutes for Mg) low, whereas Ca and Sr are kept low by equilibrium with CaCO<sub>3</sub> at the high carbonate alkalinity and pH. Aragonite needles have precipitated abundantly within the upper 2 mbsf on both of these active mud volcanoes (Figure 8), where plentiful Ca is supplied by downward diffusion from seawater [*Mottl*, 1992; *Shipboard Scientific Party*, 2002]. Precipitation of CaSO<sub>4</sub> does not play a role, as the solutions are undersaturated with gypsum and anhydrite.

### 3.2. Extremophilic Archaea

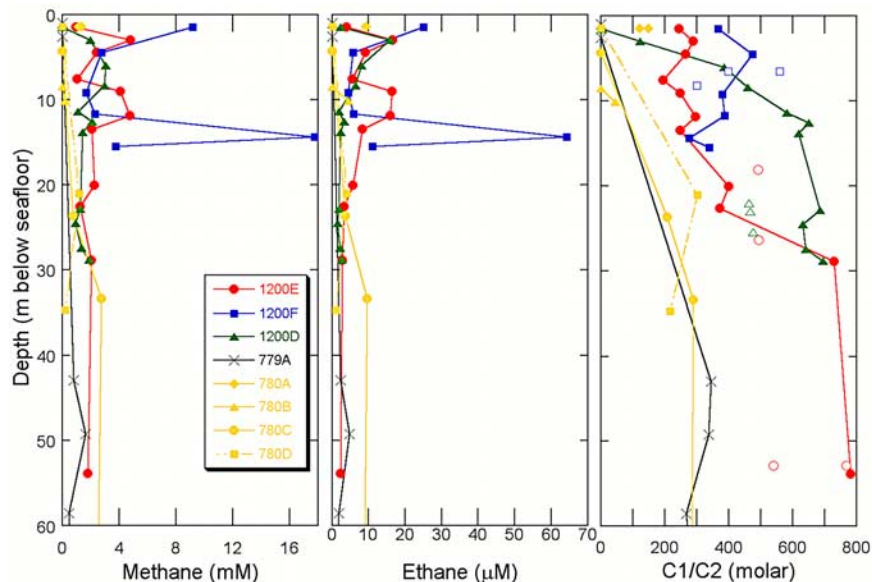
[11] Microbial sulfate reduction accompanied by production of carbonate, bisulfide, and ammonia at 1–3 and 13 mbsf, inferred from Figure 4, is remarkable for three reasons: it is accomplished at pH 12.5, by an assemblage overwhelmingly

dominated by *Archaea* rather than *Bacteria*, in a setting that has essentially no sedimentary organic carbon. We analyzed ten sediment samples from Hole 1200E for phospholipid fatty acid (PLFA) content [*Dobbs and Findley*, 1993] to characterize the microbial communities. Bacterial biomass (as defined by the total concentration of PLFA) ranged from ~10<sup>4</sup> to ~10<sup>6</sup> cells/g dry wt. It was highest at 0–0.1 mbsf but was undetectable in the deepest sample at 53.8–53.9 mbsf. The surface sample had a diverse community structure, as defined by the variety of PLFAs detected, including ~10% fatty acids that are common in anaerobic lithotrophic bacteria (e.g., branched monoenoic and mid-chain branched PLFAs). Specifically, the mid-chain branched biomarker 10me16:0 was detected, which is prevalent in the sulfate reducer *Desulfobacter*. Whereas bacteria were concentrated near the seafloor, archaeal biomass was exceptionally high in subsurface samples, based on phospholipid-derived diphytanyl diethers. Archaeal biomass showed a bimodal distribution with the highest peaks at the same depths as the two bisulfide maxima and the bounds of the sulfate minimum (Figure 4), indicating that archaea are mainly responsible for sulfate reduction. At these two peaks archaeal biomass is 932 and 571 times, respectively, higher than bacterial biomass, as defined by the total concentration of diethers to PLFAs.

[12] Of 49 samples of serpentinite mud analyzed from Site 1200 only 13 had detectable (≥0.01 wt.%) organic carbon (Figure 8); of these, nine had ≤0.1 (avg. 0.05) wt.% and the remaining four were from the upper 2.7 mbsf in Hole 1200D where some pelagic sediment is present. The reduced carbon that fuels sulfate reduction is almost certainly methane delivered by the ascending fluid, via the reaction

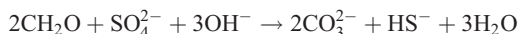


The observed increase in carbonate alkalinity of 53 meq/kg within the zone of sulfate reduction (average of ten samples from Hole 1200E), relative to its concentration in the deep upwelling fluid (Table 1), nearly matches the loss of 55 meq/kg of sulfate (Figure 4), as would be the case in the above reaction for methane oxidation at high pH.



**Figure 9.** Methane, ethane, and the methane/ethane ratio versus depth in pore waters from Site 1200 on the summit of South Chamorro Seamount, Site 779 on the flank and Site 780 on the summit of Conical Seamount. Concentrations are minima as these gases can be lost during core recovery and sampling. Solid symbols are for headspace-gas samples and open symbols (C1/C2 at Site 1200 only) are for gas collected from the core liner immediately on core recovery; this gas had already separated from the sediment. C1/C2 increases with depth between 2 and 30 mbsf at Site 1200 mainly because ethane decreases with depth over this interval.

The observed changes also match the overall stoichiometry of this reaction remarkably well, except for methane (Table 1 and Figure 9), which may have been lost from the cores by degassing prior to sampling. These changes differ greatly from those for oxidation of sedimentary organic matter



in which the increase in carbonate alkalinity is twice the loss of sulfate. The increase in ammonia of only 100  $\mu\text{mol/kg}$  (Figure 4) is far smaller than the increase of several  $\text{mmol/kg}$  that typically results from oxidation of sedimentary organic matter. The phosphate increase of only 1–6  $\mu\text{mol/kg}$  (Figure 7) is similarly too small; also, phosphate correlates with fluoride in Hole 1200E (Figure 7), suggesting that the source of phosphate is dissolution of apatite rather than oxidation of sedimentary organic matter. Thermodynamic calculations using the program PHREEQC [Parkhurst and Appelo, 1999] suggest that the small increase in ammonia may result from reduction of dissolved

nitrogen in the ascending fluid, a process that is likely microbially mediated.

[13] If our interpretation of the pore water profiles is correct then these archaea are oxidizing methane and reducing sulfate, in a process known as anaerobic oxidation of methane (AOM) (see review by Valentine [2002]), by a novel alkaliphilic-lithotrophic pathway. Whereas syntrophic aggregates of archaea and sulfate-reducing bacteria were first identified as facilitators of AOM [Boetius *et al.*, 2000; Orphan *et al.*, 2001], archaea alone may also be capable of it [Chapelle *et al.*, 2002; Orphan *et al.*, 2002]. This appears to be the case in our setting, as there is no evidence for sulfate-reducing bacteria at the key depths. Our setting adds the novelty of high pH and may act to expand the boundary conditions of deep subsurface life [D'hondt *et al.*, 2002]. Studies are ongoing to characterize these microbes.

#### 4. Conclusions

[14] Drilling of serpentinite on the summit of South Chamorro Seamount during ODP Leg 195 has

recovered deep upwelling pore water of unusual composition that is remarkably similar to that recovered from the summit of Conical Seamount on ODP Leg 125, 630 km to the north. Both seamounts are active serpentinite mud volcanoes produced by serpentinization of depleted harzburgitic mantle, and both have formed in the Mariana forearc about the same distance behind the trench axis (85 km for South Chamorro Seamount and 90 km for Conical Seamount). The main differences are that the waters upwelling through Conical Seamount have lower chlorinity and higher sulfate than those at South Chamorro. The ascending waters probably originate at the top of the subducting Pacific Plate, ~27–29 km deep, at temperatures of 150–250°C. Drilling at South Chamorro Seamount also revealed an extremophilic microbial community, dominated by *Archaea* and operating at pH 12.5, that is generating carbonate alkalinity by oxidizing methane from the upwelling fluid and reducing sulfate from both the upwelling fluid and seawater. This microbial community is therefore not only extremophile, but subsists on a source of chemical energy delivered from as deep as 27 km below the seafloor.

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