

22. SHORT-CHAIN ORGANIC ACIDS IN INTERSTITIAL WATERS FROM MARIANA AND BONIN FOREARC SERPENTINES: LEG 125¹

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ABSTRACT

For the first time, short-chain organic acids are described from serpentine-associated interstitial waters. In this geologic setting, formate typically dominates the organic acid assemblage. Within the forearc setting, the organic acids are associated only with unconsolidated serpentine. Their existence may be the result of alkaline hydrolysis of ester linkages in organic matter that has been entrained in the serpentine diapir.

INTRODUCTION

Short-chain aliphatic acid anions are common constituents of pore waters associated with Holocene through Paleozoic strata in many geologic settings: (1) associated with hydrocarbon production (Carothers and Kharaka, 1978; MacGowan and Surdam, 1988; Fisher, 1987), (2) anoxic pore waters of Holocene nearshore marine sediments (Parkes and Taylor, 1983), and (3) hydrothermally altered sediments in the actively rifting Guaymas Basin (Martens, 1990). Although the origin of these compounds is commonly attributed to either bacterial metabolism of sedimentary organic matter (Lamar and Goerlitz, 1963) or thermal alteration of organic matter (Carothers and Kharaka, 1978; Eglinton et al., 1987; Lundegard and Senftle, 1987; Barth et al., 1988), they can be produced by other means. For example, in laboratory experiments, permanganate oxidation of complex natural organics or alkaline hydrolysis of ester linkages (Morrison and Boyd, 1973) produce short-chain aliphatic acids. Regardless of origin, the presence of organic acids in all pore water indicates the existence of more complex organic precursors.

Here, we describe a novel habitat for organic acids—serpentine diapirs in a forearc setting. No complex organic compounds are present in any serpentine mineral; consequently, the organic acids present must be derived from allochthonous organic precursors. Further, because sediments directly overlying serpentine in the Torishima Forearc Seamount in the Bonin Islands contain no organic acids, we propose that the precursors for these short-chain aliphatic acids are more complex organic compounds from sediments entrained in the rising serpentine diapir. This is reflected by the association of the highest aliphatic acid concentrations with metasediment clasts and slightly higher organic carbon content of the cores from the summit region of Conical Seamount in the Mariana forearc. Moreover, the general dominance of the thermally unstable formate anion in serpentine-associated pore waters containing organic acids and the extreme pH conditions of serpentine associated pore waters (pH typically ranging from 9 to 12) strongly suggest an unconventional source for these acids: alkaline hydrolysis of ester linkages in the complex organic precursors.

The presence of organic acids in Leg 125 interstitial waters associated with serpentine materials was suspected on the basis of fluid inclusion analysis of limestones associated with serpentine material and serpentinites from the Mariana forearc. Haggerty (1989) reported the discovery of the aliphatic acid acetate in the trapped

fluids. This discovery of an aliphatic acid in fluid inclusions prompted us to collect interstitial water samples for organic acid analysis on Leg 125.

METHODS

Interstitial water was obtained on board the *JOIDES Resolution* from sediments and unconsolidated serpentine (nonindurated serpentine) by squeezing and by *in-situ* extraction using the Barnes pore-water sampler. As soon as cores arrived on deck, whole-round sections of core were removed by slicing the plastic core tube and capping both ends. No acetone was used to seal the plastic caps to the ends of the whole-round cores. The samples were removed from the plastic core liner and scraped with a stainless-steel spatula to remove the outer, possibly contaminated, layer and then were placed in a stainless-steel squeezer. Both the squeezer and the samples were handled only with plastic gloves to avoid contamination. The squeezer was placed in a Carver hydraulic press and squeezed at pressures up to about 3,300 psi. The interstitial water was retrieved in a plastic syringe and was then filtered through a polysulfone filter for removal of fine particles. See the "Explanatory Notes" chapter of the *Initial Reports* (Shipboard Scientific Party, 1990a) for a more detailed description of the extraction of interstitial waters from these cores and for a description of the Barnes pore-water sampler (Barnes, 1988).

An aliquot of the interstitial water was treated with a few milligrams of 1-hexadecylpyridinium chloride ($C_{21}H_{38}ClN$, CAS No. 6004-24-6, Kodak Product No. 05361) that dissolved in the interstitial water sample and thereafter inhibited degradation of organic molecules by bacterial action. This quaternary ammonium salt was chosen in preference to $HgCl_2$ because of its lower toxicity to mammals. Previous experiments at AMOCO Research Laboratory showed that this quaternary ammonium salt has the same preservative value for organic acids as $HgCl_2$. Best preservation is achieved when using this salt or $HgCl_2$ in glass containers.

Organic acids were determined using ion exclusion chromatography (IEC: Dionex 2000i series chromatograph, S1 separator, fiber suppressor, 800 μ M octanesulfonic acid eluant, tetrabutylammonium hydroxide regenerant, conductivity detection). Prior to injection, sulfate was removed by reacting the sample with excess $BaCl_2$ (12 mg/mL sample) and halides were removed by passing the sample through a silver-formed ion exchange resin (Dionex OnGuard-Ag cartridge). In order to remove contaminants and condition the packing, the pre-treatment cartridge was successively flushed with 5 mL of distilled water followed by 3 mL of analyte.

Sample volume (typically 5 mL) was insufficient to do recovery efficiency experiments for the pre-treatment method. The recovery efficiency was evaluated by applying the pre-treatment methodology to organic acid standard mixtures and comparing the analytical results

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for the treated standards to those of the same standard but without pre-treatment. Example chromatograms are shown in Figure 1. Recovery efficiency varied from 85% to 107% and showed no preference for individual acid anions. The average recoveries were 95%.

The pre-treatment method was necessary to resolve early eluting peaks (see Fig. 1). With an eluant flow rate of 0.8 mL/min, all peaks had eluted in 15 min. Observed peaks were identified by retention time matching to verified pure compounds; some peaks remained unidentified.

RESULTS

Observed concentrations of determined organic acids are given in Table 1. No organic acids are found in any sediment from forearc basin ODP Sites 781, 782, 785, 786, or from sediment overlying serpentine associated with Torishima Forearc Seamount from ODP Sites 783 and 784. In contrast, organic acids are consistently found in pore waters from serpentine.

The determined organic acid assemblage is dominated by formate and acetate. Propionate and malonate are rare and are found only in pore waters from the summit of Conical Seamount (ODP Site 780). Figures 2 and 3 illustrate the abundance of acetate and formate in the summit holes of Conical Seamount compared with that observed in the flank holes of Conical Seamount. Organic acid concentrations (all species) were highest in pore waters from Holes 780C and 780D from the summit of Conical Seamount. Of the 14 summit samples, 5 exceed the maximum observed formate and acetate levels of the flank samples (Figs. 2 and 3).

In the Torishima Forearc Seamount, acetate is noted in two samples from Hole 784A (Sample 125-784A-39R-2, 0–15 cm; Sample 125-784A-42R-1, 135–150 cm) and is associated with formate in Sample 125-784A-39R-2, 0–15 cm. These interstitial water samples were extracted from unconsolidated serpentine located within the main serpentine body.

DISCUSSION

Potential sources of the complex organic precursors for the aliphatic acid anions in the serpentine pore waters include (1) circulation of overlying seawater into the diapiric body, (2) organic material entrained during diapirism, and (3) organic material associated with the downgoing slab, but not entrained by the diapir. Circulation of seawater through the diapir may take place, but probably is not an important source for either organic acids or their more complex precursors. No organic acids are found in any pore waters from the sediment/water interface or from any subsurface sediments (Table 1). Although the exact identities of the acid precursor compounds are unknown, they probably are high-molecular-weight materials of sparing aqueous solubility and, hence, unlikely to be transported by circulating seawater. Further, the extremely nonradiogenic strontium isotopic values (0.70525 to 0.70751 $^{87}\text{Sr}/^{86}\text{Sr}$) of interstitial waters from sub-bottom depths in excess of about 130 m indicate minor, if any, contribution from overlying seawater to the interstitial waters (Haggerty and Chaudhuri, this volume).

Whether the complex organic precursors for the aliphatic acids are resident in material entrained in the diapir or in the downgoing slab cannot be deduced directly from these data. Because the diapir is, in fact, a conduit for fluid migration from depth, the appearance of aliphatic acids in pore waters from the diapiric body does not provide direct evidence of their ultimate source. The highest concentrations of aliphatic acids, however, are found at the summit site of Conical Seamount in association with metasediment clasts and slightly higher organic carbon contents (an average of 0.25%, $n = 19$, range 0.14% to 0.56% at Site 780 vs. an average of 0.22%, $n = 16$, range 0.0% to

0.45% at Site 779; Shipboard Scientific Party, 1990b) argues for the production of aliphatic acids from organics entrained in the diapir. Further, the general dominance of formate, which is unstable thermally, argues for either a mild (time-temperature) thermal exposure of organics in sediments associated with the downgoing slab or a less "conventional" origin linked to the peculiar chemical conditions (extremely high pH) of serpentine pore waters. One possibility is alkaline hydrolysis of ester linkages in complex organics. Ester linkages in marine-type kerogens are the second most abundant functional group and contain the largest percentage of oxygen (Behar and Vandembroucke, 1987). Alkaline hydrolysis of these linkages produce terminal carboxyl groups (organic acids).

We have not discussed the possibility of a bacterial origin for the organic acids. We submit that the data are not inconsistent with well-known abiotic production methods; however, the dominance of formate in organic acid assemblages has not been described for thermally produced organic acids in nature or laboratory settings. Formate-dominated, bacterially produced, organic acid assemblages have been described for recent marine pore waters (Barcelona, 1980). A sympathetic variation between alkalinity and ammonia concentration is observed for Conical Seamount (Shipboard Scientific Party, 1990b) which may suggest a bacterial origin, however, the pH of these waters is extremely high (pH = 12) and therefore unlikely to support a microbial population (Moat and Foster, 1988; Holt, 1984, 1986, 1989a, 1989b). Regardless of biotic or abiotic production mechanism, the presence of organic acids requires the existence of more complex organic precursors within the serpentine body.

If alkaline hydrolysis is the source of the organic acids, the complex precursor of the acids is most likely organic matter that is entrained by the diapir. If thermal maturation of organic matter is the source of the organic acids, the complex precursor of the acids is organic matter in the downgoing slab. A mixed model of local production by alkaline hydrolysis of organic matter within the serpentine body and thermal maturation of organic matter in the downgoing slab is probably the most appropriate model.

As shown in Figures 4 and 5, a sympathetic variation exists between organic acid concentration and dissolved methane and ethane. Methane, ethane, and propane are produced by both microbial (Oremland, 1975, 1981; Oremland et al., 1987; Oremland, Cloern, Sofer, et al., 1988; Oremland, Whiticar, Strohmeyer, et al., 1988) and thermal mechanisms (Tissot and Welte, 1984). Both methane and ethane also have been shown to evolve abiotically during the process of serpentinization (Abrajano et al., 1988; T. Abrajano, pers. comm., 1990). In addition to methane and ethane being present at Conical Seamount, propane has also been detected in pore-water gases from the summit region of Conical Seamount (Shipboard Scientific Party, 1990b). Because propane has not been demonstrated to be produced by serpentinization, one must conclude that propane has another source. One possible conclusion from these data is that if the hydrocarbon gases and aliphatic acids are derived from the same source, they can only be produced thermally from organic matter that was associated with the downgoing plate or microbially in the serpentine body. It is possible, however, that three (or more) mechanisms—thermal, microbial, and chemical (alkaline hydrolysis of ester linkages)—produced the organic acids.

CONCLUSIONS

Organic acids found in serpentine-associated pore waters are derived from more complex organic precursors, either from serpentine diapir entrained organic matter or from organic matter associated with the downgoing slab, but not entrained by the diapir. From the current state of knowledge, we cannot argue against either a microbial or thermal source for the organic acids and pore-fluid hydrocarbon gases, but the strong association of methane and ethane with formate

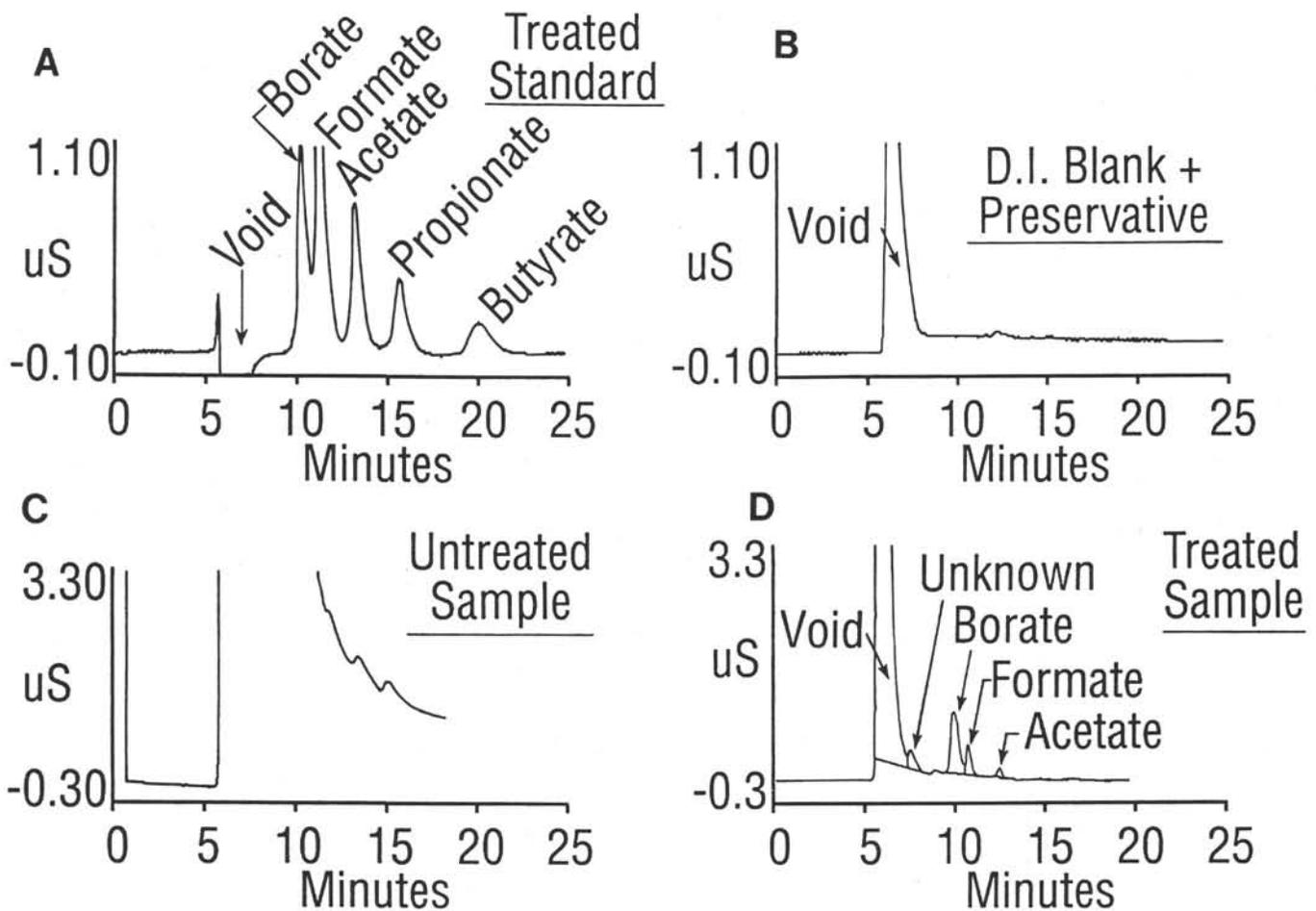


Figure 1. Example chromatograms. Chromatogram of a treated standard (A) shows that the pretreatment does not generate artifacts or affect the concentrations of the standards. Chromatogram of deionized water (D.I. Blank) and preservative (B) shows the lack of contamination with organic acids in the preservative and lack of artifact generation. Chromatogram of an untreated sample of interstitial water (C) shows the presence of organic acids and extensive ionic interferences. Chromatogram of a treated sample of interstitial water (D) shows the effects of the pretreatment on a sample for removal of ionic interferences, and lack of artifact generation.

and acetate suggests that an important source for all of these compounds is the direct result of the chemistry of serpentinization. Nearly all sediment samples lack any detectable organic acids, ethane, or propane; the only exception is at Site 783, where ethane is detected in a trace amount. In contrast, nearly all the serpentine-associated interstitial waters contain organic acids, methane, and ethane. Our expectation for a microbial source is the ubiquitous occurrence of organic acids and dissolved hydrocarbon gases in the forearc setting; the Leg 125 data demonstrate that this is not the case. Existing data show that in the Mariana and Bonin forearc settings, both organic acids and dissolved hydrocarbon gases are unique characteristics of the serpentine-associated pore waters. These materials may have a thermal origin from organic precursors associated with the downgoing slab, but may also be produced chemically in the serpentine diapir.

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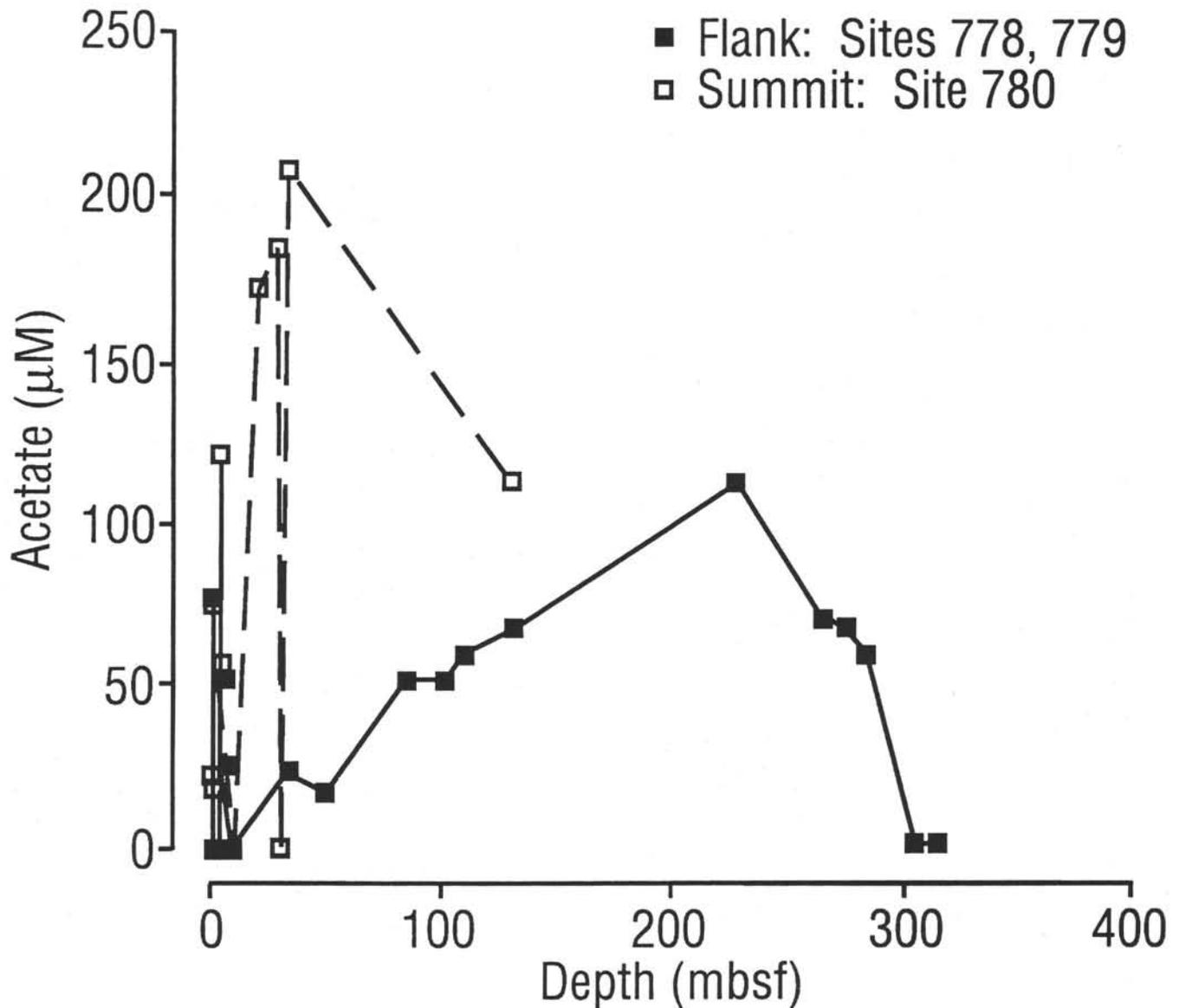


Figure 2. A comparison of acetate values of the summit with those from the flank of Conical Seamount. See Table I for data. Acetate analyses from the flank and summit of Conical Seamount in micromolar concentrations (μM) vs. depth (mbsf).

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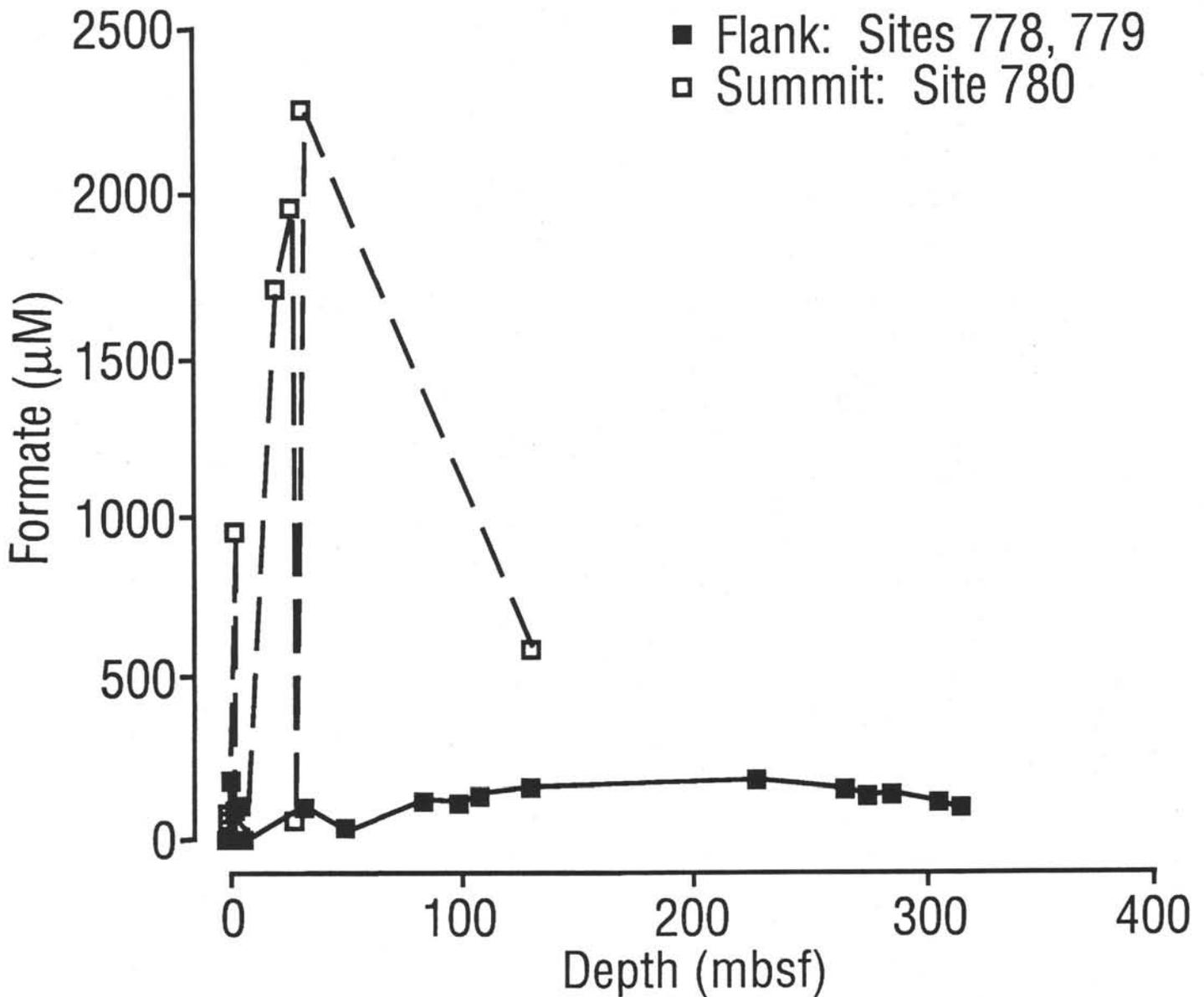


Figure 3. A comparison of formate values from the summit with those from the flank of Conical Seamount. See Table 1 for data. Formate analyses from the flank and summit of Conical Seamount in micromolar concentrations (μM) vs. depth (mbsf).

Oremland, R. S., Whiticar, M. J., Strohmaier, F. E., and Kiene, R. P., 1988. Bacterial ethane formation from reduced, ethylated sulfur compounds in anoxic sediments. *Geochim. Cosmochim. Acta*, 52:1895-1904.

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Table 1. Organic acid analyses from Leg 125 interstitial waters.

Sample identifier	Depth (mbsf)	Malonate (ppm)	Malonate (μM)	Formate (ppm)	Formate (μM)	Acetate (ppm)	Acetate (μM)	Propionate (ppm)	Propionate (μM)
Mariana Forearc Seamount (flank)									
778A-1R-1, 145-150	1.45	0.0	0	8.6	191	4.5	76	0.0	0
778A-1R-1, 145-150	5.95	0.0	0	5.4	120	1.5	25	0.0	0
778A-7R-1, 140-150	50.10	0.0	0	1.3	29	1.0	17	0.0	0
778A-11R-1, 140-150	83.70	0.0	0	5.9	131	3.0	51	0.0	0
778A-13R-1, 140-150	99.70	0.0	0	5.1	113	3.0	51	0.0	0
779A-2R-2, 145-150	4.05	0.0	0	4.5	100	3.0	51	0.0	0
779A-5R-3, 46-56	33.11	0.0	0	4.6	102	1.4	24	0.0	0
779A-13R-1, 140-150	108.50	0.0	0	6.3	140	3.5	59	0.0	0
779A-18R-2, 0-10	130.47	0.0	0	7.2	160	3.9	66	0.0	0
779A-28R-2, 95-105	227.42	0.0	0	8.4	187	6.6	112	0.0	0
779A-32R-2, 0-10	265.90	0.0	0	6.6	147	4.1	69	0.0	0
779A-33R-1, 42-52	274.42	0.0	0	5.9	131	3.9	66	0.0	0
779A-34R-1, 111-121	284.76	0.0	0	6.1	135	3.4	58	0.0	0
779A-36R-2, 135-150	305.85	0.0	0	4.8	107	0.0	0	0.0	0
779A-37R-1, 135-150	314.05	0.0	0	4.0	89	0.0	0	0.0	0
779B-1R-1, 145-150	1.45	0.0	0	0.0	0	0.0	0	0.0	0
779B-1R-3, 145-150	4.45	0.0	0	0.0	0	0.0	0	0.0	0
779B-1R-5, 145-150	7.45	0.0	0	0.0	0	0.0	0	0.0	0
779B-1R-6, 105-110	8.58	0.0	0	0.0	0	0.0	0	0.0	0
Mariana Forearc Seamount (summit)									
780A-1H-1, 45-55	0.45	0.0	0	2.9	64	1.3	22	0.0	0
780A-1H-1, 95-105	0.95	0.0	0	3.5	78	4.4	75	0.0	0
780A-1H-1, 145-150	1.45	0.0	0	3.8	84	1.1	19	0.0	0
780A-1H-2, 129-139	2.79	0.0	0	4.0	89	3.3	56	0.0	0
780B-1R-6, 106-116	8.56	0.0	0	0.0	0	0.0	0	0.0	0
780C-1R-3, 140-150	3.94	0.8	8	0.0	0	0.0	0	0.0	0
780C-5R-1, 48-58	33.48	2.2	22	102	2272	12.3	208	1.9	26
780C-15R-1, 38-48	129.93	0.0	0	26.4	586	6.7	113	0.0	0
780D-1X-2, 96-106	1.41	0.0	0	0.0	0	0.0	0	0.0	0
780D-1X-3, 68-78	2.19	0.0	0	0.6	13	1.1	19	0.0	0
780D-2X-1, 40-50	2.90	0.0	0	42.9	953	7.2	122	0.0	0
780D-6X-1, 68-78	21.08	0.0	0	77.6	1723	10.2	173	2.5	34
780D-7X-5, 135-150	29.43	0.0	0	2.9	64	0.0	0	0.0	0
780D-7P-1, 0-1	27.41	0.0	0	89.0	1976	10.9	185	5.0	68
Mariana Adjacent Horst									
781A-1R-2, 140-150	2.23	0.0	0	0.0	0	0.0	0	0.0	0
781A-4R-1, 62-67	26.52	0.0	0	0.0	0	0.0	0	0.0	0
781A-6R-1, 140-150	46.30	0.0	0	0.0	0	0.0	0	0.0	0
781A-6R-4, 140-150	50.80	0.0	0	0.0	0	0.0	0	0.0	0
781A-7R-2, 140-150	57.40	0.0	0	0.0	0	0.0	0	0.0	0
781A-8R-2, 103-113	67.03	0.0	0	0.0	0	0.0	0	0.0	0
781A-21R-CC, 30-36	188.72	0.0	0	0.0	0	0.0	0	0.0	0
781A-26R-1, 32-42	236.82	0.0	0	0.0	0	0.0	0	0.0	0
Bonin Forearc Basin									
782A-1H-3, 145-150	4.45	0.0	0	0.0	0	0.0	0	0.0	0
782A-2H-4, 145-150	15.75	0.0	0	0.0	0	0.0	0	0.0	0
782A-3H-4, 145-150	25.25	0.0	0	0.0	0	0.0	0	0.0	0
782A-4H-4, 145-150	34.75	0.0	0	0.0	0	0.0	0	0.0	0
782A-5H-4, 145-150	44.25	0.0	0	0.0	0	0.0	0	0.0	0
782A-7H-4, 140-150	63.20	0.0	0	0.0	0	0.0	0	0.0	0
782A-11X-2, 145-150	98.65	0.0	0	0.0	0	0.0	0	0.0	0
782A-13X-2, 145-150	117.90	0.0	0	0.0	0	0.0	0	0.0	0
782A-16X-2, 145-150	146.80	0.0	0	0.0	0	0.0	0	0.0	0
782A-19X-2, 145-150	175.80	0.0	0	0.0	0	0.0	0	0.0	0
782A-23X-4, 145-150	217.40	0.0	0	0.0	0	0.0	0	0.0	0
782A-26X-3, 145-150	244.70	0.0	0	0.0	0	0.0	0	0.0	0
782A-29X-4, 145-150	275.10	0.0	0	0.0	0	0.0	0	0.0	0
782A-32X-5, 145-150	301.40	0.0	0	0.0	0	0.0	0	0.0	0
782A-35X-3, 145-150	326.90	0.0	0	0.0	0	0.0	0	0.0	0
782A-39X-1, 145-150	362.30	0.0	0	0.0	0	0.0	0	0.0	0
782A-42X-1, 145-150	391.20	0.0	0	0.0	0	0.0	0	0.0	0
Torishima Forearc Seamount (Bonin Forearc Seamount)									
783A-1R-1, 145-150	1.45	0.0	0	0.0	0	0.0	0	0.0	0
783A-1R-2, 145-150	2.95	0.0	0	0.0	0	0.0	0	0.0	0
783A-1R-5, 145-150	7.45	0.0	0	0.0	0	0.0	0	0.0	0
783A-4R-3, 140-150	30.40	0.0	0	0.0	0	0.0	0	0.0	0
783A-7R-1, 140-150	53.80	0.0	0	0.0	0	0.0	0	0.0	0

Table 1 (continued).

Sample identifier	Depth (mbsf)	Malonate		Formate		Acetate		Propionate	
		(ppm)	(μ M)	(ppm)	(μ M)	(ppm)	(μ M)	(ppm)	(μ M)
783A-10R-1, 140-150	82.70	0.0	0	0.0	0	0.0	0	0.0	0
784A-3R-2, 140-150	13.80	0.0	0	0.0	0	0.0	0	0.0	0
784A-4R-2, 140-150	23.30	0.0	0	0.0	0	0.0	0	0.0	0
784A-6R-4, 140-150	45.40	0.0	0	0.0	0	0.0	0	0.0	0
784A-8R-4, 140-150	64.70	0.0	0	0.0	0	0.0	0	0.0	0
784A-14R-1, 140-150	118.10	0.0	0	0.0	0	0.0	0	0.0	0
784A-16R-5, 140-150	143.40	0.0	0	0.0	0	0.0	0	0.0	0
784A-19R-1, 0-10	165.00	0.0	0	0.0	0	0.0	0	0.0	0
784A-22R-3, 140-150	198.40	0.0	0	0.0	0	0.0	0	0.0	0
784A-26R-1, 140-150	233.90	0.0	0	0.0	0	0.0	0	0.0	0
784A-29R-4, 140-150	267.30	0.0	0	0.0	0	0.0	0	0.0	0
784A-32R-5, 140-150	297.80	0.0	0	0.0	0	0.0	0	0.0	0
784A-34R-3, 0-15	312.70	0.0	0	0.0	0	0.0	0	0.0	0
784A-35R-1, 135-150	320.65	0.0	0	0.0	0	0.0	0	0.0	0
784A-39R-2, 0-15	359.40	0.0	0	2.7	60	1.2	20	0.0	0
784A-40R-1, 135-150	368.85	0.0	0	0.0	0	0.0	0	0.0	0
784A-41R-1, 92-107	378.22	0.0	0	0.0	0	0.0	0	0.0	0
784A-42R-1, 135-150	388.25	0.0	0	0.0	0	2.8	47	0.0	0
784A-43R-2, 135-150	399.45	0.0	0	0.0	0	0.0	0	0.0	0
Bonin Outer Arc High									
785A-1H-1, 145-150	1.45	0.0	0	0.0	0	0.0	0	0.0	0
786A-1H-4, 145-150	5.95	0.0	0	0.0	0	0.0	0	0.0	0
786A-3H-4, 145-150	25.15	0.0	0	0.0	0	0.0	0	0.0	0
786A-6H-3, 140-150	52.00	0.0	0	0.0	0	0.0	0	0.0	0
786A-9H-3, 140-150	81.20	0.0	0	0.0	0	0.0	0	0.0	0

Mariana Forearc Conical Seamount, Flank: Sites 778 & 779

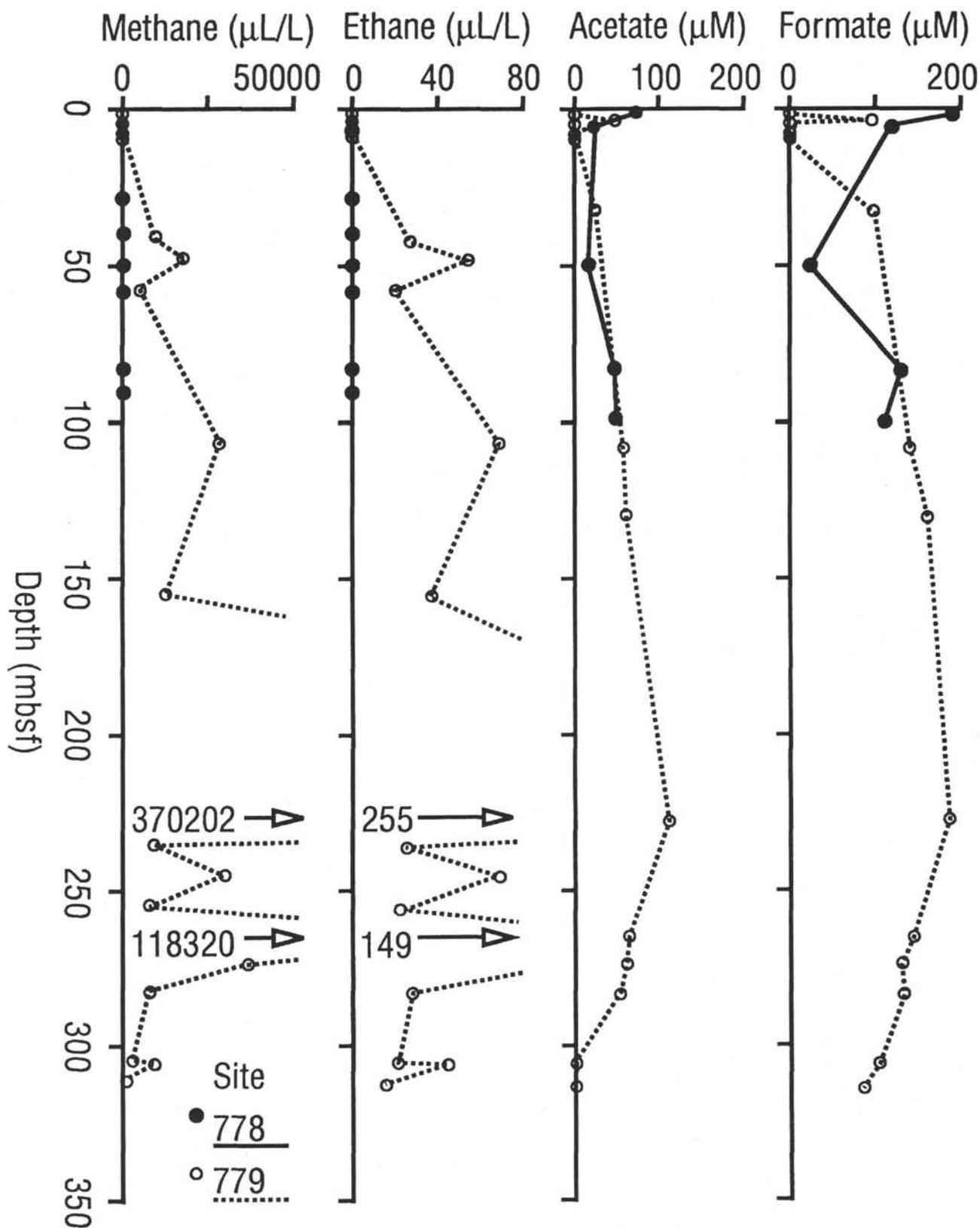


Figure 4. Methane and ethane values (in $\mu\text{L/L}$) vs. depth (mbsf) for flank Sites 778 and 779 on Conical Seamount. See *Initial Reports* for data (Shipboard Scientific Party, 1990b). Acetate and formate values (in μM) vs. depth (mbsf) for flank Sites 778 and 779 on Conical Seamount.

Mariana Forearc Conical Seamount, Summit: Site 780

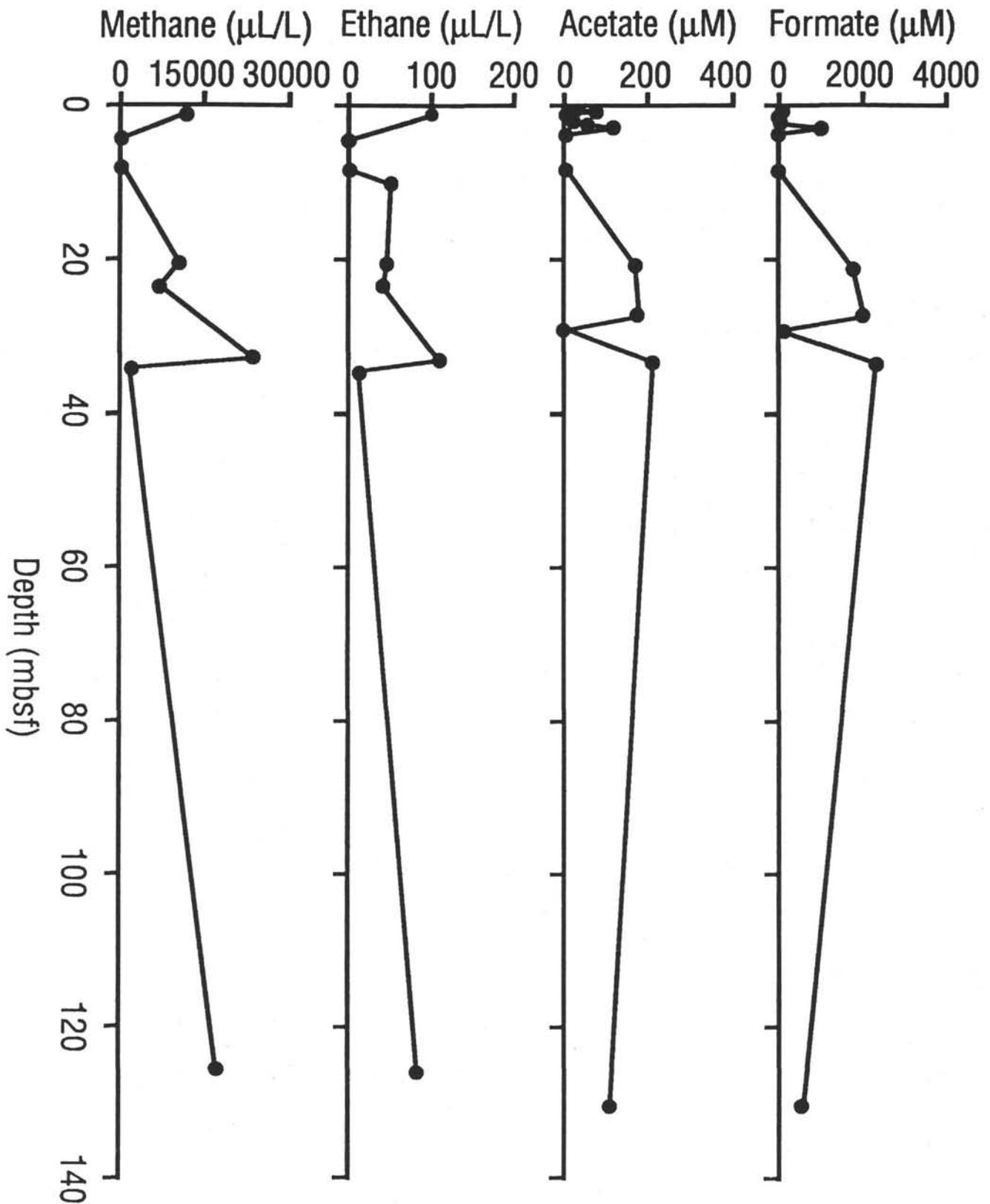


Figure 5. Methane and ethane values (in $\mu\text{L/L}$) vs. depth (mbsf) for summit Site 780 on Conical Seamount. See *Initial Reports* for data (Shipboard Scientific Party, 1990b). Acetate and formate values (in μM) vs. depth (mbsf) for summit Site 780 on Conical Seamount.