

42. DATA REPORT: MINOR AND TRACE ELEMENT AND SULFUR ISOTOPIC COMPOSITION OF PORE WATERS FROM SITES 778 THROUGH 786¹

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INTRODUCTION

Pore waters were collected from nine sites during Leg 125 of the Ocean Drilling Program (ODP). The first four sites (778–781) were drilled in the Mariana forearc on and near Conical Seamount, an active serpentine “mud volcano” located about 80 km behind the trench axis and 120 km in front of the active island arc. The last five sites (782–786) were drilled in the Izu-Bonin forearc between the trench and the outer arc high. Pore waters from the five sites from both areas that penetrated serpentine silts (Sites 778, 779, 780, 783, and 784) are discussed in detail by Mottl (this volume). Here we report analyses of the pore waters from all nine sites for Li, Rb, Sr, Ba, Mn, B, and the sulfur isotopic ratio of dissolved sulfate. Sampling methods and results of analyses for major and minor species determined aboard ship were presented by Fryer, Pearce, Stokking, et al. (1990).

ANALYTICAL METHODS

Li and Rb were determined by flame-emission spectrometry at the University of Hawaii using the method of additions, which produced a tenfold final dilution of the sample. Li was measured at 671.0 nm and Rb at 779.4 nm, using a 0.2-nm slit. For both elements, the average background intensity measured separately 0.4 nm above and below the peak was subtracted from the peak intensity to account for spectral interferences. Sr, Ba, Mn, and B were determined by inductively coupled plasma atomic emission spectrometry (ICPAES) on samples that had been diluted fivefold.

The sulfur isotopic composition of dissolved sulfate was determined for selected samples at the University of Michigan. The samples were filtered through 0.45- μ m polysulfone filters on recovery. The samples were stored in 5-mL polystyrene test tubes with polyethylene caps for shipboard analyses. At the end of Leg 125, the remaining sample solution, generally 1 to 2 mL, was transferred into polyethylene tubing and heat-sealed. In addition to these samples, two samples were treated with CdCl₂ immediately following filtration and stored in capped plastic test tubes. This treatment produced a pale yellow to white precipitate.

The two samples treated with CdCl₂ and Sample 125-780D-7X-5, 135–150 cm, were opened and poured into beakers containing distilled water under a nitrogen atmosphere. The samples were acidified with HCl to dissolve any CdS and release any H₂S. Then the beakers were sealed and purged with nitrogen, which was run through an AgNO₃ solution to trap any H₂S. No sulfide was detected by this method in any of these samples. The high alkalinity of these fluids (Mottl, this volume) suggests that the white precipitate was CdCO₃. If any CdS was initially present, causing the slight yellowish color, it apparently oxidized during storage.

Because no sulfide was detected in any of the samples specifically treated to preserve sulfide, the remaining untreated samples were not sampled for sulfide. These samples, plus the solutions remaining from the sulfide extractions, were placed in beakers, heated to near boiling, and treated with BaCl₂ to precipitate sulfate as BaSO₄. The BaSO₄ was combusted with sodium metaphosphate under vacuum at 1000°C to produce SO₂ gas (Halas et al., 1982). Sulfur isotopic ratios were measured using a VG 602 mass spectrometer at the University of Michigan and are reported in standard delta notation relative to Canyon Diablo troilite (CDT). Instrumental error for individual analyses is $\pm 0.1\text{‰}$, but replicate analyses of standards indicate errors of $\pm 0.4\text{‰}$, probably because of the variable equilibration of oxygen isotopes between SO₂ and phosphate. One sample from Hole 784A consists of the combined BaSO₄ from two adjacent pore-water samples (Table 1) because there was insufficient sulfate to analyze in the individual samples.

RESULTS AND DISCUSSION

Concentrations of Li, Rb, Sr, Ba, B, and Mn in pore waters from Sites 781, 782, 785, and 786 are plotted vs. depth in Figures 1 through 3. Site 781 was drilled just off Conical Seamount in the Mariana forearc, whereas the other three sites were drilled in the Izu-Bonin forearc. Drilling at all four sites penetrated mainly volcanogenic sediments. The pore waters reflect mainly reaction with these sediments. They exhibit changes with depth that are typical of many deep-sea sites having moderate rates of sedimentation and organic carbon deposition. Depth profiles show the effects of three main processes: (1) bacterial oxidation of organic matter using various oxidants, including seawater sulfate; (2) precipitation of CaCO₃; and (3) alteration of volcanic material in the sediments and basement. The oxidation of organic matter produces bicarbonate alkalinity and ammonia, while consuming oxidants in the order oxygen, nitrate, nitrite, MnO₂, FeO(OH), and sulfate. The enhanced alkalinity causes CaCO₃ to precipitate. The alteration of volcanic material by seawater at low temperatures removes Mg, K, and OH⁻ from solution in exchange for Ca and Si from the volcanic sediments and basement rocks. The acidity generated by these reactions consumes bicarbonate alkalinity, as does the precipitation of CaCO₃, which is favored in turn by the enhanced concentration of dissolved Ca. The depth profiles for the various dissolved species are determined primarily by the relative rates of these competing reactions. Accordingly, the solutions at these four sites show maxima in alkalinity and ammonia; decreases in sulfate, Mg, K, Li, Rb, and B; increases in Ca, Sr, Ba, and Mn; and little or no change in Na and Cl with depth (Figs. 1–3; Fryer, Pearce, Stokking, et al., 1990).

The sulfur isotopic composition of dissolved sulfate at Sites 778 through 780 in the Mariana forearc and Sites 783 and 784 in the Izu-Bonin forearc is plotted vs. depth in Figure 4. These are the five sites discussed by Mottl (this volume) that penetrated serpentine silts. The $\delta^{34}\text{S}$ values range from +13.4‰ to +31.2‰ (Table 1). Little variation is seen from Sites 778 and 783, but these samples are from the upper part of the section, where sulfate is little changed from its concentration in seawater. The wide variations seen at the other three sites are consistent with different processes affecting sulfur.

¹ Fryer, P., Pearce, J. A., Stokking, L. B., et al., 1992. *Proc. ODP, Sci. Results*, 125: College Station, TX (Ocean Drilling Program).

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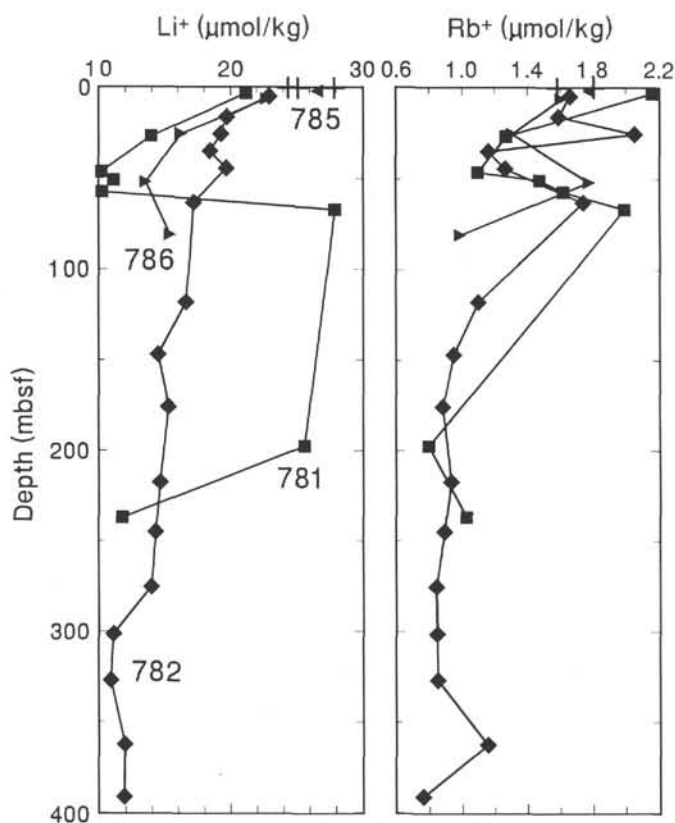


Figure 1. Composition of pore waters from cores at Sites 781 (squares), 782 (diamonds), 785 (left-pointing triangles), and 786 (right-pointing triangles) compared with that of seawater (+'s on the x axis).

At Site 784, the increase in $\delta^{34}\text{SO}_4$ above the seawater value of $+20.5\text{‰}$ (Rees et al., 1978) with depth is accompanied by a decrease in dissolved sulfate below the concentration in seawater. This correlation is characteristic of relatively closed-system bacterial reduction of seawater sulfate in marine sediments (Ivanov and Freney, 1983).

By contrast, at Site 780, a decrease in $\delta^{34}\text{SO}_4$ with depth is accompanied by an increase in sulfate concentration to well above that in seawater. This trend is opposite from that expected for bacterial sulfate reduction in sediment pore waters (Fig. 5), suggesting that seawater has mixed with a solution rich in sulfate that has a low value of $\delta^{34}\text{SO}_4$. Mottl (this volume) showed that the solutions at Site 780 are upwelling through the summit of Conical Seamount. He argued that they contain a component of a deep fluid rich in H_2O , reduced and oxidized carbon and sulfur, Na, K, Rb, and B, and that this deep fluid probably derives from the top of the subducting slab, which lies 30 km below the seafloor at Site 780. The sulfur isotopic data are consistent with this interpretation. The large decrease in $\delta^{34}\text{SO}_4$ with depth within only a few meters of the seafloor parallels a similar large decrease in chlorinity and an increase in dissolved sulfate within the surficial serpentine silts. The addition to seawater of sulfate having the $\delta^{34}\text{S}$ value of sulfur in fresh mid-ocean ridge basalt glasses ($+0.1\text{‰} \pm 0.5\text{‰}$; Sakai et al., 1984) is consistent with the data (Fig. 5). That the $\delta^{34}\text{SO}_4$ values decrease slightly above the mixing line can be attributed to isotopic fractionation produced by small amounts of bacterial sulfate reduction. Whether the deep fluids leached or transported sulfur as sulfate or as sulfide, which was subsequently oxidized, is not constrained by the isotopic data.

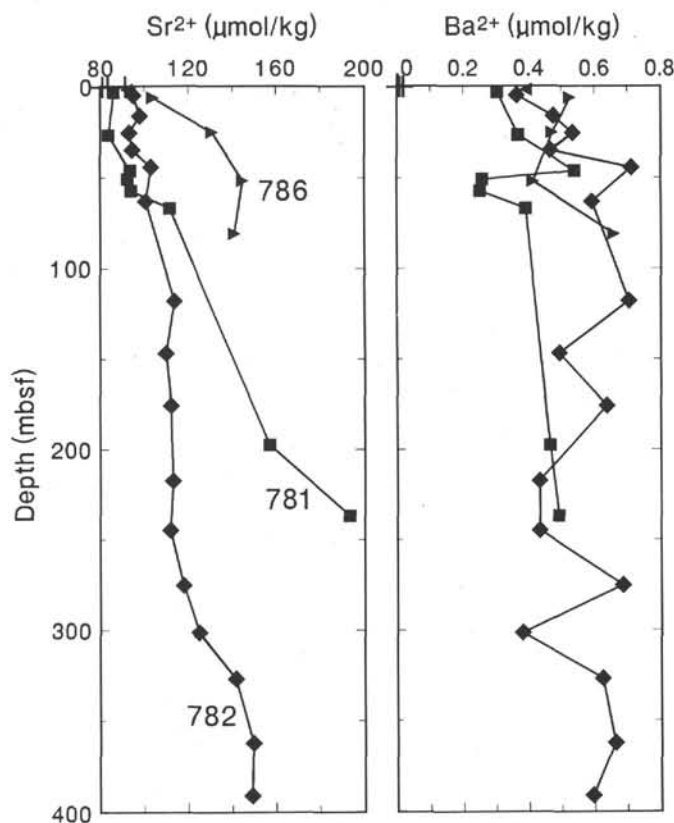


Figure 2. Composition of pore waters from cores at Sites 781, 782, 785, and 786. Symbols are the same as in Figure 1.

ACKNOWLEDGMENTS

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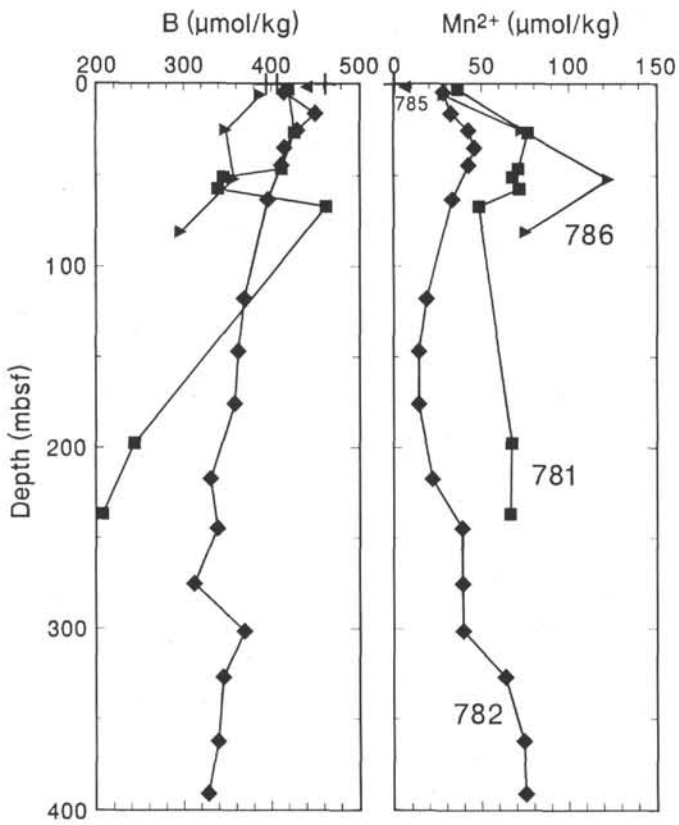


Figure 3. Composition of pore waters from cores at Sites 781, 782, 785, and 786. Symbols are the same as in Figure 1.

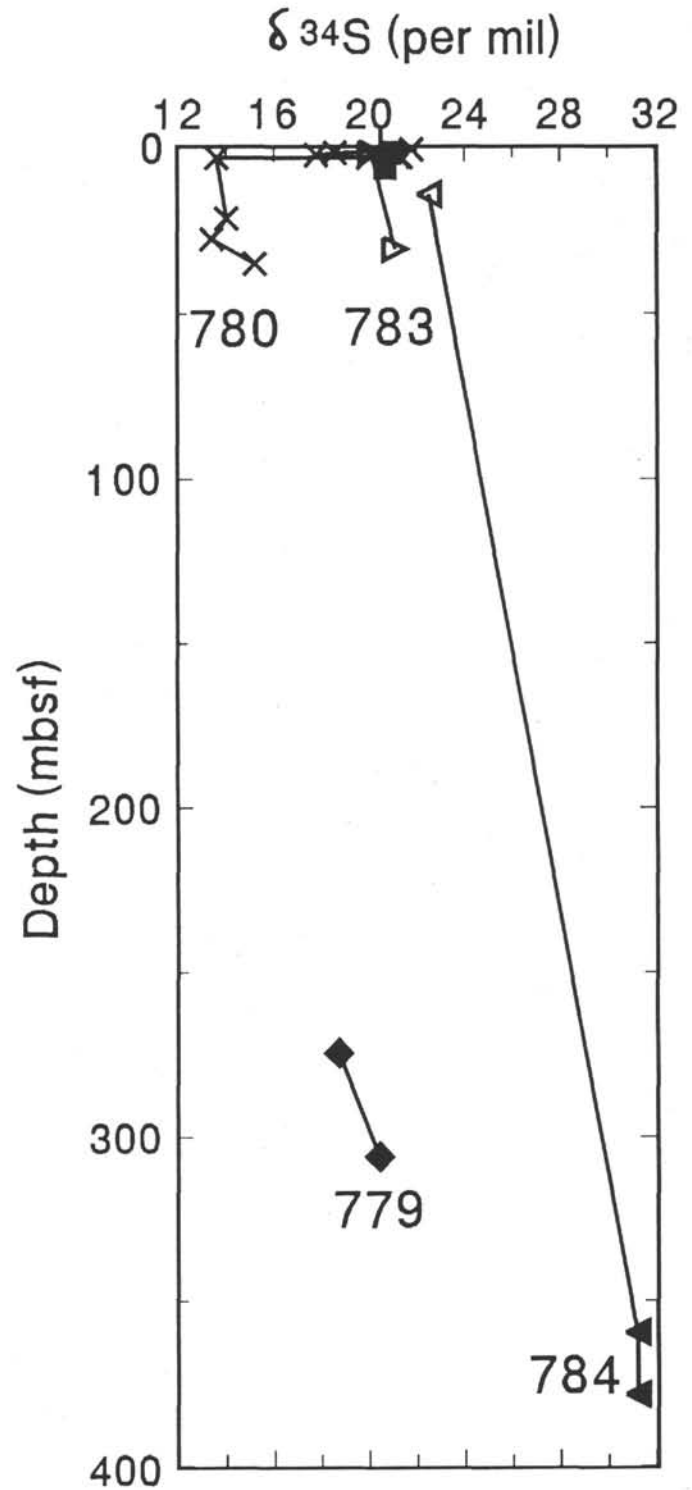


Figure 4. Composition of pore waters from cores at Sites 778 (squares), 779 (diamonds), 780 (x's), 783 (right-pointing triangles), and 784 (left-pointing triangles), compared with that of seawater (+ on the x axis). Solid triangles indicate samples from serpentine silts.

Table 1. Composition of interstitial waters from Sites 778 through 786.

Sample number ^a	Core, section, interval (cm)	Depth (mbsf)	Li (μmol/kg)	Rb (μmol/kg)	Sr (μmol/kg)	Ba (μmol/kg)	Mn (μmol/kg)	B (μmol/kg)	Sulfate δ ³⁴ S (o/oo)	Sulfate (mmol/kg)	Chlorinity (mmol/kg)
Surface seawater											
22 February 1989			25.1	1.6	83.4	0.018	0	407		28.60	539.0
4 March 1989			27.9	1.8	91.3	0.000	0	462		27.98	542.6
17 March 1989			24.4	1.2	80.8	0.007	0	394		27.78	539.2
125-778A-											
IW-1	1R-1, 145-150	1.48	20.3	1.3	121.3	0.405	8.6	292	20.9	24.46	542.6
IW-2	1R-4, 145-150	5.98	28.1	1.0	76.2	0.145	0.5	485	20.7	27.17	547.5
IW-3	7R-1, 140-150	50.15								12.15	532.0
IW-4	11R-1, 140-150	83.75	11.2	1.1	503.6	0.994	1.0	299		16.83	510.7
IW-5	12R-1, 140-150	91.25	3.4	1.1	536.6	0.994	2.5	323		16.43	502.0
IW-6	13R-1, 140-150	99.75	5.5	0.4	432.0	1.292	3.2	370		16.77	508.8
125-779A-											
IW-1	2R-2, 145-150	4.08	29.2	1.6	84.3	0.544	1.9	389		27.77	543.9
IW-2	5R-3, 46-56	33.11								22.46	529.4
IW-3	13R-1, 140-150	108.05	39.5	2.2	60.5	0.365	0.6	398		19.19	523.1
IW-4	18R-2, 7-17	156.52	134.2	2.3	16.3	0.527	0.0	733		25.56	525.5
IW-5	28R-2, 95-105	227.47								25.52	507.7
IW-6	30R-1, 140-150	246.45	105.8	3.2	83.9	0.975	0.0	944		24.90	495.1
IW-7	32R-2, 0-10	265.95	56.5	2.1	107.6	0.649	0.0	511		23.37	498.0
IW-8	33R-1, 42-52	274.47	57.6	2.7	105.3	0.369	0.0	694	18.7	23.79	491.3
IW-9	34R-1, 111-121	284.86	40.1	2.7	85.9	0.235	0.0	680		17.47	480.6
IW-10	36R-2, 135-150	305.93	12.2	0.8	120.6	1.176	0.1	326	20.4	24.06	515.5
IW-11	37R-1, 135-150	314.13	11.7	0.7	170.7	1.582	0.0	261		21.33	522.3
125-779B-											
IW-1	1R-1, 145-150	1.48	30.7	1.2	77.2	0.434	0.6	527		27.45	537.9
IW-2	1R-3, 110-115	4.08	29.5	1.2	78.8	0.353	0.7	517		27.14	536.0
IW-3	1R-5, 145-150	7.48	32.0	1.3	81.2	0.264	0.6	502		29.25	538.8
IW-4	1R-6, 105-110	8.58	30.1	1.2	81.9	0.360	1.5	411		27.65	539.8
125-780A-											
IW-1	1H-1, 45-55	0.50	2.5	6.3	32.4	0.329	0.0	2501	21.8	32.41	399.0
IW-2	1H-1, 95-105	1.00	2.5	6.9	17.9	0.252	0.0	2870		36.20	393.2
IW-3	1H-1, 145-150	1.48	1.5	7.4	15.4	0.235	0.0	3522	18.6	39.80	338.3
IW-4	1H-2, 57-67	2.12	0.9	6.7	13.2	0.999	0.2	3550	17.8	38.59	339.3
IW-5	1H-2, 129-139	2.84	1.0	6.8	11.8	0.306	0.0	3489	20.0	38.05	351.8
125-780B-											
IW-1	1R-6, 106-116	8.61	30.5	1.9	70.6	0.246	1.1	573		26.93	517.6
125-780C-											
IW-1	1R-3, 140-150	4.45	32.6	1.3	60.4	0.277	0.6	551		28.58	534.0
IW-2	5R-1, 48-58	33.53	1.2	7.7	10.2	0.209	0.0	3698		43.52	270.8
IW-3	15R-1, 38-48	129.93	1.6	7.8	32.3	0.061	0.0	3929		45.03	315.2
125-780D-											
IW-1	1X-2, 96-106	2.51	22.5	2.2	50.8	0.190	1.1	833	21.2	27.31	484.6
IW-2	1X-3, 68-78	2.73	6.3	5.0	26.5	0.170	0.0	584	21.7	33.11	364.7
IW-2	1X-3, 68-78	2.73							21.0		
IW-3	2X-1, 40-50	2.95	1.1	6.5	27.7	0.150	0.0	3034	13.6	44.33	284.4
IW-4	6X-1, 68-78	21.13	2.1	6.8	27.8	0.242	0.0	3308	14.0	44.27	285.3
BW-5	7X-1, 0-1	27.41	1.8	6.0	12.5	0.149	0.0	2185	13.4	46.84	234.1
IW-6	7X-5, 135-150	34.83	3.5	6.9	74.0	0.222	0.0	1803	15.2	36.37	369.5
125-781A-											
IW-1	1R-2, 140-150	2.95	21.2	2.2	86.0	0.304	36.4	420		26.60	548.9
IW-2	4R-1, 62-67	26.55	13.9	1.3	83.4	0.368	76.6	427		27.97	551.3
IW-3	6R-1, 140-150	46.35	10.2	1.1	93.5	0.541	71.1	412		28.34	555.2
IW-4	6R-4, 140-150	50.85	11.1	1.5	92.2	0.259	67.7	346		26.73	556.2
IW-5	7R-2, 140-150	57.45	10.2	1.6	93.9	0.252	71.7	339		28.04	559.1
IW-6	8R-2, 103-113	67.08	27.9	2.0	111.5	0.391	48.5	463		28.77	551.3
IW-7	21R-CC, 30-36	197.57	25.6	0.8	157.1	0.465	67.4	244		29.92	556.2
IW-8	26R-1, 32-42	236.87	11.7	1.0	193.5	0.491	66.4	207		25.77	560.2

Table 1 (continued).

Sample number ^a	Core, section, interval (cm)	Depth (mbsf)	Li ($\mu\text{mol/kg}$)	Rb ($\mu\text{mol/kg}$)	Sr ($\mu\text{mol/kg}$)	Ba ($\mu\text{mol/kg}$)	Mn ($\mu\text{mol/kg}$)	B ($\mu\text{mol/kg}$)	Sulfate $\delta^{34}\text{SO}_4$ (o/oo)	Sulfate (mmol/kg)	Chlorinity (mmol/kg)
125-782A-											
IW-1	1H-3, 145-150	4.48	22.9	1.7	95.0	0.364	28.2	415		26.44	545.5
IW-2	2H-4, 145-150	15.78	19.7	1.6	97.8	0.476	32.5	450		26.60	548.4
IW-3	3H-4, 145-150	25.28	19.2	2.1	93.0	0.535	42.7	430		26.93	549.4
IW-4	4H-4, 145-150	34.78	18.4	1.2	94.4	0.466	46.0	415		26.85	546.5
IW-5	5H-4, 145-150	44.28	19.7	1.3	103.1	0.713	42.7	412		26.40	546.5
IW-6	7H-4, 140-150	63.25	17.2	1.7	100.5	0.593	33.2	396		25.86	550.4
IW-7	11X-2, 145-150	98.68								24.92	546.5
IW-8	13X-2, 140-150	117.95	16.6	1.1	113.7	0.706	18.4	369		25.76	546.5
IW-9	16X-2, 140-150	146.85	14.5	0.9	109.8	0.493	14.1	362		25.21	545.5
IW-10	19X-2, 140-150	175.85	15.3	0.9	112.2	0.639	14.0	358		25.23	544.6
IW-11	23X-4, 140-150	217.45	14.6	0.9	112.9	0.432	22.0	331		24.71	546.5
IW-12	26X-3, 140-150	244.75	14.3	0.9	111.8	0.433	38.9	339		25.08	545.5
IW-13	29X-4, 140-150	275.15	13.9	0.8	117.8	0.686	39.2	312		24.82	547.7
IW-14	32X-5, 140-150	301.45	11.1	0.8	124.9	0.380	39.5	369		26.25	548.7
IW-15	35X-3, 140-150	326.95	10.9	0.9	141.5	0.624	63.7	345		25.28	546.8
IW-16	39X-1, 140-150	362.35	11.9	1.2	149.5	0.662	74.1	339		24.90	543.9
IW-17	42X-1, 140-150	391.25	11.9	0.8	149.0	0.595	75.1	328		24.75	542.9
125-783A-											
IW-1	1R-1, 145-150	1.48	24.4	1.6	86.5	0.815	24.7	417	20.1	27.31	543.6
IW-2	1R-2, 145-150	2.98	22.5	1.7	84.5	0.853	39.5	407		27.41	544.5
IW-3	1R-5, 145-150	7.48	20.0	1.5	88.1	0.558	50.6	356		28.20	547.5
IW-4	4R-3, 140-150	30.45	17.4	1.2	88.2	0.572	59.6	370	21.1	27.77	553.3
IW-5	7R-1, 140-150	53.85	16.1	1.4	87.1	0.807	61.5	355		27.11	552.3
IW-6	10R-1, 140-150	82.75	14.0	0.9	86.7	0.851	60.7	347		27.61	557.2
IW-7	15R-1, 140-150	131.05	11.4	0.7	179.6	2.154	2.9	122		11.54	554.3
IW-8	16R-1, 135-150	140.63	11.0	1.2	228.9	1.460	0.6	79		7.85	549.4
IW-9	17R-1, 140-150	150.35	15.1	1.2	282.3	2.673	0.2	105		6.06	555.2
125-784A-											
IW-1	3R-2, 140-150	13.85	15.0	1.5	93.0	0.503	102.5	388	22.5	26.14	546.5
IW-2	4R-2, 140-150	23.35	13.3	1.1	86.5	0.494	133.9	402		25.42	548.4
IW-3	6R-4, 140-150	45.45	13.9	1.2	92.0	0.594	67.1	336		25.07	552.3
IW-4	8R-4, 140-150	64.75	16.7	1.1	89.6	0.564	61.8	297		22.05	549.4
IW-5	10R-1, 140-150	79.55	16.5	1.1	103.5	0.654	53.0	313		23.34	550.4
IW-6	14R-1, 140-150	118.15	19.0	0.9	112.2	0.600	46.9	257		21.08	550.4
IW-7	16R-5, 140-150	143.45	16.7	1.0	112.3	0.514	60.7	266		21.82	549.4
IW-8	19R-3, 0-10	168.05	18.3	0.7	118.5	0.774	62.4	234		20.58	543.6
IW-9	22R-3, 140-150	198.45	20.4	0.9	127.1	0.794	72.0	232		19.61	550.4
IW-10	26R-1, 140-150	233.95	21.4	0.8	130.4	0.999	73.3	210		19.23	550.4
IW-11	29R-4, 140-150	267.35	21.1	0.8	137.7	1.208	96.1	227		17.84	549.4
IW-12	32R-5, 140-150	297.85	27.4	0.8	145.5	1.008	110.6	231		16.38	550.4
IW-13	34R-3, 0-15	312.78	27.6	0.2	151.1	2.202	109.9	442		14.36	540.7
IW-14	35R-1, 135-150	320.73	43.5	0.6	140.1	1.556	60.0	392		14.76	548.4
IW-15	39R-2, 0-15	359.48	18.8	0.9	168.5	1.373	2.2	230	^b 31.2	11.48	546.5
IW-16	40R-1, 135-150	368.93	18.1	0.7	195.5	1.044	1.2	176		9.78	553.3
IW-17	41R-1, 92-107	378.30	23.4	0.8	196.9	1.532	1.1	225	^b 31.2	10.44	550.4
IW-18	42R-1, 135-150	388.33	14.8	1.1	197.8	1.658	1.3	192		7.00	549.4
IW-19	43R-2, 135-150	399.53	20.4	1.0	201.7	1.003	0.6	175		9.33	552.3
125-785A-											
IW-1	1H-1, 145-150	1.48	26.5	1.8	92.1	0.393	6.0	440		25.81	539.7
125-786A-											
IW-1	1H-4, 145-150	5.98	22.7	1.6	103.9	0.526	28.5	388		27.02	541.9
IW-2	3H-4, 145-150	25.18	16.2	1.3	130.7	0.471	73.3	349		23.81	550.7
IW-3	6X-3, 140-150	52.05	13.6	1.8	144.8	0.415	122.7	357		24.34	551.7
IW-4	9X-3, 140-150	81.25	15.4	1.0	141.0	0.660	75.4	297		24.03	552.6

^a IW = squeezed; BW = collected *in situ* using Barnes sampler.^b These two samples were combined for sulfur isotopic analysis because of their small size.

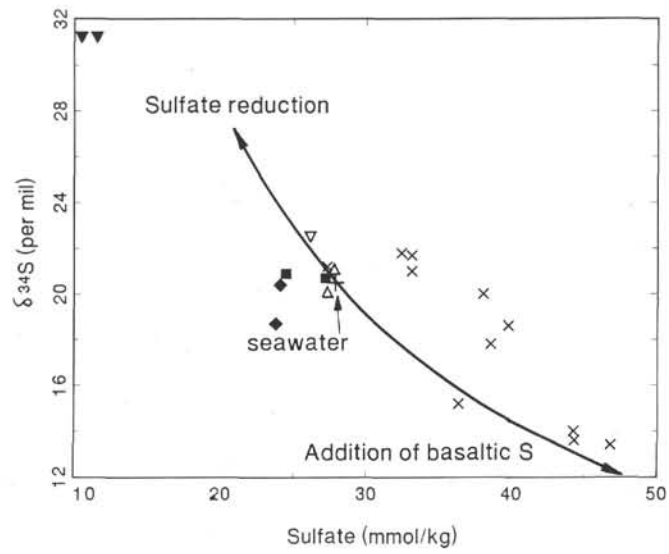


Figure 5. Sulfate-sulfur isotopic composition (in per mil CDT) vs. sulfate concentration of pore waters from Sites 778 (squares), 779 (diamonds), 780 (x's), 783 (upright triangles), and 784 (inverted triangles). Solid triangles indicate samples from serpentine silts. The line indicates the addition of basaltic sulfur and the general trend for sulfate reduction.