15. INTERSTITIAL WATER STUDIES, LEG 15 – δO^{18} IN SULFATE ION[1]

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INTRODUCTION

Thirty-nine samples of interstitial water squeezed from cores at Sites 147, 148, and 149 of DSDP Leg 15 were analyzed for oxygen isotope analysis of the dissolved sulfate. Methods of sampling the interstitial water are discussed elsewhere in this volume.

The water samples were received in heat-sealed sections of polyethylene tubing. The water sample was extracted with a hypodermic syringe, weighed, and mixed with a 0.5 molar $BaCl_2$ solution which contained 5 percent HCl. The $BaSO_4$ was filtered and washed on 0.5-micron filter membranes. The precipitate was dried and weighed and the concentration of sulfate in the original sample calculated. Fifteen of my sample intervals were also analyzed by Presley, et al. (this volume) and agreement averaged about 8 percent of the amount present with my values generally lower. Two of my samples matched those of Cescon and Macchi (this volume) and agreement was within 3 percent.

The $BaSO_4$ precipitate was mixed with graphite and combusted to CO_2 in the manner described by Lloyd (1968). The yields averaged 98±2 percent. The CO_2 was analyzed on a dual collecting mass spectrometer and the oxygen isotope composition expressed as δO^{18} relative to the SMOW standard. Only two samples contained sufficient sulfate for duplicate analysis, and these agreed within $\pm 0.2^{\circ}/_{oo}$. Previous experience indicates that this is also the routine isotopic reproducibility of the technique.

ANALYTICAL DATA

The data for sulfate concentration and δO^{18} are given in Table 1 and plotted in Figure 1.

The differences in sulfate chemistry among the three holes are quite striking. Samples from Site 149 are characterized by monotonous uniformity. Throughout the 400 meters of core, there is a barely perceptible decrease in sulfate ion concentration. The δO^{18} values of eight of the eleven samples average $9.8 \pm 0.2^{\circ}/_{oo}$ which is only a few tenths more positive than values reported for present-day oceanic sulfate (Longinelli and Craig, 1967; Lloyd, 1967). The remaining three values from the interval of 30 to 100 meters are slightly enriched in O^{18} averaging $11.7 \pm 0.2^{\circ}/_{oo}$.

Samples from Site 148 show a systematic decrease in sulfate concentration from normal seawater values near the surface (2600 ppm) to 200 to 300 ppm at 250 meters. The δO^{18} values exhibit a curious "dog leg" trend–a gradual increase in δO^{18} from the surface to 50 meters followed by O^{18} depletion back to near surface values at 250 meters.

All of the samples from Site 147, the Cariaco Trench, contain less than 500 ppm sulfate. Only one sample (147B-1-3), from a depth of five meters, contained enough sulfate (470 ppm) for isotopic analysis. The δO^{18} of this sample was $24.4^{\circ}/_{oo}$, which is an enrichment of about $15^{\circ}/_{oo}$ over values for oceanic sulfate.

DISCUSSION

The O^{18} value in oceanic sulfate is constant around a value of $9.6^{\circ}/_{oo}$; however, opinions differ as to the reason for this constancy. Longinelli and Craig (1967) suggest the value represents equilibrium exchange of oxygen between sulfate and seawater, but Lloyd (1968) postulates that the value represents a steady state system for oxidation-reductions in the sulfur cycle. If the latter viewpoint is correct then the fractionation resulting from a reduction cycle can be expressed by a form of the Rayleigh distillation equation:

$$\delta - \delta_o = 1000\,(a - 1)\,ln\,F, \qquad (1)$$

where:

$\delta_o = \delta O^{18}$ of the original sulfate,

$\delta = \delta O^{18}$ of the sulfate after bacterial reduction,

F = fraction of the sulfate remaining, and

a = kinetic fractionation factor.

At Site 149, the sulfate ion was essentially undisturbed from the time it was incorporated in the sediment with the pore water until the present. This is unusual because one would expect sulfate-reducing bacteria to be ubiquitous in oceanic sediments. Perhaps there was not a sufficient organic nutrient base to support an active bacterial population. The sediment may have been deposited in a strongly oxidizing environment (suggested by the orange and yellow tones of the sediment) which discouraged sulfate reducers.

Site 147 represents the other extreme. Here the interstitial water has been stripped of almost all of its dissolved sulfate by bacterial reduction. Inserting the one oxygen isotope analysis into equation 1 above and assuming original sulfate of oceanic concentration and isotopic composition, the value for 1000 (a - 1) would be about $-9^{\circ}/_{oo}$ for bacterial reduction as compared to the experimental value of $-4^{\circ}/_{oo}$.

Site 148 provides the most unusual data. If one assumes the uppermost three values to represent simple sulfate reduction, the kinetic fractionation term [1000 (a - 1)] would equal about $-39^{\circ}/_{oo}$. Though we have no absolute dates, the rate of bacterial reduction relative to the rate of burial is clearly much slower at Site 148 than at Site 147,

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TABLE 1
Sulfate Concentrations and δO^{18} Values

Sample	Depth (m)	Sulfate (ppm)	δO^{18}-SMOW
147A-2-3-4	8	<100	–
4-3-4	27	210	–
147B-1-3	5	470	24.4
1-4	7	220	–
1-4	7	<100	–
1-4	7	<100	–
148-1-2	3	2540	12.9
1-4	7	2160	17.5
2-3	14	2180	20.9
5-2	38	1530	25.7
7-3	59	1130	24.9
10-3	86	850	15.7
16-3	141	350	–
23-4	209	170	–
27-4	248	290	10.9
149-3-5	16	2500	9.8
3-5	16	2390	9.7
5-3	33	2420	11.7
8-4	62	2370	11.9
12-5	100	2030	11.6
18-3	156	2390	9.3
20-4	174	2130	10.0
26-2	228	2240	9.7
33-1	282	2180	9.9
37-3	324	2110	10.0
41-5	370	2080	9.7

which in turn is probably much slower than the laboratory experiment. This suggests a rate influence on the kinetic fractionation factor.

The lower samples at Site 148 show a continuing decrease in sulfate concentration but a reversal in δO^{18} toward more negative values. There are three directions one could take to explain this behavior:

1) The data on oxygen isotope exchange between sulfate and water which were obtained in high-temperature experiments cannot be extrapolated to lower temperatures; hence, 9.5°/oo does represent true isotopic equilibrium in the oceanic environment as suggested by Longinelli and Craig (1967). The lower samples from Site 148, then, represent an approach toward this equilibrium value in sulfates which have been in contact with ocean water for many thousands of years.

2) The turnover of sulfate in the interstitial environment is much more complex than we have been considering and exchange of oxygen is taking place by some as yet unknown oxidation-reduction couple(s).

3) The "dog leg" curve is an artifact. The values from the lower part of the core reflect contamination of pore water having a very low sulfate concentration by a small amount of seawater (<10%) with 2600 ppm sulfate. Such low levels of contamination might not be apparent in major element analyses where the total range of variation is small.

Mizutani and Rafter (1969b) have shown that in sulfate reduction sulfur isotope behavior parallels that of oxygen and that the change in δS^{34} is very consistently about 3.8 times the change in δO^{18}. Analysis of both sulfur and oxygen isotopes from the same samples would resolve some of the uncertainty in the interpretation of the oxygen data from Site 148. Until these data are available, it is impractical to speculate further.

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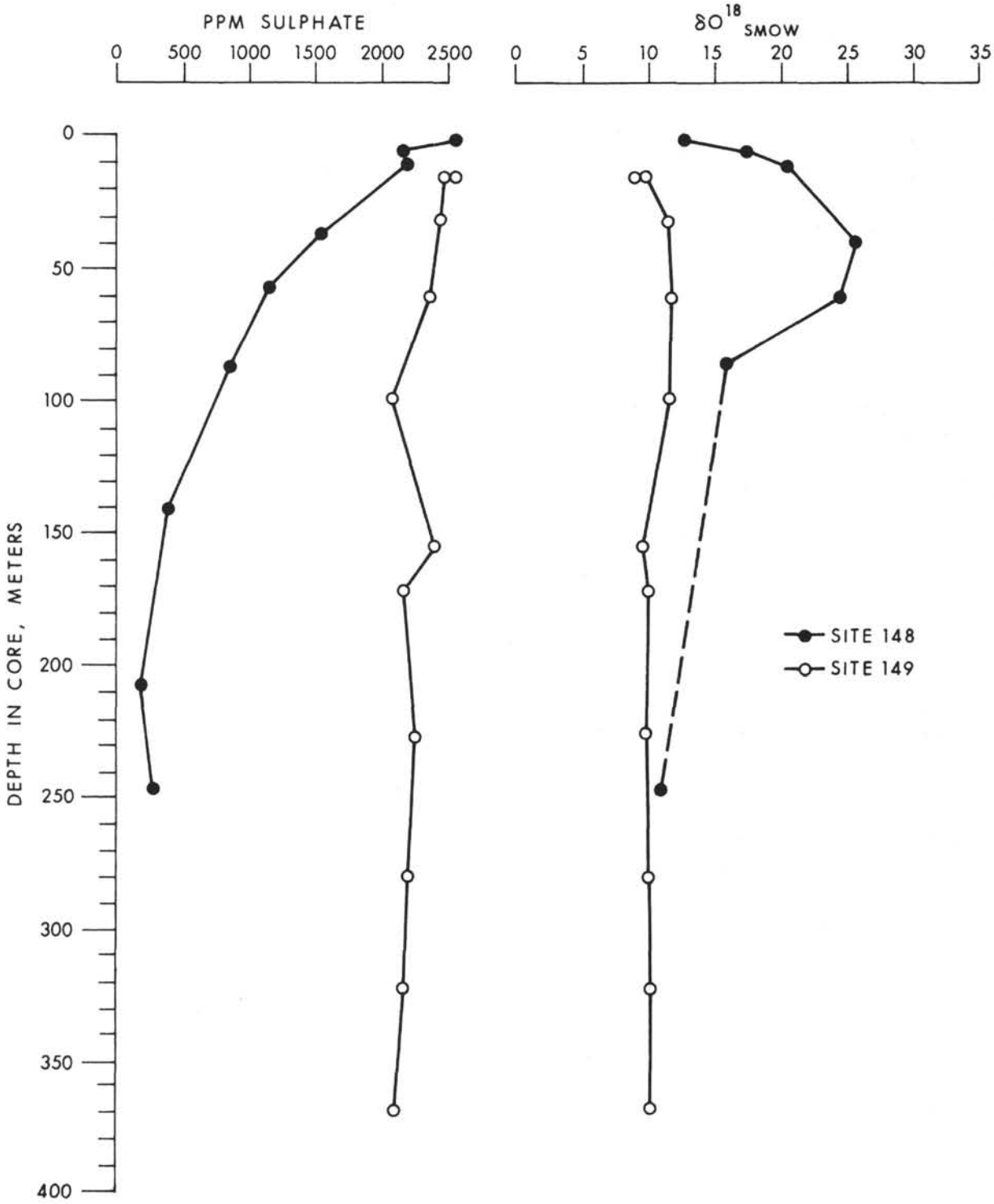

Figure 1. *Sulfate concentration and δO^{18} values for interstitial waters, Sites 148 and 149.*