# 22. STABLE ISOTOPIC COMPOSITION OF PORE WATERS AND CALCITE VEINS<sup>1</sup>

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### ABSTRACT

The oxygen isotopic composition of the pore waters from the sediments and the oxygen and carbon isotopic composition of carbonate veins from basalts of Leg 121 were analyzed. The pore-water data document the extent of the alteration of volcanic ashes and basalt. The influence of an increase in the isotopic composition of deep water as a result of the growth of polar ice caps over the last million years can also be detected in the pore waters of the upper 100 m of the sediments. Temperatures of formation of carbonate veins from basalts from sites located on the Ninetyeast Ridge increase northward along the ridge along with the increased age of the crust and depth of sediments. The temperatures calculated for carbonate veins from Site 758 indicate that a thermal event occurred at some time in the past.

### INTRODUCTION

Stable isotope studies of alteration products in basalts and pore waters from deep-sea drilling cores have been useful in determining the temperatures of formation of alteration minerals, estimating the extent of alteration of the oceanic crust, and delineating the patterns of fluid transport through the oceanic crust (Lawrence and Drever, 1981; Lawrence, 1980; Lawrence and Gieskes, 1981; and Mottl et al., 1983).

At Deep Sea Drilling Project (DSDP) Site 395 in the Atlantic Ocean in relatively young crust (7 Ma), isotopic analyses of carbonate veins from basalts indicated that pervasive circulation of cold, deep waters had taken place. Vein formation temperatures were in the 15° to -1°C range (Lawrence and Drever, 1981). At DSDP Site 417 in the Atlantic Ocean in relatively old crust (109 Ma), isotopic analyses of carbonate veins in basalts indicated formation temperatures in the range 41° to 14°C (Lawrence, 1980).

An isotopic study of pore waters from DSDP cores from 37 locations in all three major oceans is reported in Lawrence and Gieskes (1981). It was concluded that extensive alteration of the upper 500 m of the oceanic crust, up to 30%, can take place after the segment of the oceanic crust leaves the vicinity of the midocean ridge. Furthermore, slow convection of ocean water continues in the basalt layer beneath the sediments even after the sediments have largely sealed the crust from the overlying ocean, possibly until subduction.

At DSDP Site 501/504 near the Costa Rica Rift, four holes were completed within a horizontal distance of 500 m. Isotopic and chemical analyses of the pore waters revealed marked differences from one hole to another (Mottl et al., 1983). These differences were attributed to convection of water at relatively slow rates, millimeters per year, through both the basalts and the sediments. Subsequent studies of the chemical and isotopic composition of pore waters from a grid of piston cores in the same area confirmed this result (Mottl et al., 1987; Mottl and Lawrence, unpubl. data).

On Leg 121 of the Ocean Drilling Program (ODP) in the Indian Ocean, seven sites were occupied, Sites 752–758. The first four

sites were located on Broken Ridge. The last three sites were located on Ninetyeast Ridge. Basaltic basement was reached only at the last three sites. Pore waters were taken from the sediments of all seven sites. Chemical analyses of the pore waters and a discussion of the results can be found in Peirce, Weissel, et al. (1989). Carbonate veins were taken from the basalts of Sites 756–758. This chapter focuses primarily on the isotope results from the pore waters and carbonate veins.

At Broken Ridge the studies focus on the changes observed in the chemical and isotopic composition of the pore waters in the sediments from site to site on a scale of a few kilometers. Four sites were drilled on a 20-km-long north-south line perpendicular to the strike of Broken Ridge (Peirce, Weissel, et al., 1989). The stratigraphy consists of a 40- to 150-m-thick cap of Neogene and uppermost Paleogene oozes overlying older sediments. An angular unconformity separates the two sequences (Peirce, Weissel, et al., 1989). The oozes are thickest at the middle Sites 752 and 754. The uppermost underlying sediments that subcrop beneath the oozes are older from north to south, ranging in age from 45 Ma at Site 753 to 86 Ma at Site 755. A middle to late Eocene erosion event caused by rift-related uplift was followed by subsidence through the present to produce the overall stratigraphic relationships on Broken Ridge. The sediments below the unconformity are increasingly lithified from north to south. They are generally slightly indurated at Sites 753 and 752 and highly indurated at Sites 754 and 755.

Ninetyeast Ridge represents an excellent region in which to observe large chemical and isotopic gradients in pore fluids. The topography is very rough and volcanic sediments are common. Extensive faulting in the ridge and great thicknesses of ash in some locations have led to increased exposure of volcanic material to seawater. In addition, the high topographic relief of the basement relative to the surrounding oceanic crust causes thermal differences that help generate fluid flow within the crust. Finally, earlier studies of pore fluids from Ninetyeast Ridge, particularly at DSDP Site 253, showed very large chemical and isotopic changes with depth (Lawrence and Gieskes, 1981).

The basement on Ninetyeast Ridge ranges in age from Late Cretaceous at the north end (Site 758) to late Paleocene in the middle (Site 757) to late Eocene at the south end (Site 756). Some systematic changes roughly comparable to those exhibited by ocean crust as a function of distance from the ridge axis are found from south to north along the ridge. Ninetyeast Ridge becomes deeper and more heavily sedimented to the north. Its depth profile appears to subside at similar rates to normal oceanic crust (Detrick

 <sup>&</sup>lt;sup>1</sup> Weissel, J., Peirce, J., Taylor, E., Alt, J., et al., 1991. Proc. ODP, Sci. Results, 121: College Station, TX (Ocean Drilling Program).
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et al., 1977), indicating that heat flow is lower to the north. Therefore, some of the features of chemical change exhibited from south to north in pore fluids in the sediments overlying Ninetyeast Ridge may be similar to those found in ocean sediments at progressively greater distances from a mid-ocean ridge (Lawrence and Gieskes, 1981).

### **METHODS**

The oxygen isotope values of the pore waters were determined using a carbon dioxide-water equilibration technique at 50°C. Fifty-microliter water samples were placed in 5-mL tubes with carbon dioxide having a pressure of about one-half atmosphere. Equilibration took place overnight. The carbon dioxide-water sample tubes were then placed in a dry ice bath in order to produce dry carbon dioxide for analysis in an isotope ratio mass spectrometer. This technique is a modification of one described by Epstein and Mayeda (1953). All pore-water data are reported relative to standard mean ocean water (SMOW) in parts per thousand. The precision of measurement on replicate analyses of isotopic standards is better than 0.1 per mil.

Carbonate samples were analyzed by reaction with 100% phosphoric acid at 50°C in vacuo. The carbon dioxide was then transferred after drying in a dry ice bath to sample tubes for mass spectrometer analysis. This technique is a modification of one by McCrea (1950). Carbon isotope analyses are reported relative to Pee Dee belemnite (PDB) in parts per thousand. Oxygen isotope analyses are reported relative to SMOW in parts per thousand. The SMOW scale for carbonate veins is preferred here rather than the PDB scale used with carbonate fossils because the waters are reported on the SMOW scale. It logically follows that the same scale should be used in discussions of water/rock interactions.

### DISCUSSION OF RESULTS

### **Pore-Water Chemistry**

The oxygen isotopic analyses of the pore waters are reported in Table 1 and shown as a function of depth for all seven sites in Figures 1–4. The chlorinities, calcium ion, and magnesium ion concentrations of the pore waters taken from the shipboard data set (Peirce, Weissel, et al., 1989) are also shown as a function of depth in Figures 1–4. The precision of the analyses of chlorinity are slightly better than 2%. The precision of the calcium and magnesium ion analyses are better than 0.5%.

A generalized pattern of chemical and oxygen isotopic changes in the pore waters can be seen at all of the sites with the exception of Site 756, which shows a much more complex pattern (Figs. 1–4). In general, oxygen isotope values decrease with depth, chlorinities increase with depth, and calcium ion concentrations increase with depth. A clear-cut pattern of increasing chlorinities with depth is evident only at Sites 757 and 758 on Ninetyeast Ridge (Figs. 3 and 4). At Sites 752 to 755 on Broken Ridge it is not as clear that increases in chlorinities with depth are present (Fig. 1).

The generalized pattern of chemical and isotopic changes described above can be attributed to the alteration of volcanic material either in the sediments or in the basalts beneath the sediments (Lawrence et al., 1975; Lawrence and Gieskes, 1981; Gieskes and Lawrence, 1981). The decrease in the oxygen isotopic composition of the pore waters is a result of positive shifts in oxygen isotope values of solid phases as volcanic material alters to smectitic clays and to zeolites. This same reaction releases calcium to the pore waters, accounting for the increase in calcium ion concentrations with depth. Chlorinities also increase with depth because the alteration of volcanic material to smectites and zeolites is a hydration reaction and consumes water.

The most manifest display of the effects of the volcanic alteration on pore-water chemistry can be seen at Site 757. The calcium ion concentration increases with depth to a maximum of 14 times its concentration in seawater (Fig. 3). The calcium ion gradient, the change in calcium ion concentration per unit of depth change, is the highest to date ever found in the history of DSDP and ODP. These large changes are undoubtedly the result of the alteration of the thick section of ash from 220 to 360 mbsf. The increase in calcium concentration with depth also has an impact on the alkalinity and sulfate concentrations in the pore waters. Both decrease with depth because of supersaturation with respect to calcite and gypsum (Peirce, Weissel, et al., 1989, table 13, p. 341). The pore solutions are supersaturated with respect to calcite at all depths, with a marked jump in supersaturation occurring in the ashes. The ion activity product/equilibrium solubility product (IAP/KSP) ratio for gypsum increases as a function of depth and reaches supersaturation at the ash boundary.

The decrease in oxygen isotope ratios with depth at Site 757 is about average for sites located in older oceanic crust (see Lawrence and Gieskes, 1981). The increases in calcium ion concentrations and decreases in magnesium ion concentrations and oxygen isotope values are very similar to those that were observed at DSDP Site 253 on Ninetyeast Ridge. Both sites have thick basaltic ash sequences. Most other sites examined had a smaller increase in calcium ion concentration for each per mil drop in oxygen isotope value. Apparently the basaltic ash, being very rich in calcium compared to more acidic ashes at other sites, releases a higher amount of calcium per amount of ash altered. The oxygen isotope shifts can be directly related to the quantity of ash alteration (Lawrence and Gieskes, 1981).

The chloride concentrations of the pore waters also show large changes with depth. At a depth of 340 mbsf the increase in chloride amounts to about 10% over that of seawater. The water lost has gone directly into either structural sites or interlayer sites in the abundant smectitic clays found in the ashes (Peirce, Weissel, et al., 1989, table 14, p. 342). Quantitative estimates of the amount of alteration at Site 757 are discussed in the mass balance section of this chapter.

At Site 758 near the north and older end of Ninetyeast Ridge the oxygen isotope, chloride ion, calcium ion, and magnesium ion changes in the pore waters were found to be lower than those at Site 757 (Fig. 4). The maximum values for calcium concentrations and chlorinities were about half those at Site 757 and the minimum value in oxygen isotope ratios was about three-quarters of that at Site 757. The gradients in these parameters, changes per unit change in depth, were also lower than those at Site 757. Quantitative estimates of the amount of alteration at Site 758 are discussed in the mass balance section of this chapter.

At Sites 752 to 755 on Broken Ridge the changes in oxygen isotope ratios, calcium ion and magnesium ion concentrations, and chlorinities with depth were much lower than those found at Sites 757 and 758. The maximum decrease in oxygen isotope ratios was half that at Site 757, and the maximum increase in calcium ion concentration was only 20% of that at Site 757. Only a slight hint of a chloride increase was observed at the Broken Ridge sites (Fig. 1). If these changes are attributed to the alteration of volcanic material, they suggest that the amount of ash altered at these sites must be less than that at Site 757. Ashes are present at the Broken Ridge sites but there is no thick ash sequence. In addition, a thick sequence of old, highly lithified sediments exists below the younger sediments cored at Sites 752-755. Changes in pore-water chemistry that may have occurred in the pore fluids in the basalts underlying the old lithified sediments may be effectively sealed off. At Site 758, where chemical changes in the pore waters were closer to those observed at Site 757, the oldest

Table 1. Oxygen	isotopic composition
of pore waters.	
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Hole, core,	Depth	δ <sup>18</sup> O	
section <sup>a</sup>	(mbsf)	(SMOW)	
121-			
752A-1H-4	6.0	0.5	
752A-3H-4	23.8	1.7	
752A-6H-4	52.4	0.7	
752A-9H-1	75.4	1.2	
752A-9H-4	81.4	0.7	
752A-13X-3	117.4	0.4	
752A-16X-3	146.5	0.7	
752A-19X-3	175.6	0.1	
752A-22X-3	204.6	0.3	
752A-25X-2	232.1	-0.1	
752A-28X-3	262.6	0.2	
752A-31X-4	285.4	-0.1	
752B-2R-1	121.0	0.7	
752B-4W-4	131.0	0.8	
752B-5R-3	301.5	0.1	
753A-1H-4	6.0	0.5	
753A-4H-1	24.4	1.0	
753A-7H-5	53.2	0.3	
754A-6H-5	52.0	0.9	
754A-9H-5	81.0	0.8	
754A-12H-5	110.1	0.7	
755A-1R-1	0.1	0.9	
755A-3R-1	36.7	1.0	
756B-1H-4	6.0	0.6	
756B-3H-5	25.6	0.7	
756B-4H-5	34.7	0.9	
756B-5H-6	42.3	1.0	
756B-6H-5	54.4	0.6	
756B-7H-4	62.2	0.3	
756B-8H-4	71.6	0.4	
756B-9H-5	81.2	0.4	
756B-10H-5	90.9	0.4	
756B-1H-5	100.6	0.7	
756C-1H-5	7.5	0.4	
756C-3W-CC	88.2	0.5	
756C-4X-5	108.6	0.9	
756C-5X-4	115.5	1.0	
756C-6X-3	124.7	1.1	
756C-7X-4	135.8	0.7	
756C-8X-1	140.9	0.8	
756D-1R-3	6.5	0.4	
756D-2R-6	81.1	0.8	
756D-3W-1	120.0	0.8	
757B-1H-2	2.7	0.4	
757B-3H-5	21.5	0.5	
757B-4H-4	29.6	0.3	
757B-5H-4	39.2	0.3	

Hole, core, section <sup>a</sup>	Depth (mbsf)	δ <sup>18</sup> O (SMOW)
121-		
757B-6H-5	50.3	0.3
757B-7H-4	58.5	0.0
757B-8H-5	69.7	0.5
757B-9H-4	77.8	0.4
757B-11H-5	98.7	-0.2
757B-12H-5	108.5	-0.4
757B-13H-5	118.0	-0.5
757B-14H-5	127.6	-0.5
757B-15H-4	135.8	-0.6
757B-16H-4	145.5	-0.6
757B-17H-5	156.6	-0.8
757B-18H-5	166.3	-0.2
757B-21X-5	190.2	-2.2
757B-24X-4	217.7	-1.1
757B-27X-5	248.2	-1.9
757B-30X-2	272.7	-1.9
757B-35X-CC	322.0	-2.4
757B-37X-2	340.0	-1.9
757C-1R-1	1.5	0.2
757C-1R-4	6.0	0.3
757C-1R-6	9.0	0.2
757C-2R-1	123.0	-0.5
757C-2R-6	130.5	-0.5
757C-3R-1	132.6	-0.7
757C-4R-1	142.3	-0.7
757C-4R-6	149.8	0.0
757C-5R-3	155.0	-0.8
757C-5R-6	159.5	-0.9
758A-1H-3	4.5	0.5
758A-7H-6	65.4	0.2
758A-12X-5	108.9	0.1
758A-15X-2	134.4	-0.1
758A-18X-3	164.9	-0.1
758A-21X-4	195.3	-0.4
758A-28X-5	264.4	-0.6
758A-31X-5	293.4	-0.8
758A-34X-5	322.4	-0.6
758A-38X-1	354.1	-1.1
758A-41X-4	383.0	-0.9
758A-50R-1	452.1	-1.3
758A-54R-1	490.7	-1.6
758A-57R-1	519.4	-1.7

<sup>a</sup> Most of the samples were taken in the interval 140-150 cm. The exact intervals can be found in the site reports (Peirce, Weissel, et al., 1989).

sediments directly overlying the basalts were only lithified to chalks.

At Sites 752 to 755, relatively high oxygen isotope values are observed in all of the sediments of Sites 753, 754, and 755, and in the upper sediments of Site 752 (see Fig. 1). The oxygen isotopic composition of deep water in the oceans is presently between 0.0 and 0.2 per mil (Craig and Gordon, 1965). The oxygen isotopic composition of the shallowest pore-water sample is very near this value (see Fig. 1). But samples deeper than this have oxygen isotope values averaging near 1.0 per mil. The oxygen isotopic composition of the oceans over the last 1 m.v. has usually been higher than the present value by 0.5-0.9 per mil (Craig, 1965; Shackleton, 1967). Sediment pore waters were therefore higher in <sup>18</sup>O in the last 1 m.y. In addition, the deep water which was generally enriched in <sup>18</sup>O over most of the last 1 m.y. would have diffused downward into the sediments. Observations of higher oxygen isotope ratios accompanied by increases in chlorinity in the uppermost sediments from DSDP Leg 86 have been made by McDuff (1985).

The decrease in oxygen isotope values with depth may not, therefore, be the result of the alteration of volcanic material. The increase in calcium ion and decrease in magnesium ion concentrations with depth at Sites 752 to 755 and the slight suggestion of an increase in chloride with depth, however, indicate that volcanic alteration has been going on at these sites. This point is discussed in more detail in the mass balance section of this report. Part of the problem in interpreting the chloride data is that the precision of the analyses are no better than 1%.

High oxygen isotope values in the upper 100 m of the sediments are not as evident at Sites 757 and 758 as they are at the Broken Ridge sites (see Figs. 3 and 4). This may be because of the diffusion of pore waters from below having low oxygen isotope ratios. The pore waters at Site 757 suggest a slight enrichment over the 0.0 to 0.2 per mil level. At Site 758 it is not possible to make an evaluation because very few samples were taken in the upper 100 m of sediment.

The most complex pattern of chemical and isotopic changes in the pore waters observed on Leg 121 was at Site 756 at the south and young end of Ninetyeast Ridge. Site 756 was located in 6-km-wide sediment pond situated in very rough topography. A



Figure 1. Oxygen isotope values, chlorinities, and calcium ion and magnesium ion concentrations of pore waters from Sites 752, 753, 754, and 755 plotted as a function of depth.



Figure 2. Oxygen isotope values, chlorinities, and calcium ion and magnesium ion concentrations of pore waters from Holes 756B, 756C, and 756D plotted as a function of depth. All samples come from carbonate ooze, as there was no ash section at this site. Hole 756B is interpreted as being in the upwelling zone of a convection cell, Hole 756C as a downwelling zone, and Hole 756D as an intermediate zone.



Figure 3. Oxygen isotope values, chlorinities, and calcium ion and magnesium ion concentrations of pore waters from Site 757 plotted as a function of depth.



Figure 4. Oxygen isotope values, chlorinities, and calcium ion and magnesium ion concentrations of pore waters from Site 758 plotted as a function of depth.

prominent fault lies about 3 km to the southeast. The sediments in the pond are about 150 m thick at the site location. Four holes were drilled at Site 756, three of which reached basement. These three holes were located in a southwest to northeast direction (in the order 756B, 756D, 756C) with about 100-m spacing between them.

The simple pattern in the pore-water data is seen in the calcium ion concentrations (see Fig. 2). There is a clear-cut increase in calcium and decrease in magnesium ion concentrations with depth at Hole 756B to the southwest, lesser changes at the next hole, 756D, and no changes at Hole 756C. These changes over a relatively short distance cannot be a result of differences in the ash content of the sediments. The sediments have a low concentration of volcanic ash and essentially no variation from site to site at any given horizon. In the same way it seems unlikely that alteration rates would be different in the underlying basalts from one hole to another.

Another possible explanation for the observed differences is that slow convection of water is taking place through the sediments in the pond. Studies by Mottl et al. (1983; 1987) have shown that differences in calcium ion gradients from location to location on a scale of a few hundred meters can be caused by slow convection of seawater through the oceanic crust. The sediment columns with high calcium ion concentrations represent upwelling zones and the sediment columns with calcium ion concentrations close to that of seawater represent downwelling zones. The high calcium ion concentrations coming up are a result of alteration of the basalts. The advection rates postulated by Mottl et al. (1987) from modeling their data were from 1 to 5 mm per year.

The oxygen isotope values in the pore waters do not show such a simple pattern from hole to hole as do the calcium data (see Fig. 2). The oxygen isotope values at both Holes 756B and 756C vary with depth, with some suggestion of a sinusoidal pattern. Unfortunately, no cores were taken at shallower depths at Hole 756C, with one exception, and no cores were taken below 105 m at Hole 756B. It is therefore not clear whether there are sinusoidal patterns at Hole 756C at shallower depths and at Hole 756B at deeper depths.

As pointed out earlier oxygen isotope values of deep waters show an oscillation in time connected to the grow and decay of the polar ice caps. The oxygen isotope values of the deep waters are high during the glacial periods and low during the interglacial periods.

With this in mind a possible explanation for combined calcium and oxygen isotope data sets seems possible. At Hole 756B an upwelling rate of 0.8 mm per year would move water upward about 80 m in 100,000 yr, the approximate spacing between glacial maximums or periods of high oxygen isotope values in deep waters. There is a suggestion of an 80-m oscillation in the oxygen isotope data of the pore waters at Hole 756B. The oxygen isotope decreases associated with alteration of the basalts below would be superimposed on the glacial to interglacial isotope signal. If reaction rates were uniform the sinusoidal variation in oxygen isotopes would still be present.

At Hole 756C, a downwelling rate of 0.8 mm per year would produce a similar sinusoidal pattern in the oxygen isotope values but calcium ion concentrations would be near those of seawater at all depths because of the downward flow. Upward diffusion of high calcium ion concentrations caused by basalt alteration would be suppressed by the downward flow. Of course, no data are available in the 10- to 80-m interval at Hole 756C, so this interpretation assumes that the suggestion of a sinusoidal pattern with depth at Hole 756C continues to the sediment/water interface.

If it is assumed that the oxygen isotope values at Hole 756C are uniform with depth between the two uppermost sampling intervals, then a much higher downward flow rate would be required. The rate would have to be 100 m in 10,000 yr, the approximate length of the present interglacial, or about 10 mm per year. The oxygen isotope data then represent a step function with higher isotope values, representing large polar ice caps, below 100 m.

The chloride data show similarities to the oxygen isotope data. Although an exact match is not evident, the data sets may match when the error in the chloride analyses is considered. The chloride results are no better then 1% of the number given, leaving an error of more than 5 mmol/L. The oxygen isotope data are good to within 0.1 per mil. If the chloride data mirror the oxygen isotope data this adds support to the pore water convection hypothesis given.

## **Mass Balance Calculations**

Oxygen isotopic decreases in pore waters of deep-sea sediments can be used to estimate the extent of alteration of the oceanic crust (Lawrence and Gieskes, 1981). The reaction that produces these decreases has been identified as the alteration of volcanic material to smectitic clays and zeolites. By knowing the increase in the oxygen isotopic composition of the solids in this reaction and the observed decrease in the pore waters, it is possible to estimate the amount of volcanic material that had to have been altered to produce the observed decrease. The methodology of the calculation and the assumptions made are given in Lawrence and Gieskes (1981; table 2).

Three sites from Leg 121, 752, 757, and 758, lend themselves to mass balance estimates of the amount of volcanic alteration. Each of these sites showed distinct and steady decreases in the oxygen isotope ratios of the pore waters with depth (see Figs. 1, 3, and 4).

Site 757 showed the largest decrease in oxygen isotope ratios with depth. The calculations (see Lawrence and Gieskes, 1981, for methodology) indicate that a minimum of 15 m of ash or 7 m of basalt had to be altered to explain the <sup>18</sup>O depletion found in the pore waters (see Table 2). This calculation takes into account only the observed depletion of oxygen isotopes in the pore waters and represents the minimum required. A second calculation (see Lawrence and Gieskes, 1981, for methodology) is done to account for the fact that diffusion has been constantly adding <sup>18</sup>O to the sediment column from the ocean above through time. If this process is considered, much larger amounts of alteration are indicated at Site 757. The calculations indicate that 225 m of ash or 161 m of basalt would have to be altered over the entire history of the site if the rates of alteration were half those going on presently (see table 2 in Lawrence and Gieskes, 1981). The thickness of the ash layer at Site 757 is about 140 meters thick. This ash is highly altered but certainly not completely altered. This suggests that the basalts underlying the ash must also have been altered. Alternatively reaction rates could have been slower in the past yielding a much lower gradient in the oxygen isotope ratios of the pore waters and thereby less alteration.

Similar mass balance calculations can be made for Site 758. The calculations suggest minimum amounts of alteration of 20 m of ash or 9 m of basalt. Amounts that consider alteration through the entire history of the site are much larger, amounting to 176 m of ash or 124 m of basalt. Ash is dispersed throughout the sediment column and 90 m of tuff were found in lowest sediments of Site 758. If 10% of the sediments overlying the tuff are composed of ash then the total thickness of ash material at Site 758 would be about 130 m. The tuffs, however, are not completely altered. If the second mass balance estimate is accepted then it requires that tens of meters of basalt below Site 758 must also have been altered.

Mass balance calculations at Site 752 consider only ash alteration because a thick section of highly lithified sediments almost

Table 2. Reaction zo	ne thickness fron	i oxygen isotope	material balance.
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	Basement		Mean $\delta^{18}$ O		Volume of fluid in sediments	Reaction zone thickness			
	Depth Age			<sup>18</sup> O balance		<sup>18</sup> O influx			
Site	(m)	(m.y.)	pore fluid <sup>a</sup>	Xb	(cm <sup>3</sup> )	Ash	Basalt	Ash	Basal
752	434	60	-0.5	0.023	20,623	8		109	
757	367	55	-1.0	0.045	19,011	15	7	225	161
758	520	77	-0.8	0.038	29,173	20	9	176	124

<sup>a</sup> The equivalent values in table 2 of Lawrence and Gieskes (1981) would be -0.3 per mil lower. The value for G in the second equation in table 2 of Lawrence and Gieskes (1981) is obtained by dividing the value given here by the depth.

<sup>b</sup> The mole fraction of oxygen in the solid phase (Lawrence and Gieskes, 1981, table 2).

certainly exists below the deepest sediments cored at Site 752. This can be seen from seismic data (see Peirce, Weissel, et al., 1989; Driscoll et al., this volume). This lithified layer would most probably isolate the basaltic crust below the lithified sediments from the sediments above. The amounts calculated are a minimum of 8 m of ash and 109 m if isotopic gradients have been present over the entire history of the site. Ash sediments are dispersed throughout the sediment column. Sediments were cored to a depth of 430 m. If 10% of the sediments were composed of ash the amounts needed to satisfy the calculation are insufficient. This suggests that the rate of alteration of the ash in the past was lower.

Another consideration ignored in the above calculations is that the observed gradient in the oxygen isotopic composition of the pore waters at Site 752 is not due only to the alteration of volcanic material. This is very likely because the upper sediments at Site 752 contain pore waters which appear to be residual from a time during which deep waters were higher in oxygen isotope ratios due to the presence of a large polar ice cap. This would produce an oxygen isotope gradient in the pore waters which was not caused by the alteration of volcanic material. If 50% of the gradient observed is due to ash alteration then the estimates given above would be reduced by half. The same reasoning applies to Sites 757 and 758. Therefore, the amounts calculated for those sites using the <sup>18</sup>O flux method (see Table 2) would also be high. The depletions in oxygen isotope ratios, however, are greater at these two sites so that most of the effect is probably the result of alteration of volcanic material.

### **Alteration Temperatures**

Carbonate veins in the basalts from Sites 756, 757, and 758 on Ninetyeast Ridge were analyzed for their oxygen and carbon isotope ratios. The data are given in Table 3 and plotted in Figure 5. The oxygen isotope values were also used to calculate the formation temperatures of the carbonate using the calcite-water relationship of O'Neil et al. (1969). The oxygen isotope ratios of the waters assumed to be in equilibrium with the calcites were either the present-day pore waters or present-day deep-ocean water. These temperatures are plotted as a function of depth in Figure 6.

In Figure 5 it can be seen that the isotope values of the three sites plot in different regions on the diagram. The samples with the lowest oxygen and carbon isotope values are from Site 758, followed by higher values in both these ratios at Site 757, to still higher values at Site 756. Also shown are the ranges of isotope values for carbonate veins from DSDP Site 395 (Lawrence and Drever, 1981) and DSDP Site 417 (Lawrence, 1980). Overall there appears to be a linear relationship between the oxygen and carbon isotope values. Furthermore, the youngest sites, Sites 395 and 756, have the highest isotope values. Their ages are 7 Ma and 35 Ma, respectively. The other sites have older ages of 55 Ma (Site 757), 77 Ma (Site 758), and 109 Ma (Site 417).

The temperatures calculated for the carbonate veins (O'Neil et al., 1969) show a general increase from Sites 756 to 757 to 758 (see Fig. 6). This increase corresponds to an increase in the age of the sites and an increase in the depth of burial of the sites and thereby the present *in-situ* temperature. The line drawn in Figure 6 represents the temperature at the depth shown assuming a geothermal gradient of  $4^{\circ}$ C per 100 m. The data in Figures 5 and 6 suggest that the carbonate veins at Sites 756 and 757 were formed by the interaction of seawater with the basalts at relatively cold temperatures. The carbon isotope ratios are within the range of that of seawater.

The temperatures calculated at Sites 756 and 757 using the oxygen isotope ratios of the carbonates and those of the pore water or deep-ocean water (see Fig. 6) do not constrain the time of formation of the veins. They indicate that the carbonate veins could have been formed at any time from the time of extrusion of the basalts to the present. The veins are currently very close to being in isotopic equilibrium with the *in-situ* waters at the *in-situ* temperatures. Because deep waters were warmer going back in time toward the Cretaceous by  $5^{\circ}$ -10°C (Savin, 1977), the carbonate veins may also reflect formation at an earlier time than the present because temperatures would have been warmer at shallower depths in the crust. The veins, however, could not have been formed at high temperatures before the extruded basalts had time to cool down to near-bottom-water temperatures.

The carbonate veins from Site 758 appear to be different from those at the other two sites on Ninetyeast Ridge. The calculated temperatures (see Fig. 6) are high. The temperatures are too high to reflect in-situ temperatures and the in-situ isotopic composition of the pore fluids. This suggests that they may have been formed by a thermal event either when the basalts were extruded or later. It is unlikely that they were formed at temperatures reflecting a normal geothermal gradient in pore waters having a very low isotopic composition. Such pore waters would have had to have an oxygen isotopic composition of -6 per mil. Only one DSDP site has ever shown such low isotope values, Site 348 in the Norwegian Sea (Lawrence and Gieskes, 1981). The carbon isotope values of the carbonate veins from Site 758, although lower than those from the other two sites (see Fig. 5), are still within the range of deep-ocean waters. This suggests that the fluid phase that interacted with the basalts to produce the veins was seawater.

The general relationship between the oxygen and carbon isotopic composition of the carbonate veins both from Leg 121 and two earlier DSDP legs (see Fig. 5) deserves additional comment. The relationship is compatible with continuous formation of carbonate veins in aging oceanic crust. The decreasing oxygen isotope values suggest average higher temperatures with age. The decreasing carbon isotope values are compatible with increasing depth of formation of the carbonate veins with age. First, let us consider the earlier history of a segment of oceanic crust representing the time before the sediment cover seals off the crust. In

Table 3. Oxygen and carbon isotopic composition of carbonate veins.

Hole, core, section,	Denth	δ <sup>18</sup> O	δ <sup>13</sup> C (PDB)	Temperatures <sup>a</sup>	
interval (cm)	(mbsf)	(SMOW) <sup>b</sup>		(°C)	(°C)
121-					
756C-10N-1, 44-45	150.7	32.8	1.9	5.8	10.2
756C-10N-2, 6-7	151.9	32.5	1.6	7.3	11.7
756D-4R-2, 12-13	140.6	31.8	1.9	10.0	14.6
756D-6R-1, 103-104	159.3	31.9	1.9	9.4	13.9
756D-7R-2, 68-69	170.2	31.3	1.5	10.6	15.3
756D-7R-2, 68-69	170.	31.3	1.1	11.9	16.6
756D-7R-3, 11-12	171.1	32.2	1.1	8.2	12.7
756D-7R-3, 11-12	171.1	31.6	1.4	10.6	15.3
756D-7R-3, 99-100	172.0	28.2	0.5	25.4	30.6
756D-8R-1, 50-51	178.2	32.4	1.7	7.6	12.1
756D-9R-3, 27-28	190.3	32.1	1.4	8.8	13.3
756D-9R-4, 31-32	191.8	30.0	1.4	17.4	22.5
756D-10R-1, 28-29	197.3	32.6	1.7	6.6	11.1
756D-10R-3, 77-78	200.8	26.3	0.6	34.7	40.6
756D-10R-3, 77-78	200.8	32.6	1.7	6.8	11.2
756D-11R-2, 91-92	209.0	31.8	0.9	9.9	14.5
756D-12R-2, 130-131	218.7	32.0	1.7	9.2	13.8
757C-9R-2, 55-56	383.7	27.4	1.5	17.1	29.2
757C-9R-6, 52-53	388.1	27.7	1.5	16.7	27.8
757C-10R-3, 57-59	395.3	27.9	0.9	15.8	26.8
757C-10R-3, 57-59	395.3	28.7	1.2	12.5	23.2
757C-11R-3, 136-137	405.6	27.3	0.6	18.3	29.6
757C-12R-3, 73-75	414.4	27.8	1.1	16.1	27.1
758A-55R-1, 72-73	499.6	24.4	0.0	35.5	44.9
758A-55R-4, 85-86	504.0	22.5	-0.1	45.9	56.3
758A-55R-4, 85-86	504.0	22.7	-0.1	44.6	55.0
758A-56R-1, 37-38	508.8	24.0	-0.6	37.1	46.6
758A-60R-1, 84-85	546.7	22.1	0.2	47.7	58.4
758A-62R-1, 106-107	565.4	25.0	0.0	32.1	41.2
758A-62R-1, 106-107	565.4	24.7	0.0	33.9	43.1
758A-62R-2, 54-55	566.3	20.9	-1.1	55.2	66.6
758A-63R-5, 62-63	579.8	24.8	-2.4	33.0	42.1
758A-64R-3, 142-143	587.4	20.6	0.4	57.4	69.1
758A-65R-2, 68-69	594.7	20.4	-0.4	58.3	70.1
758A-66R-4, 16-17	606.4	20.9	-1.0	55.1	66.5
758A-66R-4, 21-22	606,4	20.6	-1.0	57.1	68.7
758A-67R-3, 5-6	614.5	21.4	-0.8	52.3	63.3
758A-67R-4, 72-73	616.7	22.2	-1.1	57.4	58.0
758A-67R-4, 72-73	616.7	20.7	-1.0	56.3	67.9
758A-68R-5, 30-31	626.8	20.3	-0.8	59.1	71.0
758A-69R-1, 135-136	631.6	21.2	-1.3	53.1	64.3
758A-69R-5, 94-95	636.5	20.1	-1.3	60.5	72.4
758A-70R-1, 90-91	640.3	22.6	-0.6	45.3	55.6
758A-70R-1, 133-134	640.7	23.2	-1.1	41.6	51.6
758A-72R-1, 48-49	658.5	21.8	-0.6	50.0	60.8
758A-72R-5, 117-118	664.9	23.2	-1.2	41.7	51.8
758A-73R-3, 53-54	671.1	23.8	-1.1	38.3	48.0

<sup>a</sup> Two temperatures are given, one calculated assuming that the water was 0.0 per mil and the other calculated assuming the water had the same isotopic composition as that of the deepest pore water found in the sediment. For Site 756 the pore water value assumed was +1.1 per mil; Site 757, -2.4 per mil; and Site 758, -1.7 per mil. <sup>b</sup> The conversion of the oxygen isotope values to the PDB scale can be made

using the equation:  $\delta_{PDB} = (\delta_{SMOW} - 30.86) / 1.03086$ .

general, the deeper ocean water has to circulate into the crust, the greater will be the removal of inorganic dissolved carbon from the seawater due reaction with the basalts. Because carbonate solid under isotopic equilibrium conditions is enriched in the heavy isotope of carbon relative to the bicarbonate in seawater (Emrich et al., 1970), progressive reaction decreases the carbon isotopic composition of the remaining bicarbonate. This means that laterformed carbonate veins will have lower carbon isotopic values.

After the sediment cover seals the oceanic crust, additional factors can act to decrease the carbon isotopic composition of any carbonate veins formed. Organic matter in the sediments can be oxidized by sulfate reduction causing a lowering of the carbon isotopic composition of the sediment pore waters (Lawrence, 1973). If this fluid diffuses or advects into the underlying basalts



Figure 5. Oxygen isotope values plotted as a function of carbon isotope values for carbonate veins in basalts from Sites 756, 757, and 758. Also shown are the isotope ranges for carbonate veins from DSDP Sites 395 and 417.



Figure 6. Calculated temperatures of formation of carbonate veins from basalts from Sites 756, 757, and 758.

the carbonate veins formed will have lower carbon isotopic values. In addition any carbon dioxide outgassing from the lower crust or mantle of the Earth has a lower carbon isotopic composition than that of seawater (Fuex and Baker, 1973). As pointed out previously, the carbonate veins of Site 758 have the lowest oxygen isotopic values of the Ninetyeast Ridge sites and may have formed under the influences of a thermal event. If that event involved outgassing of carbon dioxide from a magma chamber, the carbon isotopic composition of that gas would be lower than that of seawater and such carbon may have been incorporated in the carbonate veins.

### CONCLUSIONS

The chemical and isotopic changes with depth seen in the pore waters of the sediments drilled on Leg 121 are in large part the result of the alteration of volcanic material both in the sediments and in the basalts below. Extensive alteration of basaltic ash and basalts has occurred at Sites 757 and 758. A much lower degree of alteration primarily of volcanic ash has occurred at Sites 752–755 with the highest amounts being at Site 752. The pore waters in the sediments of Sites 753–755 and in the upper sediments of Site 752 have unusually high oxygen isotope values most probably reflecting higher oxygen isotope values in the deep waters of the oceans over the last 1 m.y. or so. At Site 756 the chemical and oxygen isotope data suggest that slow convection of seawater through the sediments is occurring in the sediment pond where Site 756 is located. The convection rates are on the order of 0.5–10 mm per year.

Calculated temperatures of formation of carbonate veins from basalts cored on Ninetyeast Ridge show a progressive increase from south to north. This increase corresponds to greater depth of burial and greater age along Ninetyeast Ridge. Temperatures calculated for Sites 756 and 757 are the same as *in-situ* temperatures at the sites presently. Temperatures calculated for Site 758 are higher than present-day *in-situ* temperatures and may reflect the influence of a thermal event in the past.

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