

### 30. OXYGEN ISOTOPE MATERIAL BALANCE CALCULATIONS, LEG 35

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#### INTRODUCTION

The isotopic and chemical compositions of pore fluids from Deep Sea Drilling Project cores frequently exhibit large changes with depth. Some of these changes have been shown (Drever, 1971; Sayles et al., 1973; Manheim and Sayles, 1974) to be related to sulfate reduction. Alteration of basalts of layer 2 or volcanic ash in the sediments to clay minerals or zeolites also appears to be a major cause of observed changes (Lawrence et al., 1975; Perry et al., 1976). Usually Ca increases with depth while  $Mg^{+2}$ ,  $K^+$ , and  $^{18}O/^{16}O$  decrease with depth.

Oxygen isotope variations in the pore fluids are the most easily utilized in delineating the amount of alteration that has taken place in the sediments or underlying basalts. In the sediment column the pore fluids contain only a minor fraction of the total cations. In contrast, the amount of oxygen in the pore fluids is roughly the same as the amount in the solids phase (Table 1). Therefore, minor mineralogical changes can produce large changes in the chemical composition of the pore fluids, but major changes are necessary to produce major changes in the  $^{18}O/^{16}O$  of the pore fluids. Mineralogical changes in which a large  $^{18}O/^{16}O$  shift occurs are more effective in changing the  $^{18}O/^{16}O$  of pore fluid than those in which a small shift occurs.

cussion of the oxygen isotopic composition of the sediment and basalts is presented by Anderson, Lawrence, and Gieskes, and by Eslinger and Savin (this volume). Gieskes and Lawrence (this volume) discuss the chemical changes in the pore waters and relate them to the isotope changes. The reports of Donnelly, Drever, Kastner, and Perry (all in this volume) on the mineralogy and chemistry of the solids are essential in trying to pinpoint the specific mineralogical transitions.

#### MATERIAL BALANCE CALCULATIONS

Diagenetic reactions in the sediment or alteration reactions in the basalt must be responsible for the different isotopic and chemical gradients observed from site to site. Some possible reactions include the alteration of (1) volcanic ash to montmorillonite, (2) basalt to montmorillonite, (3) basalt to zeolites, (4) detrital minerals to authigenic minerals, (5) biogenic silica to chert, or (6) fossil carbonate to chalk or limestone. The change in the  $\delta^{18}O$  of the pore waters that these reactions produce can be calculated. Two closed-system models are considered. In the first model (Model A) complete equilibration of all of the recrystallized solids with the pore fluid is assumed. In the second model (Model B) local equilibrium between a small amount of recrystallizing solid and the pore fluid is assumed with the subsequent isolation of each increment of solid after recrystallization.

Either of the above models utilizes the following basic initial conditions and equations. If the mole fraction ( $x_1$ ) and isotopic composition of a component of the sediment ( $\delta_a$ ) and of the pore water ( $\delta_b$ ) prior to diagenesis or halmyrolysis are known, as well as the isotopic fraction factor between the newly forming authigenic phase and the pore water ( $\alpha_d^c$ ), the  $\delta^{18}O$  of the authigenic phase ( $\delta_c$ ), and the pore water ( $\delta_d^c$ ) can be calculated by using a material balance equation

$$x_1\delta_a + (1-x_1)\delta_b = x_1\delta_c + (1-x_1)\delta_d$$

and the equation

$$\alpha_d^c = \frac{1 + 10^{-3}\delta_c}{1 + 10^{-3}\delta_d}$$

relating the  $^{18}O/^{16}O$  of the authigenic phase and the pore water to the isotopic fractionation factor  $\alpha_d^c$ . Equations 1 and 2 give the solutions for  $\delta_d$  and  $\delta_c$ .

TABLE 1

Relationship Between Porosity and the Mole Fraction of Oxygen in the Solid Phase for a Variety of Minerals in Water

Porosity	$x_1$				
	Plagio-clase	Quartz	Diopside	Montmor-illonite	Calcite
100	0.000	0.000	0.000	0.000	0.000
90	0.137	0.149	0.143	0.133	0.140
80	0.263	0.283	0.272	0.257	0.268
70	0.379	0.403	0.391	0.372	0.386
60	0.487	0.513	0.500	0.480	0.494
50	0.588	0.612	0.600	0.581	0.594
40	0.682	0.702	0.692	0.675	0.687
30	0.769	0.786	0.778	0.764	0.773
20	0.851	0.863	0.857	0.847	0.854
10	0.927	0.934	0.931	0.926	0.929
0	1.000	1.000	1.000	1.000	1.000

Oxygen isotope material balance calculations for the Leg 35 sites are the principal subject of this report. The question we hope to answer here is how much alteration of basalt, ash, or continental detritus is needed to explain the observed  $^{18}O/^{16}O$  depletions. A detailed dis-

$$\delta_d = \frac{x_1 \delta_a + (1 - x_1) \delta_b - 1000x_1 (\alpha_d^c - 1)}{x_1 (\alpha_d^c - 1) + 1}$$

$$\delta_c = 1000 (\alpha_d^c - 1) + \alpha_d^c \cdot \delta_d$$

where

$x_1$  = mole fraction of oxygen in the solid phase  
 (1 -  $x_1$ ) = mole fraction of oxygen in the pore water phase

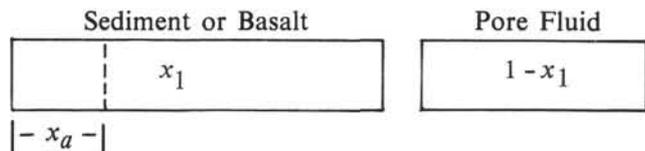
$\delta_a$  =  $\delta^{18}O$  of the solid phase prior to alteration  
 $\delta_b$  =  $\delta^{18}O$  of the pore water prior to alteration  
 $\delta_c$  =  $\delta^{18}O$  of the authigenic phase  
 $\delta_d$  =  $\delta^{18}O$  of the pore water after alteration  
 $\alpha_d^c$  = isotopic fractionation factor between the authigenic phase and the pore water

The solid lines in Figure 1 illustrate the variation in  $\delta_d$  for Model A as a function of  $x_1$  and fixed values of  $\delta_a$  and  $\alpha_d^c$ . The dashed line illustrates the variation in  $\delta_d$  for Model B for the reaction, volcanic ash to montmorillonite for 100 alteration steps to a value of  $x_1 = 0.5$ . The  $^{18}O$  depletion is somewhat larger in the second model. Values of  $\delta_a$  were chosen to be representative of the  $\delta^{18}O$  values of typical unaltered components. It was assumed the prealteration pore waters had a  $\delta^{18}O = 0$  ( $\delta_b$ ) equal to that of present-day deep ocean water. Values of  $\alpha_d^c$  have been estimated or taken from data on natural samples or experimental work (O'Neil et al., 1969; Savin and Epstein, 1970a, b; Mopper and Garlick, 1971; Sheppard et al., 1971; Wenner and Taylor, 1971; Lawrence and Taylor, 1971, 1972).

The following modifications to the models permit a consideration of the change in  $\delta_d$  as a function of the percent of solid component altered in which partial alteration takes place or inert components are present.

**Model A**

(Complete Isotopic Equilibration of the Authigenic Phase)



$$\text{Percent alteration} = \frac{x_a}{x_1} \times 100$$

Mole fraction of oxygen in the solid phase for partial alteration

$$x_1' = \frac{x_a}{x_a + 1 - x_1}$$

where  $x_a \leq x_1$

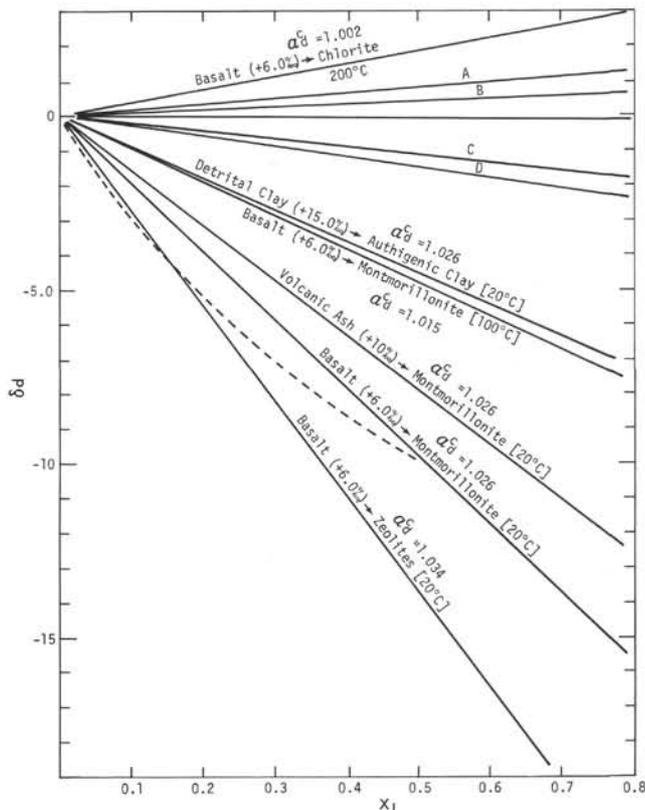


Figure 1. The  $\delta^{18}O$  of the pore water ( $\delta_d$ ) after alteration of reactants to products under isotopic equilibrium conditions in a closed system plotted as a function of the mole fraction of oxygen in the solid phase ( $x_1$ ). Each line represents a specific reaction in the closed system as illustrated. The initial value of the reactant ( $\delta_a$ ) (Taylor, 1968; Savin and Epstein, 1970a; Mopper and Garlick, 1971), the equilibrium fractionation factor  $\alpha_d^c$  (Banks and Melson, 1966; O'Neil et al., 1969; Savin and Epstein, 1970a, b; Lawrence, 1970; Mopper and Garlick, 1971; Sheppard et al., 1971; Wenner and Taylor, 1971; Lawrence and Taylor, 1971, 1972) between the authigenic product and the pore water, and the approximate temperature are given for each reaction. Curves A, B, C, and D represent the following reactions:

$$\alpha_d^c = 1.034$$

A. Biogenic Silica (+36‰) → Chert [~30°C]

$$\alpha_d^c = 1.029$$

B. Fossil Carbonate (+30‰) → Recrystallized Carbonate [22°C]

$$\alpha_d^c = 1.038$$

C. Biogenic Silica (+36‰) → Chert [~10°C]

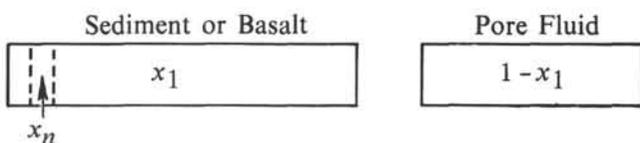
$$\alpha_d^c = 1.033$$

D. Fossil Carbonate (+30‰) → Recrystallized Carbonate [7°C]

The initial value of the pore water ( $\delta_b$ ) is assumed to equal that of present-day ocean water. The dashed curve represents isotopic equilibration of volcanic ash with the same initial conditions but with the alteration proceeding in 100 steps to a value of  $x_1 = 0.5$  with the montmorillonite being removed at each step from further reaction in the system.

### Model B

(Stepwise Isotopic Equilibration of the Authigenic Phase)



$$x_1 = \sum_{n=1}^n x_n$$

$$\text{Percent alteration (m steps)} = \frac{mx_n}{x_1} \times 100$$

where  $m \leq n$

Mole fraction of oxygen in the solid phase for one step of alteration

$$x_1' = \frac{x_n}{x_n + 1 - x_1}$$

Mole fraction of oxygen in the solid phase for  $m$  steps of alteration

$$m x_1' \text{ where } m < n$$

$$x_1 \text{ where } m = n$$

Table 1 gives the relationship between porosity and  $x_1$  for a variety of minerals. Note that  $x_1$  has a fairly restricted value for a particular porosity for a diverse group of minerals. Figure 2 illustrates the change in  $\delta_d$  as a function of the percent of a particular component altered for three reactions at three different porosities for Models A and B. Note that Model B yields slightly lower  $\delta_d$  values. Also note that the lower porosity the greater the effect on  $\delta_d$  for a given percent alteration. For example, alteration of a few percent basalt with a porosity of 15% can decrease  $\delta^{18}\text{O}$  of the in situ pore waters by several per mil. In ash as a sediment with a porosity of 40%, 10%-20% alteration would be required to produce the same effect. At 70% porosity, 50% alteration would be required. This effect is principally a reflection of a higher value for  $x_1$ .

## RESULTS AND DISCUSSION

The  $\delta^{18}\text{O}$  of the pore waters from all of the sites of Leg 35 decreases with depth (Figure 3). The change in  $\delta^{18}\text{O}$  per unit of depth, however, differs markedly from site to site. For example, Site 323 exhibits a decrease of 0.4‰ per 100 meters whereas Site 322 exhibits a decrease of only 0.1‰ per 100 meters. Differences in  $\delta^{18}\text{O}$  gradients at different locations from sites of Legs 8 and 15 Lawrence et al., 1975; (Perry et al., 1976) were attributed principally to differential alteration of basalts of layer 2 or alteration of ash in the sediments.

The sediments found on Leg 35 are composed principally of continental detritus with moderate amounts of biogenic silica and montmorillonite clays which were derived at least in part from the alteration of volcanic ash (Drever, Perry, this volume). Basalts were cored at Sites 322 and 323, but basement at Site 325 is a few hundred meters below the bottom of the hole and almost 2 km from the sea floor at Site 324. Alteration of continental detritus, basalt, or volcanic ash must be the cause of the observed  $^{18}\text{O}$  depletion at Sites 322 and 323 and probably also at Sites 324 and 325. Biogenic silica recrystallization simply cannot produce the  $^{18}\text{O}$  depletion observed. (See Figure 1.)

How much alteration of each of the principal constituents must have taken place to produce observed depletions in  $\delta^{18}\text{O}$ ? The quantities can be calculated using the average  $\delta_d$  for each site and taking the entire sediment-basalt column as the closed system. Table 2 gives a list of the amounts of alteration of basalt (15% porosity), of ash (40%-60% porosity), and of continental detritus (55%-60% porosity) to montmorillonite necessary for each site. As no account for loss by diffusion or advection due to compaction is considered, these quantities must be viewed as minimum values. Also given in Table 2 are the calculated times needed to replenish the observed  $^{18}\text{O}$  depletion for each site assuming a diffusion coefficient of  $3 \times 10^{-6} \text{ cm}^2/\text{sec}$  for  $\text{H}_2\text{O}^{18}$  and the presence of  $^{18}\text{O}/^{16}\text{O}$  gradients like those presently existing for the entire history of the cored sediments.

### Site 322

At Site 322 relatively small amounts of the major constituents could have been altered to produce the observed  $^{18}\text{O}$  depletions. For example, the complete alteration of 3 meters of basalt or 10% alteration of 30 meters of basalt can account for the observed  $^{18}\text{O}$  depletion. Perry (this volume) found smectite present in ultrasonically cleaned slightly altered basalts. Donnelly (this volume), however, reports that the basalts from Site 322 were only slightly altered.

Larger amounts of ash alteration or continental detritus alteration are necessary to explain the observed  $^{18}\text{O}$  depletion. Considering the amount of continental detritus present, however, only 2% alteration of all the sediments would be necessary. Likewise, ash alteration making up 1.5% of the sediments would be sufficient. In the lower part of Site 322, Perry (this volume) reports that the clay minerals of the sediment are dominated by a smectite probably derived by alteration of volcanic ash. Alteration of ash making up 10% of the sediments in a 70-meter interval would have been sufficient.

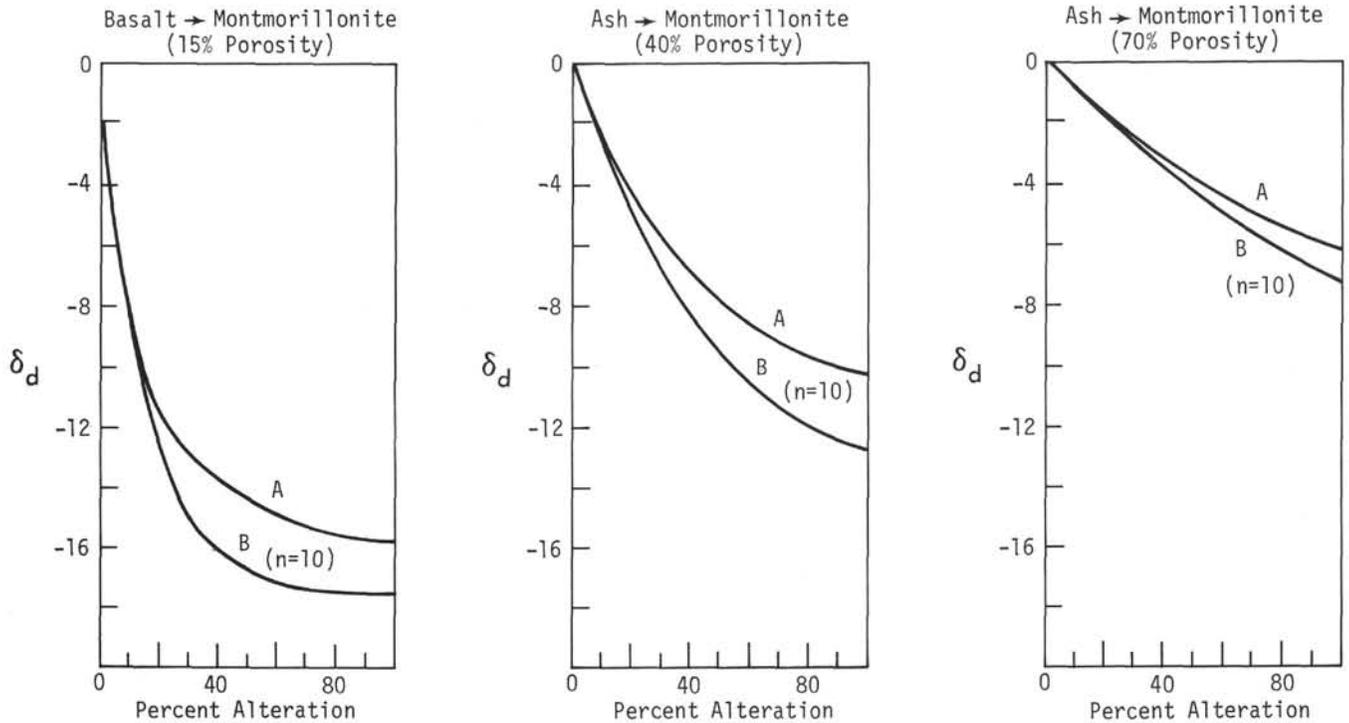


Figure 2. The  $\delta^{18}\text{O}$  of the pore water ( $\delta_d$ ) after alteration as a function of the percent alteration of the solid phase for three reactions:



$$\delta_a = +6.0^\circ/\text{‰}$$

$$\delta_b = 0.0^\circ/\text{‰}$$

$$\alpha_d^c = 1.024$$

$$x_1 = 0.9$$

$$\text{Porosity} = 15\%$$



$$\delta_a = +10.0^\circ/\text{‰}$$

$$\delta_b = 0.0^\circ/\text{‰}$$

$$\alpha_d^c = 1.025$$

$$x_1 = 0.7$$

$$\text{Porosity} = 40\%$$



$$\delta_a = +10.0^\circ/\text{‰}$$

$$\delta_b = 0.0^\circ/\text{‰}$$

$$\alpha_d^c = 1.026$$

$$x_1 = 0.4$$

$$\text{Porosity} = 70\%$$

Curves labeled A were calculated using Model A in which complete equilibration of all of the alteration product with the pore fluid was assumed. Curves labeled B were calculated using Model B in which alteration proceeded in 10 steps. At each step 10% of the solid was altered. The altered solid was then removed from further isotopic equilibration. The pore fluid equilibrated at each step.

If the observed  $^{18}\text{O}/^{16}\text{O}$  gradient were active during the entire history of the sedimentary column all the estimates made above would have to be multiplied by a factor of three, 25 m.y./8 m.y. (see Table 2). If increasing temperature with increasing depth of burial increases the rate of any of the possible reactions, one might have expected a lower  $^{18}\text{O}/^{16}\text{O}$  gradient in the past and therefore intermediate amounts of alteration would have been sufficient. A larger gradient in the past would mean even greater amounts than the mentioned factor of three greater.

### Site 323

In contrast to Site 322, the pore fluids at Site 323 are depleted in  $^{18}\text{O}$  by a large amount. The amount of alteration of major constituents necessary to account for this depletion must have been correspondingly larger (see Table 2). For example, if basalt alteration were the sole cause, 28 meters of basalt would have to have been completely altered or 280 meters would have to have

been 10% altered. The basalts of Site 323 do contain numerous clay veins and  $\delta^{18}\text{O}$  values of the basalts analyzed for the upper 30 meters of basalt range from +6.9 to +11.2 $^\circ/\text{‰}$ . The clay veins (Drever, Kastner, this volume) are composed of saponite and celadonite and have  $\delta^{18}\text{O}$  values (Anderson, Gieskes, and Lawrence, this volume) of +19.6 to +24.2 $^\circ/\text{‰}$ . Evaluating the altered state of the basalts overall is difficult because only partial recovery of the basalts took place. Probably highly altered parts are preferentially lost during drilling, thereby biasing our sample on the fresh side.

The quantity of ash alteration needed to account for the  $^{18}\text{O}$  depletion is on the order of 45 to 65 meters (Table 2). A brown claystone about 60 meters thick composed mostly of montmorillonite occurs in the basal sediments. Drever (this volume) suggests that the source of the material was largely volcanic. Donnelly (this volume) from major element ratio data of the bulk sediments argues against a volcanic source for the

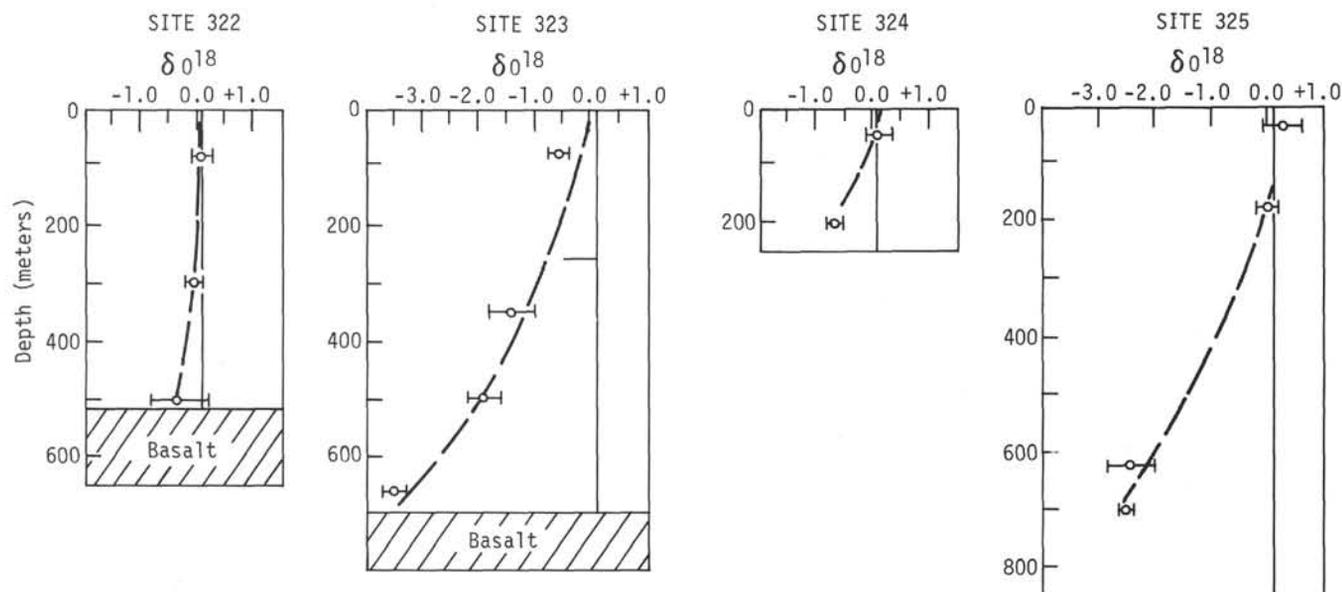


Figure 3. The measured  $\delta^{18}\text{O}$  values (relative to SMOW) of the pore fluids of Leg 35. Duplicate extractions were made on each sample using the method of Epstein and Mayeda (1953). Error bars are shown. The vertical line shown for each site is the  $\delta^{18}\text{O}$  value of present-day Pacific Deep Water.

TABLE 2  
Material Balance Calculations of Oxygen Isotopes for Leg 35

Site	$^{18}\text{O}$ Sink	Meters Needed to Cause Observed $^{18}\text{O}$ Depletion	Age at the Bottom of Site (m.y.)	Time Needed to Replenish $^{18}\text{O}$ Depletion (m.y.)
322	Basalt (15%)	3.1	25	7.9
	Ash (60%)	7.1		
	Continental Detritus (60%)	10.7		
323	Basalt (15%)	27.8	70	13.2
	Ash (60%)	64.9		
	Ash (40%)	46.4		
324	Basalt (15%)	1.8	4	1.0
	Ash (55%)	3.8		
	Continental Detritus (55%)	5.8		
325	Basalt (15%)	16.5	25	10.9
	Ash (55%)	34.7		
	Continental Detritus (55%)	54.1		

Note: A value of  $x_1$  sufficient to explain  $\delta_d$  taking each site as a closed system was determined. From  $x_1$  determination of the number of meters of pre-alteration component needed was possible.  $\delta_d$  used for each site was the average value.  $\delta_d$  was set equal to  $+6.0\text{‰}$  for basalt,  $+10.0\text{‰}$  for volcanic ash, and  $+15.0\text{‰}$  for continental detritus.  $\delta_b$  was set equal to  $0.0\text{‰}$ .

$\alpha_d^c$  was set equal to 1.025.

brown claystone. The  $\delta^{18}\text{O}$  of the unit has a range of  $+18.8$  to  $+20.8\text{‰}$  with one sample at  $+25.0\text{‰}$  (Anderson, Gieskes, and Lawrence, Eslinger and Savin, this volume). Eslinger has suggested that the unit is only partially composed of, perhaps one half, volcanic material altered in place because of the low  $\delta^{18}\text{O}$  values. Montmorillonite formed in seawater at  $20^\circ\text{C}$  should have a  $\delta^{18}\text{O}$  in the range  $+24$  to  $+26\text{‰}$ . This assumed  $\delta^{18}\text{O}$  range, however, is for an infinite reservoir of water. If alteration of ash occurred under closed-system

conditions and a pore water with a  $\delta_d = -3.0$  resulted, the  $\delta^{18}\text{O}$  of the montmorillonite formed assuming  $\alpha_d^c = 1.025$  would be  $+21.9\text{‰}$  (see Figures 1 and 2 and Equation 2). Therefore, the low  $^{18}\text{O}/^{16}\text{O}$  values of the montmorillonite need not require a low  $^{18}\text{O}/^{16}\text{O}$  continental source for the montmorillonite.

Could ash alteration higher in sediment column be an important  $^{18}\text{O}$  sink? Significant quantities of ash higher up in the sediments is not indicated. X-ray data (Drever, this volume) indicate clay mineral compositions fairly

typical of continental detritus. Therefore if ash alteration is a contributing factor at these higher levels, the quantity of ash must have been small and evenly distributed, <10% spread over the whole sediment column.

The alteration of continental detritus to montmorillonite or any other similar clay mineral as a sink for  $^{18}\text{O}$  requires quantities in excess of 100 meters (see Table 2), or alteration of more than 15% of continental detritus over the entire sediment. No obvious trends in clay mineralogy suggest an effect of such magnitude (Drever, this volume). Also, Eslinger and Savin (this volume) show that even the finest grained quartz has not undergone  $^{18}\text{O}/^{16}\text{O}$  exchange with the pore waters. Because quartz is a major constituent of continental detritus, the quantities needed to explain the  $^{18}\text{O}$  depletion must be much greater than 100 meters.

If the observed  $^{18}\text{O}/^{16}\text{O}$  gradient in the pore waters has been active for the entire history of the sediment column, all of the above estimates made would have to be multiplied by a factor greater than five, 70/13 (see Table 2). If the gradient has increased with time perhaps as a result of higher reaction rates at higher temperatures resulting from deeper burial, intermediate amounts of alteration would be sufficient. If the gradient has decreased with time, even greater amounts than those suggested by the factor of five would have been required.

#### Site 324

At Site 324 alteration of continental detritus or volcanic ash must be the principal cause of the observed  $^{18}\text{O}$  depletion in the pore fluids. Basalt basement is almost 2 km distant from the sediment-water interface and the sedimentation rate undoubtedly must be very high so close to the Antarctic continent. The amount of alteration needed to explain the  $^{18}\text{O}$  depletion in the pore waters requires only 3.8 meters of ash or 5.8 meters of continental detritus. Therefore alteration of only 2% ash or 3% continental detritus distributed throughout the column can explain the  $^{18}\text{O}$  depletion. Traces of volcanic glass were found in Cores 4, 5, and 6. Also volcanic ash may be present at depths greater than 200 meters. If the  $^{18}\text{O}/^{16}\text{O}$  gradient observed has been present for the 4 m.y. history of these sediments the amount of alteration needed would increase by a factor of four, 4/1.

#### Site 325

Moderate amounts of alteration of basalt, ash, or continental detritus are necessary to explain the  $^{18}\text{O}$  depletion at Site 325 (see Table 2). Alteration of continental detritus and volcanic ash are probable causes of  $^{18}\text{O}$  depletion. Perry (this volume), using X-ray diffraction studies, finds a high smectite content of the clays in the lower portion of this hole. He suggests that the source of these smectites was volcanic ash. Alteration of continental detritus may also be a sink for  $^{18}\text{O}$ , but the quantities needed exceed 50 meters and are probably double this because quartz is a major constituent. Eslinger and Savin's work (this volume) at Site 323 indicates that quartz does not undergo significant  $^{18}\text{O}/^{16}\text{O}$  exchange. Because recovery of deeper sediments and basalt at this site was not achieved, it is difficult to

evaluate possible  $^{18}\text{O}$  sinks at greater depth. The estimates made here must be increased to a degree depending on whether the  $^{18}\text{O}/^{16}\text{O}$  gradient were higher or lower on the average in the past at this site.

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