# 16. INTERSTITIAL WATER STUDIES, LEG 15 – STABLE OXYGEN AND CARBON ISTOTOPE VARIATIONS IN WATER, CARBONATES, AND SILICATES FROM THE VENEZUELA BASIN (SITE 149) AND THE AVES RISE (SITE 148)<sup>1</sup>

James R. Lawrence<sup>2</sup>, Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York

#### INTRODUCTION

The detrital components of sediments almost immediately after deposition begin to undergo chemical reactions involving specific mineral or chemical components and the pore waters. The qualitative and quantitative character and the sequence of diagenetic reactions that take place from the initial soft sediment state to the lithification stage are poorly understood. The overall objective of this investigation is to combine studies of pore water chemistry, mineralogy, and  $O1^8/O1^6$ ,  $C1^3/C1^2$ , and D/H studies of ocean sediments to gain a more thorough understanding of diagenetic changes.

The specific purpose of this investigation is to determine to what degree the  $O^{18}/O^{16}$  and/or  $C^{13}/C^{12}$  of the pore waters, carbonates, and silicates are unchanged since the time of deposition as opposed to what degree they have changed as a result of diagenetic processes. If little or no isotopic exchange has taken place between the sediments and the pore waters, isotopic studies of carbonate fossils, for example, can be used to determine paleotemperatures in the ocean and changes in surface or deep water  $O^{18}/O^{16}$ and  $C^{13}/C^{12}$ . If, on the other hand, significant isotopic changes have taken place as a result of isotopic exchange between the pore waters and sediments or recrystallization of the solids, isotopic studies of the pore waters and authigenic minerals should reveal details about the mechanisms of diagenesis.

The pore waters and sediments were sampled at 20 horizons at each site. Immediately after the squeezing of the sediment for pore water analyses, several 5 mg samples of the pore water were sealed, using a torch, in pyrex glass capillaries for later  $O^{18}/O^{16}$  analysis by the method of O'Neil and Epstein (1966). The remaining cake of sediment was sealed in an airtight bag for later sampling. A slice of each of these cakes was sampled at Lamont-Doherty Geological Observatory several months later. The samples were air dried and ground up using a mortar and pestle. These bulk samples, representing stratigraphic horizons of a few cm in thickness, were analyzed for the  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  content of the carbonate fraction by the method

described by McCrea (1950). A separate portion of the bulk sediment was treated with a sodium acetate-acetic acid buffer to remove the carbonate. This carbonate-free portion was analyzed for  $O^{18}/O^{16}$  by the method of Clayton and Mayeda (1963). All  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  analyses are reported with respect to SMOW and PDB, respectively.

The continuous 400-meter section of calcareous and siliceous-rich sediments from Site 149, ranging in age from Pleistocene to Eocene, is described in Table 1. The variations of carbonate and nonbiogenic silicate content in this core are illustrated in Figures 1 and 2, respectively. Figure 3 illustrates the variation with depth of X-ray amorphous material consisting mostly of biogenic silica in the lower half of the hole. The determinations were made by subtracting the carbonate and nonbiogenic silicate percentages from 100 percent, thereby giving a rough estimation of the quantity of X-ray amorphous material.

TABLE 1 Description of Sediments, Leg 15

| Depth<br>(m) | Description<br>Site 149   |  |  |  |  |  |  |  |
|--------------|---|--|--|--|--|--|--|--|
|              |   |  |  |  |  |  |  |  |
| 0-75         | Foraminiferal and nannoplankton chalk and marl ooze with carbonate content decreasing downward.   |  |  |  |  |  |  |  |
| 75-96        | Brown clay with a very low carbonate content.   |  |  |  |  |  |  |  |
| 96-139       | Foraminiferal and nannoplankton marl and clay with<br>carbonate content increasing erratically downward.  |  |  |  |  |  |  |  |
| 139-185      | Foraminiferal and nannoplankton chalk and marl.   |  |  |  |  |  |  |  |
| 185-270      | Foraminiferal nannoplankton chalk and radiolarian<br>nannoplankton marl with a large increase in radiolar-<br>ian and volcanic debris downward.   |  |  |  |  |  |  |  |
| 270-381      | Calcareous radiolarian ooze and indurated radiolarian<br>nannoplankton marl with a large variation in propor-<br>tions of radiolarian versus carbonate. Ash layers and<br>pumice fragments are common. Chert horizons occur<br>at 285 and 380 meters. |  |  |  |  |  |  |  |
|              | Site 148  |  |  |  |  |  |  |  |
| 0-64         | Soft foraminiferal and nannoplankton greenish gray marl.  |  |  |  |  |  |  |  |
| 64-111       | Soft foraminiferal and nannoplankton dark greenish-<br>gray clay with a few scattered ash beds in the upper   |  |  |  |  |  |  |  |
| 111-249      | Foraminiferal and nannoplankton dark greenish-gray<br>marl with increasing compactness in the lower<br>40 meters.   |  |  |  |  |  |  |  |
| 249-272      | Lithified volcanic sand and clay, deeply oxidized.  |  |  |  |  |  |  |  |

The continuous 250-meter section of marl and calcareous clay from Site 148, ranging in age from early

<sup>&</sup>lt;sup>1</sup>Lamont-Doherty Geological Observatory Contribution No. 1904.

 $<sup>^{2}</sup>$  The author gratefully acknowledges financial support for this work by the National Science Foundation under contract GA 17724.



Figure 1. Weight percent CaCO<sup>3</sup> in the bulk sediment as a function of depth at Site 149. Quantities were determined by standard LECO (decarbonation) techniques of DSDP.



Figure 2. Weight percent nonbiogenic detrital silicates (sum of quartz, feldspar, and clay minerals) as a function of depth at Site 149. Quantities were determined by X-ray diffration techniques as part of standard mineralogical determinations by DSDP.

Pliocene to the present and unconformably overlying Miocene volcanic sand and clay, is described in Table 1. The variation in carbonate content is illustrated in Figure 8. The remainder of the sediments is composed almost entirely of nonbiogenic detrital silicate material. The amount of biogenic silica is relatively low throughout the hole.

### DISCUSSION OF RESULTS

#### Site 149

The most significant changes in  $O^{18}/O^{16}$  at Site 149 were in the pore waters (see Figure 4). The  $O^{18}/O^{16}$ decreases from a  $\delta O^{18} = +0.3\pm0.2^{\circ}/_{\circ\circ}$  in the pore waters near the sediment-water interface, a value very near Atlantic Deep Water (+ $0.12^{\circ}/_{\circ\circ}$ , Craig and Gordon, 1965) to a minimum value of  $-2.7\pm0.3^{\circ}/_{\circ\circ}$  at 285 meters in Eocene sediments. Such a large change in the  $O^{18}/O^{16}$ might be explained by (a) diagenesis of a major portion of the sediments, (b) an influx of isotopically light waters from a deep source, or (c) an increase in the  $O^{18}/O^{16}$  of the ocean of  $> 3^{\circ}/_{\circ\circ}$  since the Eocene. Also the fact that



Figure 3. Calculated weight percent X-ray amorphous solids at Site 149. Calculated by subtracting CaCO3 (from Figure 1) plus detrital silicates (from Figure 2) from 100%.

diffusion of Atlantic Deep Water into the sediments is decreasing the contrast between the O18/O16 of ADW and the pore waters must be considered. The fact that the minimum O18/O16 does not occur at the deepest horizon would appear to eliminate possibilities (b) and (c) as singular explanations. If a deep source were responsible, the  $O^{18}/O^{16}$  should be lowest at the greatest depth. Also it is unlikely that the  $O^{18}/O^{16}$  of the pore waters represents paleo ocean water because even the most extreme model for change in the O18/O16 of ocean water (Perry and Tan, 1972) suggests and O18/O16 increase of only 0.5 to 1°/00 over the last 40 m.y. That the observed variation in  $O^{18}/O^{16}$  is a result of recrystallization of the sediments or isotopic exchange between the sediments and the pore waters is suggested by the fact that the minimum  $O^{18}/O^{16}$ value is observed at the first chert horizon in a region with a high content of X-ray amorphous sediment consisting primarily of biogenic silica (see Table 1 and Figure 3). Biogenic silica has been shown to be very subject to isotopic exchange (Mopper and Garlick, 1971).

Several diagenetic reactions may be important in lowering the  $O^{18}/O^{16}$  of the pore waters. These include (a) the alteration of volcanic ash to chert, authigenic clay



Figure 4.  $\delta O^{18}$  of the pore waters (relative to SMOW) from Site 149 plotted as a function of depth. Also shown are  $\delta O^{18}$  values of carbonate-free bulk solids.

minerals, and/or zeolites, (b) the alteration of biogenic silica to chert, (c) the recrystallization of fossil carbonate to authigenic carbonate, and (d) the alteration of detrital clay minerals to authigenic clay minerals.

The probable relative importance of each of these reactions in lowering the  $O^{18}/O^{16}$  of the pore water depends on the ratio of the oxygen reservoir of each of these materials to the oxygen reservoir of the pore water. It also depends on the degree of enrichment in  $O^{18}$  in going from the unaltered sediment to its authigenic counterpart. In order to consider the effect of the above reactions on bringing about changes in the  $O^{18}/O^{16}$  of the pore waters, it is instructive to consider a closed system model of diagenesis in which diffusion of Atlantic Deep Water into the sediments is ignored. Diffusive effects may then be considered separately.

Table 2 gives a list of the relative sizes of the oxygen reservoir in pore waters compared to the oxygen reservoir in the sediments as a function of the porosity for sediments composed of calcite or opal. Porosities of 40 to 70% are commonly found in the sediments at Site 149. Thus for a given volume of wet sediment the pore water commonly makes up from 30 to 60% of the total oxygen reservoir. If the mole fraction  $(x_1)$  and isotopic composition of a component of the sediment  $(\delta_a)$  and the pore water  $(\delta_b)$  prior to diagenesis are known, as well as the isotopic fractionation factor between the newly forming authigenic phase and the pore water  $(\alpha_d^{\zeta})$ , the  $\delta O^{18}$  of the authigenic phase  $(\delta_c)$ , and the pore water  $(\delta_d)$  can be calculated by

using the material balance equation (1) and an equation (2) relating the O<sup>18</sup>/O<sup>16</sup> of the authigenic phase and the pore water to the isotopic fractionation factor  $\alpha_d^c$ . Equations (3) and (4) give the solutions for  $\delta_c$  and  $\delta_d$ .

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

$$\alpha_d^c = \frac{1 + \frac{\delta_c}{1000}}{1 + \frac{\delta_d}{1000}}$$
(2)

- $x_1$  = mole fraction of oxygen in the sediment phase
- $(1-x_1)$  = mole fraction of oxygen in the pore water phase
  - $\delta_a = \delta O^{18}$  of the sediment phase prior to diagenesis
  - $\delta_b = \delta O^{18}$  of the pore water prior to diagenesis
  - $\delta_c = \delta O^{18}$  of the authigenic phase
  - $\delta_d = \delta O^{18}$  of the pore water after diagenesis
  - $\alpha_d^c$  = isotopic fraction factor between the authigenic phase and the pore water during diagenesis

$$\delta_d = \frac{x_1 \delta_a + (1 - x_1) \delta_b - 1000 x_1 \left( \alpha_d^c - 1 \right)}{x_1 \left( \alpha_d^c - 1 \right) + 1}$$
(3)

$$\delta_c = 1000(\alpha_d^c - 1) + \alpha_d^c \cdot \delta_d \tag{4}$$

Table 3 contains a list of solutions for  $\delta_c$  and  $\delta_d$  from various values of  $x_1$ ,  $\delta_a$ ,  $\delta_b$  and  $\alpha_d^c$  for a selection of diagenetic reactions. Values of  $x_1$  and  $\delta_a$  have been chosen to be representative of the concentrations and  $\delta O^{18}$  values of the prediagenetic components in the sediments. It has been assumed that the prediagenetic pore waters had a  $\delta O^{18}$  equal to that of ADW. Values of  $\alpha_d^c$  have been estimated or taken from data on natural samples or experimental work. From Table 3 it can be seen that the most favorable diagenetic reactions for lowering the  $O^{18}/O^{16}$  of the pore waters involve converting volcanic ash

TABLE 2

Oxygen Reservoirs in Sediments and Pore Waters Ratio of Mole Percent Oxygen in Pore Waters to Opal Calcite (SiO2 · 0.1 H2O) Sediment Porosity Sediment 100 90 0.86 0.87 80 0.73 0.75 70 0.63 0.61 60 0.51 0.53 0.40 50 0.43 40 0.32 0.33 30 0.22 0.24 20 0.15 0.16 10 0.07 0.08 0 0.00 0.00

to chert or detrital clay minerals to authigenic clay minerals. This is because the reaction results in a large uptake of  $O^{18}$  by the newly formed authigenic mineral in comparison to its prediagenetic counterpart. However, because these components are not the most abundant components in the sediments at Site 149, this importance is reduced.

As can be seen from Table 3 the conversion of biogenic silica to chert or fossil carbonate to authigenic carbonate may decrease or increase the O<sup>18</sup>/O<sup>16</sup> in the pore waters depending on the selection of values of  $x_1$ ,  $\delta_a$ ,  $\delta_b$ , and  $\alpha_d^c$ . Also it can be seen that even in choosing favorable values for the parameters  $\delta_a$ ,  $\delta_b$  and  $\alpha_d^c$ , a large value for  $x_1$  is needed to get significantly low values for  $\delta_d$ . This means that even though biogenic silica and fossil carbonate are abundant in the sediments, a very large portion of each must undergo diagenesis to result in low values for  $\delta_d$ .

The minimum  $\delta O^{18}$  value in the pore waters occurs at 285 meters at the horizon at which the first appearance of a chert layer 0.3 meters thick is observed (see Figure 4 and Table 1). This chert has resulted almost entirely from the alteration of a volcanic ash layer as is indicated by the prevalence of relic ash textures (F. Maurrasse, personal communication). Using a value of  $x_1 = 0.05$ , which corresponds to reaction with a column of pore water 5 to 10 meters thick, a  $\delta_c$  of  $-1.1^{\circ}/_{\circ\circ}$  will result from complete alteration of the ash. Although this is significant, it is apparent that only a small part of the low  $O^{18}$  anomaly can be explained by the formation of this chert layer.

The fact that the lowest  $O^{18}/O^{16}$  of pore waters is observed in the region of the core where the biogenic silica content is very high (see Table 1 and Figure 3) suggests that the alteration of biogenic silica to chert may be important in lowering the  $O^{18}/O^{16}$  of the pore waters. But the importance of this reaction is not easily evaluated until values for  $\delta_a$  and  $\alpha_d^c$  can be determined. Note from the selection of values for these parameters in Table 3 that a decrease or increase in  $O^{18}/O^{16}$  of the pore waters may result during diagenesis.

The  $\delta O^{18}$  of the noncarbonate portion of the sediment consisting of biogenic silica and detrital silicates (see Figure 4) increases from  $+25^{\circ}/_{oo}$  at 235 meters to  $+32^{\circ}/_{oo}$ at 380 meters suggesting a possible increase in the O<sup>18</sup>/O<sup>16</sup> of biogenic silica as a result of isotopic exchange or recrystallization, which in turn would decrease the O<sup>18</sup>/O<sup>16</sup> of the pore waters. However, the biogenic silica to detrital silicate ratio also increases with depth (see Figures 2 and 3), which may explain the observed increase in O<sup>18</sup>/O<sup>16</sup>. Nonbiogenic detrital silicates have a much lower  $\delta O^{18}$  than biogenic silica,  $\sim +15^{\circ}/_{oo}$  (Savin and Epstein, 1970).

Another possible important reaction may be the alteration of detrital clay minerals to authigenic clay minerals in the 220 to 390 meter region. Using a reasonable value of  $x_1 = 0.1$  (see Figure 2) and reasonable values for  $\delta_a$  and  $\alpha_d^c$  (see Table 3), the reaction results in a 1.0% decrease in the O<sup>18</sup>/O<sup>16</sup> of the pore water.

The effect of recrystallization of carbonate fossil debris on the O<sup>18</sup>/O<sup>16</sup> of the pore waters can be evaluated in detail because the parameters  $x_1$ ,  $\delta_a$  and  $\alpha_d^c$  can be determined within narrow limits. Figure 5 shows the observed variations of the O<sup>18</sup>/O<sup>16</sup> of bulk carbonate at Site 149. Also illustrated is a temperature curve for Site 149 using a geothermal gradient of 4°C/100 meters (calculated geothermal gradient from temperature measurements in the holes [> 200 m] from Leg 19 of DSDP).

From the pore water  $O^{18}/O^{16}$  values and this temperature curve, a curve representing CaCO<sub>3</sub> in isotopic equilibrium with these pore waters has been calculated. From a comparison of the natural sample data with this curve it can be seen that the carbonates in the *upper* portions of the core are far out of isotopic equilibrium with

TABLE 3 Diagenetic Reaction Effects on the O18/O16 of Pore Waters

| Prediagenetic<br>Component | Authigenic<br>Product          | <i>x</i> <sub>1</sub> | δα    | δb   | $a_d^c$ | Temp.<br>°°C | δ <sub>c</sub> | δd   | Comments  |
|----------------------------|--------------------------------|-----------------------|-------|------|---------|--------------|----------------|------|---|
| Volcanic ash               | Chert                          | 0.05                  | +12.0 | +0.1 | 1.036   | 12-20        | +34.9          | -1.1 | $a_d^c$ estimated from data by Savin (1967) and Mopper and                              |
|                            |                                | 0.10                  | + 8.0 | +0.1 | 1.039   | 4-12         | +35.9          | -3.0 | Garlick (1971)  |
| Detrital clay<br>minerals  | Authigenic<br>clay<br>minerals | 0.05                  | +18.0 | +0.1 | 1.026   | 12-20        | +25.7          | -0.3 | $a_d^c$ estimated from data by Savin and Epstein (1970a) and Lawrence and Taylor (1971) |
|                            |                                | 0.10                  | +15.0 | +0.1 | 1.026   | 12-20        | +25.0          | -1.0 |   |
|                            |                                | 0.20                  | +12.0 | +0.1 | 1.028   | 4-12         | +24.8          | -3.1 |   |
| Biogenic<br>silica         | Chert                          | 0.10                  | +38.0 | +0.1 | 1.036   | 12.20        | +36.3          | +0.3 | $a_{d}^{C}$ estimated from data by Savin (1967) and Mopper and                          |
|                            |                                | 0.20                  | +35.0 | +0.1 | 1.036   | 12-20        | +35.9          | -0.1 | Garlick (1971)  |
|                            |                                | 0.30                  | +35.0 | +0.1 | 1.036   | 12-20        | +35.8          | -0.2 |   |
|                            |                                | 0.50                  | +38.0 | +0.1 | 1.036   | 12-20        | +37.1          | +1.0 |   |
|                            |                                | 0.50                  | +35.0 | +0.1 | 1.036   | 12-20        | +35.5          | -0.4 |   |
|                            |                                | 0.50                  | +35.0 | +0.1 | 1.038   | 4-12         | +36.5          | -1.5 |   |
| Fossil<br>carbonate        | Authigenic<br>carbonate        | 0.20                  | +32.0 | +0.1 | 1.029   | 22           | +29.7          | +0.7 | $a_d^c$ Epstein et al. (1953)   |
|                            |                                | 0.20                  | +29.0 | +0.1 | 1.031   | 15           | +30.6          | -0.3 |   |
|                            |                                | 0.50                  | +32.0 | +0.1 | 1.029   | 221          | +30.6          | +1.5 |   |
|                            |                                | 0.50                  | +28.0 | +0.1 | 1.029   | 22           | +28.5          | -0.4 |   |
|                            |                                | 0.50                  | +29.0 | +0.1 | 1.031   | 15           | +30.0          | -0.9 |   |
|                            |                                | 0.50                  | +29.5 | +0.1 | 1.033   | 7            | +31.3          | -1.7 |   |
|                            |                                | 0.50                  | +28.0 | +0.1 | 1.033   | 7            | +30.5          | -2.4 |   |



Figure 5.  $\delta O^{18}$  (measured) of the bulk carbonate (relative to SMOW) from Site 149 plotted as a function of depth. The temperatures of the sediments are estimated using a geothermal gradient of 4°C/100 meters (from temperature data in sediments of Leg 19, DSDP). Using the above geothermal gradient and the  $\delta O^{18}$  of the pore waters (from Figure 4), the  $\delta O^{18}$  of a hypothetical calcite in equilibrium with those waters is calculated using the calcite-water curve of Epstein et al. (1953).

the pore waters, and recrystallization of these fossil carbonates will decrease the  $O1^8/O1^6$  of the pore waters. An examination of Table 3 illustrates the degree to which recrystallization using a variety of parameters can decrease the  $O1^8/O1^6$  of the pore waters. For example, using  $\delta_a$  of  $+29^\circ/_{oo}$  and recrystallizing at 7 to  $15^\circ$ C can result in a 0.3 to  $0.9^\circ/_{oo}$  reduction in the  $O1^8/O1^6$  of the pore waters. Thus in the upper portion of the core the diagenesis of the carbonate may be contributing significantly to lower the  $O1^8/O1^6$  of the pore waters. However, the  $O1^8/O1^6$  of the fossil carbonate in the Pleistocene has probably not undergone much diagenesis. The  $O1^8/O1^6$ , variations in this region are typical of  $O1^8/O1^6$  variations found in unrecrystallized forams of the Caribbean (Emiliani, 1966; Broecker and van Donk, 1970).

In the lower part of the core, the comparison of the  $\delta O^{18}$  data with the equilibrium curve indicates that the carbonate is very near to equilibrium with the pore waters, perhaps suggesting it has recrystallized or been exchanged. However, this comparison suggests that recrystallization of the carbonate currently will bring about an increase in the  $\delta O^{18}$  of the pore waters in the lower portion of this hole. Therefore, presently, recrystallization of the carbonate in this region cannot explain the observed anomaly of low  $O^{18}$  pore waters. If the geothermal gradient were lower,

perhaps  $3^{\circ}C/100$  meters, the equilibrium curve would be shifted to the right and recrystallization of the carbonate might contribute under those conditions to a lowering of the  $O^{18}/O^{16}$  of the pore water. Also at an earlier time such as the Pliocene, when the depth to this region was less, the temperatures may have been lower, and at that time recrystallization of the carbonate may have been important in lowering the  $O^{18}/O^{16}$  of the pore waters.

Taking all of the possible diagenetic reactions into account suggests that they may contribute significantly to a lowering of the O<sup>18</sup>/O<sub>16</sub> of the power waters but may not be the only cause of the observed low O18 of the pore waters. Certainly the evidence is strong that a significant portion of the pore water in the vicinity of the O18/O16 minimum is a result of diagenetic reactions. However, it cannot be ruled out that this effect may be superimposed on a general decrease in  $O^{18}/O^{16}$  of the pore waters with depth caused by a deep source of low O<sup>18</sup>/O<sup>16</sup> water. The Eocene to Cretaceous sediments at Site 146 directly below the sediments at Site 149 may be a source because they exhibit a much greater degree of recrystallization than those from Site 149. Another possibility is that the alteration of basaltic material to authigenic clays or zeolites below the base of Hole 146 may generate a source of low O18 water.



A study of changes in the ionic species in the pore waters at Site 148 suggests that a small amount of authigenic carbonate is being precipitated as a result of the reduction of sulfate and oxidation of organic matter by sulfate-reducing bacteria (Gieskes and Broecker, personal communication). In the interval from 40 to 80 meters there is a maximum in the alkalinity of the pore waters and the sulfate concentration drops sharply (see Figure 6). Over this same interval the  $C^{13}/C^{12}$  of the bulk carbonate changes from a  $\delta C^{13} = +0.7\pm0.2^{\circ}/_{\circ\circ}$  to  $-0.8\pm0.2^{\circ}/_{\circ\circ}$  (see Figure 7). Thus the  $C^{13}/C^{12}$  of the bulk carbonate appears to be a reflection of this diagenetic process.

Broecker, in his evaluation of the decrease of sulfate and the existence of an alkalinity maximum, calculates that 0.5% by weight of the dry solids in the sediment column are composed of authigenic calcium carbonate. The calculation is as follows:

 $240 \times 10^{-9}$  moles/cm<sup>2</sup> yr of SO<sub>4</sub><sup>=</sup> reduced, supplied mostly by diffusion

 $4MG^{++} + 4SO_4^{=} + 9CH_2O$  (organic matter)

- + 2Fe<sub>2</sub>O<sub>3</sub> + 5Ca silicate
- $4\text{FeS} + 4 \text{MgCa}(\text{CO}_3)_2 + \text{CaCO}_3 \Rightarrow$
- $+9H_2O + 5$  silicate (minus CaO)

 $300 \times 10^{-9}$  moles carbonate/cm<sup>2</sup> yr

 $5.0 \times 10^{-5} \text{ gm/cm}^2 \text{ yr carbonate}$ 

The core is  $4 \times 10^6$  years old

200 gm/cm<sup>2</sup> carbonate deposited

250 meters (depth of core) × 100 cm/m × 1.5 gm/cm<sup>3</sup> (density)

## 3.8 × 104 gm/cm<sup>2</sup> total sediment

$$\frac{200 \text{ gm carbonate}}{3.8 \times 10^4 \text{ gm sediments}} = 5.3 \times 10^{-3}$$

0.5% by weight authigenic carbonate

Organic matter in the sediment appears to be the source of carbon for the authigenic carbonate. Because marine organic matter has a  $\delta C^{13} = -15$  to  $-25^{\circ}/_{\circ\circ}$  (Schwarz et al., 1969) and the fact that the total weight percent of calcium carbonate from 60 to 150 meters (see Figure 8) is only about 10%, the effect of precipitating 0.5% by weight of authigenic carbonate should be detectable.

In order to determine more specifically whether the observed change in the  $C^{13}/C^{12}$  of the bulk carbonate is compatible with Broecker's evaluation, the amount of authigenic carbonate precipitated at each horizon must be estimated.

This may be done if two assumptions are made. First, because it appears that the rate of precipitation of authigenic carbonate is directly related to the alkalinity with the rate being greatest in the vicinity of the alkalinity maximum with rates decreasing away from that maximum to zero at the present sediment-water interface and to zero below 250 meters, it is assumed that the rate of precipitation at any depth is directly proportional to the excess in alkalinity above the base (zero) level of 0.225 X 10-3 moles/liter (see Figure 6). Thus, for example, the present rate of precipitation of authigenic carbonate is twice as high at 70 meters depth as it is at 100 meters. Secondly, it is assumed that the alkalinity curve seen presently has been in existence since the Pliocene, which means, for example, that the rate of precipitation seventy meters below the sediment-water interface at any time has always been twice as high as at 100 meters below the sediment-water interface at that same time. To further



Figure 6. Alkalinity and sulfate concentration of the pore waters from Site 148 plotted as a function of depth. The rate of precipitation of authigenic carbonate is assumed to be directly proportional to the alkalinity at any depth minus a base level alkalinity of  $2.25 \times 10^{-3}$  moles liter. The amount of authigenic carbonate at 250 meters is estimated to be 0.75% by weight of the dry solids. Under these conditions the weight percent of authigenic carbonate at any depth X may be calculated by utilizing the area under the alkalinity curve to the depth X and the area under the curve to the 250 meter level. The weight percent authigenic carbonate at depth X equals:

 $\frac{Area under the curve to depth X}{Area under the curve to 250 meters} \times 0.75\%$ 



Figure 7.  $\delta C^{13}$  of the bulk carbonate at Site 148 plotted as a function of depth. Curves a, b, and c represent model calculations of the  $\delta C^{13}$  of the bulk carbonate assuming a  $\delta C^{13}$  for the authigenic carbonate of -15, -20, and -25%, respectively. The quantity of authigenic carbonate at each horizon was taken from the curve in Figure 8.

clarify, this means that when the sediment-water interface was at the 20 meter level in the present core that the site of maximum carbonate precipitation at that time was at the 90 meter level in the present core.

Using these two assumptions the calculation of the amount of authigenic carbonate precipitated at each horizon is as follows. Broecker's calculation indicates that 0.5% by weight of authigenic carbonate has been deposited in the sediment column. This 0.5% is distributed with the greatest amount being present at greater depths. For the purpose of determining the quantity at each horizon it is assumed that 0.75% is present at 250 meters and none is present at the surface.

Under the assumptions made the rate of precipitation of authigenic carbonate at 250 meters is now zero. When the sediment-water interface was at the 250 meter level, the rate of precipitation at the 250 meter level was also zero. When the sediment-water interface was in the vicinity of the present 180 meter level, the rate of precipitation was at its highest at the 250 meter level. The total amount precipitated at 250 meters is assumed to be 0.75% by weight. It can be seen that under the model the amount precipitated at a horizon X meters in depth is equal to  $A_X/A_{250} \times 0.75^{\circ}/_{\circ\circ}$  where  $A_{250}$  is the area under the curve from 0 to 250 meters and  $A_X$  is the area under the curve from 0 to X meters in depth.

Figure 8 illustrates the amount precipitated at each horizon using this model. That the average amount of authigenic carbonate precipitated in the sediment column is 0.5% by weight can be seen by comparing the curve with a line drawn through 0.5%.

Using the curves in Figure 8 it is now possible to calculate the  $\delta C^{13}$  of the bulk carbonate at each horizon by making a set of material balance calculations. A  $\delta C^{13}$  of +0.66°/<sub>oo</sub> (average  $\delta C^{13}$  of the two uppermost bulk carbonates) is used for the fossil carbonate containing no authigenic carbonate. Values of -15, -20, and -25°/<sub>oo</sub> are used for the carbon going into the authigenic carbonate. The quantities of authigenic carbonate versus fossil carbonate can be taken from Figure 8. The calculations can then be made as follows:

 $\delta C^{13}$  of bulk =  $x_1 \delta_a + (1 - x_1) \delta_b$ 

(carbonate at horizon X)

where

- $x_1$  = mole fraction of authigenic carbonate at horizon X
- $\delta_a = \delta C^{13}$  of carbon going into authigenic carbonate (-15°/..., -20°/...)
- $(1 x_1) =$  mole fraction of fossil carbonate at horizon X  $\delta_b = \delta C^{13}$  of fossil carbonate (+0.66°/<sub>00</sub>)

The three curves, a, b, and c, shown in Figure 6 illustrate the fit of the model using  $\delta C^{13}$  values of -15, -20, and -25°/<sub>00</sub>, respectively, for the authigenic input with an average weight percent authigenic carbonate of 0.5% for the sediment column (0.75% maximum at the bottom). If a  $\delta C^{13}$  value of  $-20^{\circ}/_{00}$  is used exclusively, curves a, b, and c illustrated the fit of the model using 0.37%, 0.50%, and 0.65% by weight, respectively, for the average amount of authigenic carbonate precipitated in the sediment column. The curves b and c fit the data reasonably well. Therefore, using the model presented, precipitation of 0.50 to 0.65% by weight of authigenic carbonate in the sediment column with derivation of the carbon from organic matter having a  $\delta C^{13}$  of -20 to  $-25^{\circ}/_{00}$  explains the observed  $C^{13}/C^{12}$ variations.

#### REFERENCES

- Broecker, W. S. and van Donk, J., 1970. Isolation changes, ice volumes and the O<sup>18</sup> record in deep-sea cores. Rev. Geophys. Space Phys. 8, 169.
- Clayton, R. N. and Mayeda, T. K., 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. Geochim. Cosmochim. Acta. 27, 43.
- Craig, H. and Gordon, L. I., 1965. Isotopic oceanography. In Symposium on Marine Geochimestry. Narragansett Marine Lab, Univ. Rhode Island Publ. 3, 277.
- Emiliani, C., 1966. Paleotemperature analysis of Caribbean cores P6304-8 and P6304-9 and a generalized temperature curve for the past 425,000 years. J. Geol. 73, 209.
- Epstein, S., Buchsbaum, R., Lowenstam, H. A. and Urey, H. C., 1953. Revised carbonate-water isotopic temperature scale. Bull. Geol. Soc. Am. 64, 1315.
- Lawrence, J. R. and Taylor, H. P., 1971. Duterium and O<sup>18</sup> correlation: clay minerals and hydroxides in Quaternary soil compared to meteoric waters. Geochim. Cosmochim. Acta. 35, 993.
- McCrea, J. M., 1950. The isotopic chemistry of carbonates and a paleotemperature scale. J. Chem. Phys. 18, 849.



Figure 8. Weight percent of the bulk carbonate and authigenic carbonate plotted as a function of depth at Site 148. The bulk weight percentages were measured from the determinations of carbon dioxide released during treatment with  $H_3PO_4$ . The authigenic carbonate weight percentages were calculated by means of a model utilizing the alkalinity curve of Figure 6.

- Mopper, K. and Garlick, G. D., 1971. Oxygen isotope fractionation between biogenic silica and ocean water. Geochim. Socmochim. Acta. 35, 1185.
- O'Neil, J. R. and Epstein, S., 1966. A method for oxygen isotope analysis of milligram quantities of water and some of its applications. J. Geophys. Res. 71, 4955.
- Perry, E. C. and Tan, F. C., 1971. Significance of oxygen and carbon isotope determinations in early Precambrian cherts and carbonate rocks of southern Africa. Bull. Geol. Soc. Am, 83(3), 647.
- Savin, S. M., 1967. Oxygen and hydrogen ratios in sedimentary rocks and minerals. PhD Thesis, California Institute of Technology.
- Savin, S. M. and Epstein, S., 1970a. The oxygen and hydrogen isotope geochemistry of clay minerals. Geochim. Cosmochim. Acta. 34, 25.
- \_\_\_\_\_, 1970b. The oxygen and hydrogen isotope geochemistry of ocean sediments and shales. Geochim. Cosmochim. Acta. 34, 43.
- Schwarz, H. P., Hoefs, J. and Welle, D., 1969. Carbon. Handbook of Geochemistry. Springer-Verlag.