40. CAUSES OF THE OXYGEN ISOTOPIC DEPLETION OF INTERSTITIAL WATERS FROM SITES 798 AND 799, JAPAN SEA, LEG 128[1]

Ryo Matsumoto[2]

ABSTRACT

Oxygen isotope compositions of the interstitial waters have been measured for 21 samples taken from the depth intervals of 1.5 to 398.9 mbsf at Site 798 (Oki Ridge) and 16.5 to 435.6 mbsf at Site 799 (Kita-Yamato Trough) in Japan Sea. The $\delta^{18}O$ values decrease with depth from −0.49 to −3.38 ‰ (SMOW) at Site 798 and from −0.71 to −4.36 ‰ (SMOW) at Site 799 corresponding to an average depletion gradient of −0.8 ‰ per 100 m. Material balance calculations reveal that the $\delta^{18}O$-variations at Sites 798 and 799 were principally controlled by low-temperature alteration of basement basalt and andesite, resulting in negative shifts in pore water $\delta^{18}O$ values, and by the polymorphic transformations of biogenic opal-A to opal-CT and opal-CT to microquartz, which tend to increase $\delta^{18}O$ of interstitial waters. Carbonate diagenesis and ash alteration also caused weakly negative shifts in pore water $\delta^{18}O$ values.

INTRODUCTION

Isotopic studies of interstitial waters recovered from sediments at hundreds of DSDP/ODP sites in the world ocean demonstrate that, in most cases, the $\delta^{18}O$ values are depleted relative to seawater (e.g., Lawrence, 1973; Lawrence et al., 1975; Matsuhisa and Matsumoto, 1985; Vrolijk et al., 1990; Boulegue and Bariac, 1990). The mechanisms ascribed to these variations include: (1) secular variation of seawater $\delta^{18}O$ (Bath and Shackleton, 1984), (2) migration and mixing of isotopically light oxygen waters (Vrolijk et al., 1990; Boulegue and Bariac, 1990), (3) diagenetic reactions within sediments during burial (Lawrence, 1973; Matsuhisa and Matsumoto, 1985), (4) alteration of basement rocks (Lawrence el al., 1975; Stern et al., 1976; Vrolijk et al., 1990), (5) hyperfiltration and osmotic effects (Matsuhisa and Matsumoto, 1985; Boulegue and Bariac, 1990), and (6) decomposition of gas hydrates (Hesse and Harrison, 1981; Jenden and Gieskes, 1983; Matsumoto, 1989). The present study reveals that $\delta^{18}O$ values of interstitial waters extracted from Neogene sediments at two Japan Sea sites decrease with depth with an average gradient of −0.80 ‰ per 100 m. The purpose of this report is to evaluate the relative contribution of sediment diagenetic reactions and basalt alteration in controlling observed $\delta^{18}O$-variations of interstitial waters at ODP Sites 798 and 799 in the Japan Sea.

SITE DESCRIPTIONS AND SEDIMENT LITHOLOGY

Site 798

Site 798 is located in a small basin atop Oki Ridge, under 903 m of water (Fig. 1). The seismic records show that total sediment thickness at Site 798 is approximately 710 m (Shipboard Scientific Party, 1990a–g). A 519.7-m-thick, upper lower Pliocene through Holocene sedimentary section is divided into three lithologic units.

Unit I (0–220 mbsf; latest Pliocene to latest Quaternary) is composed of clay, diatomaceous clay, and diatomaceous ooze. This unit is characterized by decimeter- to meter-thick rhythmic interbeds of dark-colored, thinly laminated sediments and light-colored, bioturbated intervals. Biogenic carbonate content ranges up to 40% but averages around 15%. A hard dolomitic layer 33 cm thick occurs at 143 mbsf. Unit II (220–455 mbsf; late Pliocene) consists of moderately indurated, bioturbated diatomaceous clay interbedded with dia-

tom ooze and silty clay. Biogenic carbonate content is less than in Unit I, mostly less than 4%. Fragments of dolomite concretions, 1–3 cm in diameter, were found at 334.0 mbsf and 334.9 mbsf. Unit III (455–518 mbsf; late early to late Pliocene) is made up of siliceous claystone and claystone. The transition of opal-A to opal-CT coincides with the top of Unit III. Biogenic carbonate is scarce throughout this unit.

SITE 799

Site 799 is situated in the Kita-Yamato Trough (Fig. 1), at a water depth of 2084 m. Seismic profiles indicate that the sedimentary sequences filling this failed rift basin are as thick as 1200–1400 m (Shipboard Scientific Party, 1990a,f,g). A 1084.0-m-thick sedimentary section drilled in Holes 799A and 799B has been divided into five lithologic units.

Unit I (0–170 mbsf; late Pliocene to Quaternary) is similar in lithology and compositions to the Unit I at Site 798, being characterized by distinctive light/dark rhythmic interbeds of bioturbated intervals and thinly laminated layers. Thin turbidite units of foraminiferal sands and a meter-thick slumped interval are conspicuous in this unit. Biogenic carbonate content is mostly between 10% and 20%. Authigenic calcite and rhodochrosite occur as disseminated crystals or small concretions, 0.5–1.8 cm in diameter, below 12 mbsf (Matsumoto, this volume). Unit II (170–457 mbsf; late Miocene to late Pliocene) is composed of diatomaceous ooze and diatomaceous clay. Biogenic silica content ranges up to 65% as measured in smear slides. Terrigenous clay content is less than Unit I and biogenic carbonate content is less than 5%. The opal-A to opal-CT transition occurs in the lower part of Unit II at around 410–450 mbsf. Millimeter- to centimeter-thick beds and lenses and small concretions of calcite, rhodochrosite, dolomite, and lansfordite (hydrous Mg-carbonate) are common throughout this unit (Matsumoto, this volume). Unit III (457–800 mbsf; middle to late Miocene) is made up of siliceous claystone and opal-CT (<528 mbsf) or quartz-porcellanite (585 mbsf). Authigenic calcite, rhodochrosite and magnesite are more abundant in the upper part of Unit III, whereas the carbonate in the lower part is principally dolomite (Matsumoto, this volume). Unit IV (800–1020 mbsf; early to middle Miocene) consists of laminated and bedded siliceous claystone and quartz-porcellanite. Millimeter- to centimeter-thick layers and lenses of dolomite are abundant throughout this unit. Altered rhyolitic tuff and tuff breccia occur between 981 and 1003 mbsf. Unit V (1020–1084 mbsf; early Miocene) is dominantly composed of siliceous claystone and claystone with abundant intercalations of siliciclastic turbidites.
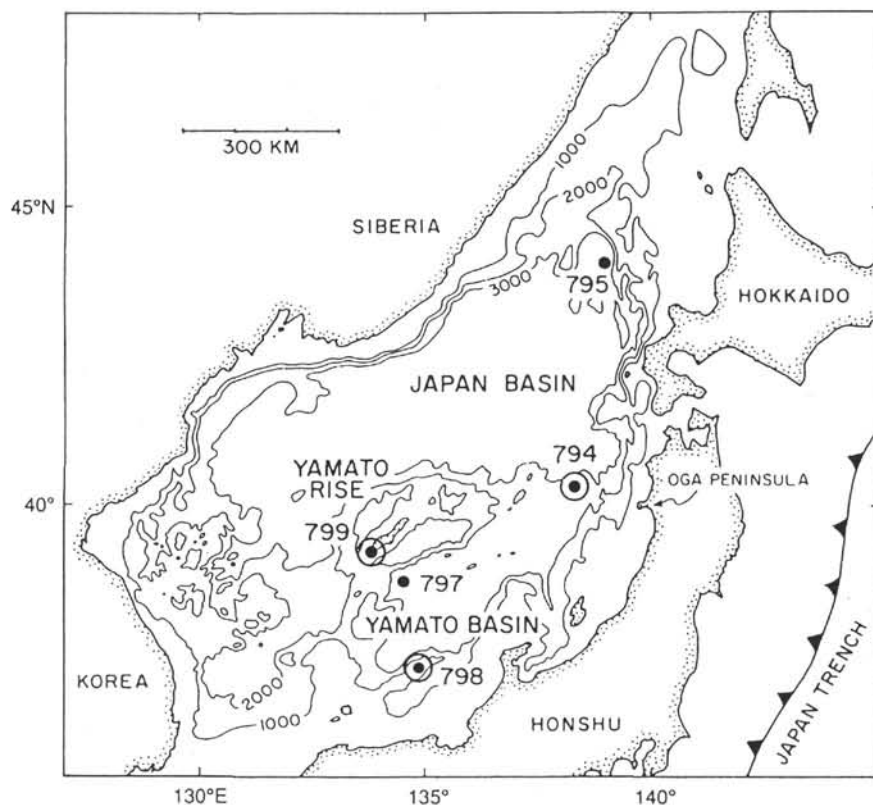
Figure 1. Location map showing bathymetry (in meters) and locations of Sites 794 and 795 in Japan Basin, Site 797 in Yamato Basin, Site 798 on the Oki Ridge, and Site 799 in the Kita-Yamato Trough of Japan Sea.

SAMPLING AND ANALYSIS

Twenty to 80 mL of interstitial water were squeezed from core samples 5–10 cm in length by means of a stainless steel, hydraulic squeezer (Manheim, 1966). Approximately 5 mL of the water recovered by squeezing were collected in a sealed glass ampule immediately after extraction for isotope analysis. At Site 798, nine interstitial water samples were selected for isotope analyses. Among these, five samples were taken from Unit I and four samples from Unit II. No samples were acquired below the opal-A diagenetic zone. At Site 799, four samples were collected from Unit I and eight samples from Unit II. The deepest sample (435.80 mbsf) from Site 799 is from the opal-A/opal-CT transition zone.

CO_2 gas was extracted from 1.5–2.5 mL aliquots of interstitial waters using the CO_2-H_2O equilibration method of Epstein and Mayeda (1953). Measurements of the oxygen isotope ratio were made with a Finnigan MAT Delta-E mass spectrometer. Standard deviation for replicate measurements of a single gas sample is less than 0.04 o/oo. Precision of the method was tested by analyzing two individual CO_2 gas extracted from a single interstitial water sample. Two individual aliquots generally agree to better than 0.15 o/oo. The results of the analyses are reported in terms of δ per mil notation relative to SMOW (Table 1).

RESULTS AND DISCUSSION

δ^{18}O-depth Profiles at Sites 798 and 799

The δ^{18}O values at Site 798 range between −0.49 and −3.38 o/oo, with the overall δ^{18}O-gradient being −0.70 o/oo per 100 m (Fig. 2). At Site 799, the δ^{18}O values decrease from −0.71 o/oo at 16.6 mbsf to −4.36 o/oo at 435.8 mbsf with an average depletion gradient of −0.87 o/oo per 100 m, similar to that for Site 798.

The remarkable aspect of δ^{18}O-depth profiles at Sites 798 and 799 is a large and systematic decrease with depth. This feature is conspicu-

ous when compared with somewhat random fluctuation and small gradients in tectonically-deformed accretionary prisms at Sites 582 and 583 in the Nankai Trough and Site 584 of the Japan Trench (Matsuhisa and Matsumoto, 1985). Within accretionary prisms, evolution of water chemistry and isotopic compositions can be significantly affected by migration and mixing of waters along fault planes (e.g., Boulegue and Bariac, 1990). In contrast, a large and systematic decrease at Sites 798 and 799 might be explained as a result of isotopic

Table 1. Oxygen isotopic composition of interstitial waters from Sites 798 and 799.

| Hole, core, section, interval (cm)	Depth mbsf	δ^{18}O o/oo SMOW
798A-1H-1, 145–150	1.45	−0.49
798A-6H-1, 145—150	47.65	−0.92
798B-8H-4, 140–150	70.67	−1.09
798A-12H-4, 145–150	109.02	−1.16
798B-18X-6, 25–35	169.47	−1.29
798B-24X-2, 140–150	222.9	−1.86
798B-30X-2, 140–150	279.94	−2.34
798B-36X-2, 65–75	336.75	−2.94
798B-42X-5, 140–150	398.85	−3.38
799A-3H-4, 135–140	16.55	−0.71
799A-9H-3, 140–145	72.70	−0.96
799A-12H-4, 145–150	103.15	−1.11
799A-18H-4, 145–150	161.15	−1.43
799A-24X-5, 140–145	220.50	−1.88
799A-30X-5, 145–150	267.95	−2.31
799A-33X-5, 145–150	295.35	−2.71
799A-36X-3, 145–150	321.35	−3.40
799A-39X-3, 145–150	350.35	−3.47
799A-42X-4, 145–150	380.95	−3.62
799A-45X-3, 145–150	408.35	−4.11
799A-46X-2, 140–150	435.60	−4.36
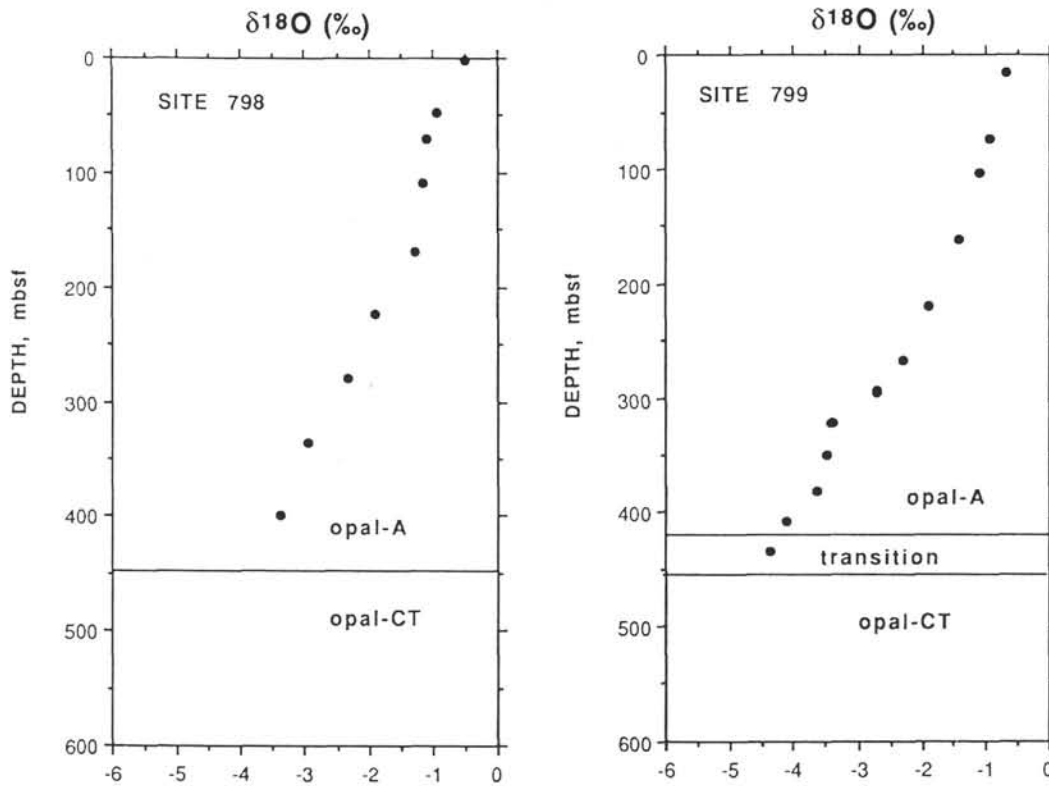
Figure 2. Variations of oxygen isotope composition of the interstitial waters at Sites 798 and 799 of Leg 128. Zones of silica diagenesis are also given.

exchange between water and sediments and by the alteration of basement rocks during burial diagenesis.

Diagenetic reactions that might be important in controlling $\delta^{18}O$ of the interstitial waters include (1) low temperature alteration of basalt, (2) alteration of volcanic ash, (3) transformation of biogenic silica (opal-A) through opal-CT to quartz, (4) recrystallization of biogenic carbonates and precipitation of authigenic carbonates, (5) transformation of detrital clay minerals, and (6) formation of gas-hydrates. Several of these may be ruled out or rendered highly unlikely. In particular, formation of gas-hydrates would decrease $\delta^{18}O$ of ambient interstitial waters (Hesse and Harrison, 1981; Matsumoto, 1989), but this process is not likely to have contributed in changing $\delta^{18}O$ at Sites 798 and 799, because neither frozen gas-hydrates nor gas-hydrate-related BSR (bottom simulating reflector) have been found in these sites. Possibility (5) can be ruled out, or at least minimized, partly because the sediments at Sites 798 and 799 are dominated with biosiliceous and calcareous components. Also, the transformation of swelling clay minerals to non-swelling clays in Neogene sediments of northern Japan has been found to occur at about 100°C (Aoyagi et al., 1987). Clay transformations at such high temperatures would not significantly change $\delta^{18}O$ of the water (Lawrence, 1973). Therefore, the observed $\delta^{18}O$-variations at Sites 798 and 799 might be attributed to reactions (1) basalt alteration, (2) ash alteration, (3) silica diagenesis, and (4) carbonate diagenesis. The relative contribution of these reactions in lowering $\delta^{18}O$ of the interstitial waters are examined using material balance calculations in a closed system model. I will proceed by assessing each of these candidates individually.

Effect of Basalt Alteration

Sediments at Site 798 and Site 799 directly overlie basaltic rocks as suggested by seismic records and other drilling results. Hole 798A terminated only about 190 m above the acoustic basement, and Hole 799B, 100–300 m above basement (Shipboard Scientific Party, 1990a,f,g).

The $\delta^{18}O$ values of fresh submarine basalts recovered by DSDP/ODP drilling cluster around 5.7 ± 0.3 ‰ (SMOW), whereas those of altered basalts range from 6 to 25 ‰ $\delta^{18}O$ (e.g., Muehlenbachs and Clayton, 1972; Kyser and O'Neil, 1978). The $\delta^{18}O$-enrichment in the altered basalt has been ascribed to high $\delta^{18}O$ secondary minerals formed by low temperature alteration. Results from Hole 504B on the East Pacific Rise clearly demonstrate that the uppermost 600-m-thick pillow basalt section is variably altered and enriched in $\delta^{18}O$ with an average $\delta^{18}O$ of 7.0 ‰ (Alt et al., 1986). Further, altered terrestrial ophiolites record the substantial isotopic enrichment of the uppermost 1.5–2 km, with $\delta^{18}O$ = 7–13 ‰ (Stern et al., 1976; Gregory and Taylor, 1981; Cocker et al., 1982).

According to onboard XRF analyses, the entire 200-m-interval of basalt and dolerite at Site 794 has been moderately altered and hydrated, with loss-on-ignition in the range of 0.76%–5.01% (Shipboard Scientific Party, 1990a,f,g). Based on the empirical relationship between $\delta^{18}O$ and H_2O^+ of submarine basalt (Muehlenbachs and Clayton, 1972), $\delta^{18}O$ of Site 794 basalts and dolerites are estimated to be about 10 ‰ (SMOW). The empirical relationship between $\delta^{18}O$ and age of basalts (Muehlenbachs and Clayton, 1972) also suggests that the early Miocene(?) basalts at Site 799 contain approximately 10–11 ‰ (SMOW) of $\delta^{18}O$.

Assuming that the lowering of $\delta^{18}O$ of the interstitial waters at Site 799 could be entirely ascribed to the low temperature alteration and ^{18}O-enrichment of the underlying basalt, the approximate thickness of altered basalt can be calculated by using a material balance equation:

$$X_B(\delta_{B2} - \delta_{B1}) + X_W(\delta_{W2} - \delta_{W1}) = 0 \qquad (1)$$

where, X_B, X_W = moles of oxygen of altered basalt and the interstitial water; δ_{B1}, δ_{B2} = $\delta^{18}O$ of basalt before and after alteration; δ_{W1}, δ_{W2} =

$\delta^{18}O$ of the interstitial water before and after diagenesis, respectively. $\delta_{B1} = 5.7$ ‰ (SMOW) and $\delta_{B2} = 10.0$ ‰ (SMOW) as discussed above, and δ_{W1} is assumed to be 0 ‰ (SMOW). Contribution of the water contained in basalt is not considered in this calculation, partly because the water contained in basalt is relatively small compared with the interstitial water of the overlying sediments and because $\delta^{18}O$ of the water contained in basalt is not given. Therefore, the above calculation would give the minimum value for the thickness of altered basalt.

Chemical composition and dry density used for the following calculations have been taken from those of Site 794 basalts (Shipboard Scientific Party, 1990a–g). Site 794 basalt contains 45.99 wt% oxygen, hence, 1 g of basalt contains 0.0144 moles of O_2. Oxygen molecules contained in basalt of 1 m^3 is calculated to be 2.8 (g/cm^3) × 10^6 (cm^3) × 0.0144 (moles O_2/g) = 4.03×10^4 (moles). Therefore,

$$X_B(\delta_{B2} - \delta_{B1}) = (4.03 \times 10^4) \times (10.0 - 5.7)$$

$$= 17.33 \, A \times 10^4 \text{ (moles ‰)} \quad (2)$$

where A = thickness (in meters) of altered basalt.

Moles of oxygen of the interstitial waters can be obtained from the porosity-depth relationship (Fig. 3; Shipboard Scientific Party, 1990a,f,g). For the depth ranges of (I) 0–150 mbsf and (II) 150–450 mbsf in Figure 3, sediment porosities are roughly constant at around 70% and 75%, respectively. For (III) 450–850 mbsf and (IV) 850+ mbsf, sediment porosities are given by,

$$P = 90 - 0.064 \, D \quad \text{and} \quad P = 60 - 0.026 \, D$$

respectively, in which P = porosity (%) and D = depth (in meters). One cubic meter of interstitial waters contains about 2.78×10^4 moles of oxygen. Therefore, the total moles of oxygen contained in the interstitial waters of sediment column with 1 m^2 basal area is calculated to be (P/100) × (sediment thickness) × (2.78×10^4).

($\delta_{W2} - \delta_{W1}$) varies with depth, reflecting $\delta^{18}O$-depth profiles. For the depth ranges (I) and (II), $\delta^{18}O = -0.5 - 0.0087D$. Hence, $\delta_{W2} - \delta_{W1} = \delta_{W2} = -0.5 - 0.0087D$. For (III) and (IV), where $\delta^{18}O$ values are not given, three cases are considered as shown by thin solid lines in Figure 3. Case 1 is an extrapolation of the gradients for Zones (I) and (II), in which $\delta_{W2} = -0.77 - 0.0087D$. Case 2, $\delta_{W2} = -2.3 - 0.005D$, was taken from the gradient for opal-CT and quartz zones (approximately 300+ mbsf) at Sites 794 and 797 (Brumsack, this volume). Case 3 represents the condition that $\delta^{18}O$ remains constant at −4.5 ‰.

In general, $X_W(\delta_{W2} - \delta_{W1})$ is given by an integral equation as,

$$X_W(\delta_{W2} - \delta_{W1}) = 2.78 \times 10^4 \int (P/100)\delta_{W2}dD \quad (3)$$

Equation (3) is integrated for the respective depth range, using P and δ_{W2} given above. The results are given in Table 2. Substituting the results in Table 2 in equation (2), the thickness of altered basalt is given as,

Case 1: A = 547.7 m
Case 2: A = 480.3 m
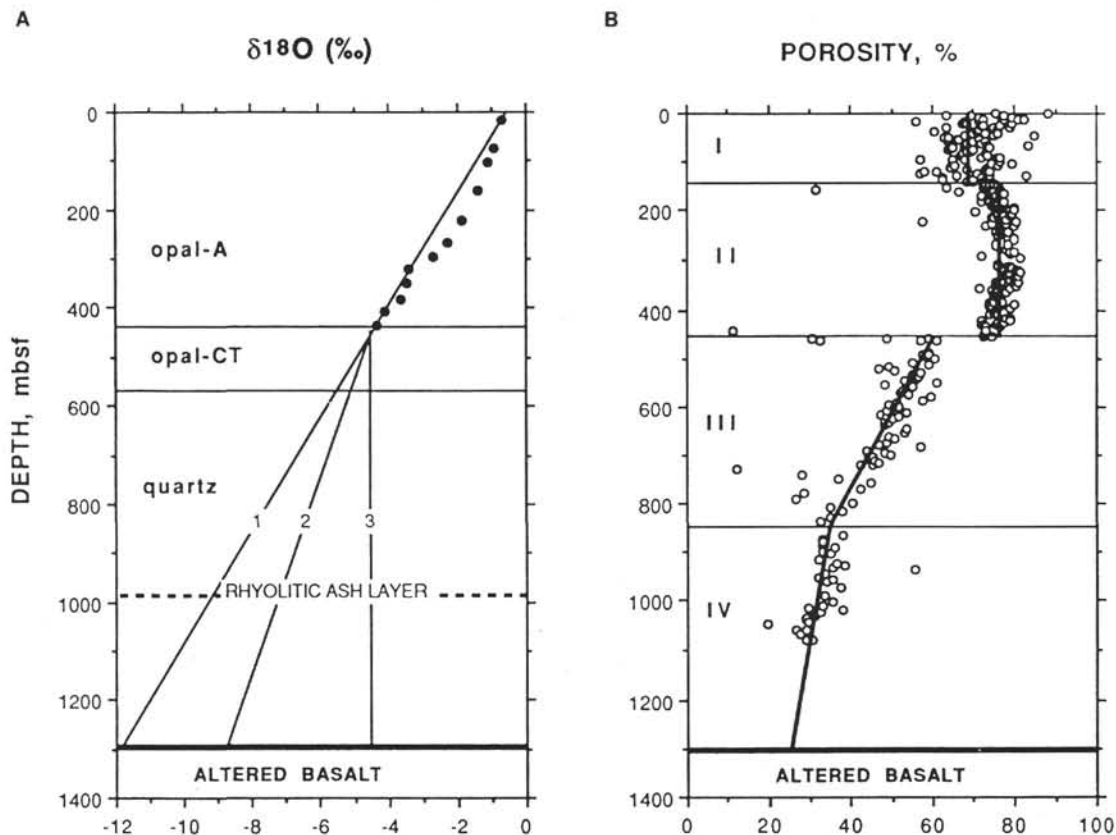Case 3: A = 379.4 m.

A

$\delta^{18}O$ (‰)

B

POROSITY, %

Figure 3. **A.** Diagram showing $\delta^{18}O$-depth profiles at Site 799. Diagonal lines represent the gradient below 450 mbsf; (1) −0.87 ‰ per 100 m, (2) −0.5 ‰ per 100 m, and (3) 0 ‰ (constant). Zones of silica diagenesis and depth of thick rhyolitic ash bed are also shown. Total thickness of sediment column has been assumed to be 1300 m based on seismic records. **B.** Porosity-depth relations at Site 799. Based on the relation, 1300-m-thick sedimentary section has been divided into four zones, I, II, III, and IV.

Table 2. Amount of oxygen molecules, X_W, and degree of depletion in ^{18}O, $X_W(\delta_{W2}-\delta_{W1})$, of the interstitial waters contained in sediment column with 1 m^2 basal area in Holes 799A and 799B.

Depth zone	X_W mole O_2	$X_W(\delta_{W2}-\delta_{W1})$ mole o/oo
I (0–150 mbsf)	2.92×10^6	-3.50×10^6
II (150–450 mbsf)	6.25×10^6	-20.00×10^6
III (450–850 mbsf)	5.33×10^6	
Case 1		-32.39×10^6
Case 2		-29.14×10^6
Case 3		-24.25×10^6
IV (850–1300 mbsf)	4.00×10^6	
Case 1		-39.03×10^6
Case 2		-30.58×10^6
Case 3		-18.00×10^6
I + II + III + IV	18.50×10^6	

These values are somewhat similar to the thickness of altered zones observed in Layer II basalt at DSDP/ODP sites and on-land ophiolites, supporting the hypothesis that basalt alteration was responsible for lowering $\delta^{18}O$ of the interstitial waters at Sites 798 and 799.

Alteration of Ash Layers

Sites 798 and 799 sediments are commonly intercalated with ash layers, but most of them are less than 1 cm in thickness, total thickness being only 1.5 m at Site 798. However, at Site 799, a thick rhyolitic ash layer, 21.2 m thick, occurs at 981.3–1002.5 mbsf in Hole 799B. Most of the volcanic glasses in Holes 798A, 798B, and 799A are fresh or very slightly altered, whereas glasses in Hole 799B (490+ mbsf) have been totally altered to quartz, smectite, and subordinate iron oxides and rare zeolite (Shipboard Scientific Party, 1990a,f,g). Assuming that volcanic glasses of ash layers in Hole 799B total approximately 23 m in thickness and have been altered to an aggregate of 50% quartz and 50% smectite during burial diagenesis, the effect of ash alteration on $\delta^{18}O$ may be assessed by material balance calculation:

$$0.5X_{ash}(\delta_{qtz} - \delta_{gl}) + 0.5X_{ash}(\delta_{smct} - \delta_{gl})$$
$$+ X_w(\delta_{W2} - \delta_{W1}) = 0 \qquad (4)$$

in which, X_{ash}, X_w = oxygen moles in ash layers and interstitial waters responsible for ash alteration, respectively, δ_{gl}, δ_{qtz}, δ_{smct} = $\delta^{18}O$ of fresh glass, authigenic quartz, and authigenic smectite, respectively, δ_{W1}, δ_{W2} = $\delta^{18}O$ of the interstitial waters before and after ash alteration. δ_{W1} is assumed to be 0 o/oo. Porosity (34%) and grain density (2.64 g/cm^3) were taken from those of the thick rhyolitic ash layer (Shipboard Scientific Party, 1990a,f,g). Rhyolitic glass is estimated to contain approximately 47.6 wt% oxygen, 0.0149 moles of oxygen per 1 g. Hence, oxygen moles in a 23-m-thick pile of ash layers is calculated to be, $23 \times (1 - 0.34) \times 10^6 \times 2.64 \times 0.0149 = 0.60 \times 10^6$ mole O_2. $\delta^{18}O$ values of fresh glass, authigenic quartz, and smectite are assumed to be 10 o/oo, 26 o/oo (Lawrence, 1973), and 24 o/oo (Murata and others, 1977), respectively. Substituting these values in equation (4),

$$X_w\delta_{W2} = -9.0 \times 10^6.$$

Supposing that the ash alterations in Hole 799B affected $\delta^{18}O$ of the interstitial waters in the depth ranges of Zone (III) and (IV), 450–1300 mbsf, X_w is 9.3×10^6 mole O_2 (Table 2), then δ_{W2} = −0.98 o/oo. This implies that ash alteration in Hole 799B might have lowered $\delta^{18}O$ of the ambient waters over the depth range of 450–1300 m by approximately 1 o/oo. These modeled changes alone are insufficient to account for the observed trend of pore water $\delta^{18}O$ values.

Silica Diagenesis

Miocene to Pliocene sediments at Sites 798 and 799 are highly siliceous, ranging in SiO_2 content mostly between 62 and 80 wt% (Minai and others, this volume). As the ratio Al_2O_3/SiO_2 for terrigenous suites has been given to be 0.321 (Shipboard Scientific Party, 1990a,f,g), biogenic silica content is calculated by total $SiO_2 - Al_2O_3/0.321$. Based on 32 analyses of diatomaceous clay samples by Minai et al. (this volume), biogenic SiO_2 for opal-CT zone is about 22 wt% and for quartz zone, 39 wt%.

Among 21 water samples examined in this report, only the deepest sample of Site 799 was taken from opal-CT zone (Fig. 3). Probably for this reason, the effect of silica diagenesis has not been clearly recognized at Sites 798 and 799. However at Sites 794, 795, and 797, interstitial waters demonstrate remarkable isotopic enrichment at around opal-A/opal-CT transition (Brumsack, this volume), suggesting that silica diagenesis played an important role in changing $\delta^{18}O$ of the interstitial waters.

Opal-A contains waters as a trapped form in micropores of the structure and as a hydroxyl form chemically bound to the silicon atoms. The former is in isotopic equilibrium with the ambient waters, but the latter, only about 3% of oxygen in silica, has isotopic composition of approximately −40 o/oo compared to the silica (Labeyrie, 1974). Hence, the material balance calculation for silica diagenesis is given by the equation,

$$X_{CT}(\delta_{CT} - \delta_{OP}) + X_{QT}(\delta_{QT} - \delta_{OP}) + 0.03(X_{CT} + X_{QT})\delta_H$$
$$+ X_w\delta_{W2} - (X_w - 0.03(X_{CT} + X_{QT}))\delta_{W1} = 0 \qquad (5)$$

where X_{CT}, X_{QT}, X_w = moles of oxygen in opal-CT, authigenic quartz, and in the interstitial waters, δ_{OP}, δ_{CT}, δ_{QT} = $\delta^{18}O$ of opal-A, opal-CT, authigenic quartz, δ_H = $\delta^{18}O$ of the hydroxyl water originally bound to opal-A, δ_{W1} = 0 o/oo, and δ_{W2} = $\delta^{18}O$ of the interstitial waters after silica diagenesis. Given the thickness, porosity, and density for the opal-CT zone at Site 799 of 135 m (450–585 mbsf), 56.5%, and 2.30 g/cm^3, and for quartz zone, 715 m (585–1300 mbsf), 35.3%, and 2.65 g/cm^3 and given the oxygen content of 0.0167 mole O_2 per 1 g SiO_2, then, the total oxygen content in opal-CT and authigenic quartz in the respective zone are calculated to be $X_{CT} = 135 \times 0.435 \times 10^6 \times 2.30 \times 0.22 \times 0.0167 = 0.50 \times 10^6$ (mole O_2) and $X_{QT} = 715 \times 0.647 \times 10^6 \times 2.65 \times 0.39 \times 0.0167 = 7.98 \times 10^6$ (moles O_2).

According to the oxygen isotopic study on biosiliceous shale recovered during ODP Leg 127 (Pisciotto et al., this volume), $\delta^{18}O$ of opal-CT is 25.0 o/oo, and quartz, 23.2 o/oo. $\delta^{18}O$ value of opal-A is assumed to be 37.4 o/oo (Murata and others, 1977). Hence, $\delta_{CT} - \delta_{OP} = 25.0 - 37.4 = -12.4$ o/oo, $\delta_{QT} - \delta_{OP} = 23.2 - 37.4 = -14.2$ o/oo, and $\delta_H = 37.4 - 40.0 = -2.6$ o/oo. Supposing that the interstitial waters contained in opal-CT and quartz zone (zones III and IV in Fig. 3) reflect the effect of silica diagenesis, X_w in equation (5) should be 9.3×10^6 (Table 2). Substituting these values in equation (5),

$$\delta_{W2} = 141.6/9.3 = 15.2 \text{ o/oo}$$

Silica diagenesis at Site 799 is thus likely to have increased $\delta^{18}O$ of the ambient waters by approximately 15 o/oo. Likewise, the effect of silica diagenesis at Site 798 is roughly calculated to be 7.0 o/oo. No isotopic enrichment of the overlying sediments in zones I and II suggests that silica diagenesis did not significantly affect the isotopic trend for the depth range of 0 and 438 mbsf observed in this report.

Carbonate Diagenesis

Authigenic calcite, dolomite, rhodochrosite, magnesite, and hydro-magnesite occur either as disseminated grains, concretions, and beds with variable size and thickness in Sites 798 and 799 sediments

(Matsumoto, this volume). In particular Site 799 sediments are commonly intercalated with carbonate concretions and beds. The thickness mostly ranges from 1 to 10 cm, but >100-cm thick beds have been recognized by borehole logging. The burial depth of precipitation of authigenic carbonates have been estimated to be 0–550 mbsf (Matsumoto, this volume). Some carbonates are considered to have been originated from biogenic carbonates. Recrystallization of biogenic carbonates is not likely to have greatly affected $\delta^{18}O$ of the interstitial water, because $\delta^{18}O$ values of recrystallized carbonates are generally quite similar to that of the precursor (Lawrence, 1973; Lawrence et al., 1975). However, carbonate diagenesis at Sites 798 and 799 can dramatically affect pore water isotopic composition, since oxygen isotopes are fractionated during precipitation of authigenic carbonates forming during organic matter decomposition and bacterial fermentation (Matsumoto, this volume). Precipitation of carbonates should lower $\delta^{18}O$ of interstitial waters because oxygen isotopic fractionations between carbonates and water ($10^3 \ln \alpha_{\text{carb-water}}$) are approximately +35 to +15 o/oo at 10°–50°C (Friedman and O'Neil, 1977). Hence, formation of carbonate concretions and beds might be responsible for the observed $\delta^{18}O$ variations. Material balance calculation of carbonate precipitation is,

$$X_{\text{carb}}\delta_{\text{carb}} + (X_w - X_{\text{carb}})(\delta_{w2} - \delta_{w1}) = 0 \qquad (6)$$

in which X_{carb}, X_w = moles of oxygen of authigenic carbonates and of the interstitial waters, respectively, before carbonate precipitation, δ_{carb} = average $\delta^{18}O$ of authigenic carbonates, and $\delta_{w2}, \delta_{w1} = \delta^{18}O$ of the interstitial waters before and after carbonate precipitation. $\delta_{w1} = 0$ o/oo.

Authigenic carbonates are estimated to be about 10 vol% of the host sediments, based on the core descriptions and logging results. This indicates that the equivalent thickness of solid carbonates at Site 799 attains 130 m. Assuming that 50% of the authigenic carbonates is of "inorganic origin," density of carbonates is 3.2 g/cm^3, and oxygen content in 1 g of carbonates is 0.0145 moles O_2, total moles of oxygen contained in "inorganic" carbonates (= X_{carb}) are $130 \times 10^6 \times 0.5 \times 3.2 \times 0.0145 = 2.32 \times 10^5$ moles O_2. The $\delta^{18}O$ value of authigenic carbonates at Sites 798 and 799 ranges mostly between 20 and 35 o/oo SMOW (Matsumoto, this volume), averaging 28 o/oo. Substituting these values in equation (6),

$$\delta_{w2} - \delta_{w1} = 2.32 \times 10^5 \times (-28)/(185 - 2.32) \times 10^5, \text{ then}$$

$$\delta_{w2} = -0.36 \text{ o/oo}$$

This low value of −0.36 o/oo indicates that carbonate precipitation is not likely to have greatly lowered $\delta^{18}O$ of the interstitial waters. Even if the "inorganic" carbonates were twice as thick as assumed in the calculations, the effect on $\delta^{18}O$ is still smaller than 1 o/oo. This seems to be consistent with the observations that $\delta^{18}O$-depth profile at Site 798, in which authigenic carbonates are scarce, is similar to that of Site 799.

SUMMARY AND CONCLUSIONS

The isotopic depletion of the interstitial waters from depths of 16.5–436 mbsf at Site 799 describe a trend of isotopic depletion equalling −0.8 o/oo per 100 m. A similar trend is recorded for Site 798 over the range of 1.5–337 mbsf. Model results yielded predicted isotopic changes associated with different diagenetic processes. Volcanic ash alteration and carbonate diagenesis–respectively capable of decreasing ambient $\delta^{18}O$ by 1 o/oo and 0.4 o/oo–are insufficient to account for the observed trend. The amount of depletion in ^{18}O of the interstitial waters at Site 799 correspond roughly to predicted changes associated with low temperature alteration of basement basalt to the approximate depth of 380–550 m.

Taking the negative effects of ash alterations and carbonate diagenesis into account and considering the fact that submarine basalt and on-land ophiolites have usually been altered to the depth up to 1 km, the magnitude of isotopic depletion observed at Sites 798 and 799 is smaller than expected. This discrepancy can be interpreted as a result of (1) positive shifts caused by silica diagenesis, and (2) flux of isotopically light waters into the ocean from sediment piles due to compaction. $\delta^{18}O$ of interstitial waters in opal-CT and quartz zones has been increased by approximately 7 o/oo (Site 798) and 15 o/oo (Site 799) by a singular effect of silica diagenesis. This effect would largely compensate the negative effects caused by basalt alterations, ash alterations, and carbonate diagenesis.

In conclusion, $\delta^{18}O$-depth profiles at Sites 798 and 799 are largely attributable to the negative shift by basalt alteration and subordinately positive shift by silica diagenesis. To elucidate the effect of these offsetting processes, and their effect upon $\delta^{18}O$ of overlying seawater, the $\delta^{18}O$-depth profiles for the entire sediment column should be determined.

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