

28. MINERALOGY AND O¹⁸/O¹⁶ RATIOS OF FINE-GRAINED QUARTZ AND CLAY FROM SITE 323

Eric V. Eslinger, West Georgia College, Carrollton, Georgia
and

Samuel M. Savin, Case Western Reserve University, Cleveland, Ohio

INTRODUCTION

Mineralogic and oxygen isotopic analyses were made of the fine-grained quartz and clay from 14 samples randomly selected from the cored sediments of Site 323. The main purposes of the study were to identify the modes of origin of the clay mineral components and to determine whether or not quartz was formed as a diagenetic reaction product in a typical, primarily detrital, deep-sea sedimentary sequence in which the temperature did not rise above 50°C. Recent work strongly suggests that in thick sequences of Tertiary sediments from the Gulf Coast, in which temperatures commonly exceed 50°C, quartz is formed as a diagenetic reaction product (Hower and Eslinger, 1973; Yeh and Savin, 1974). This diagenetic quartz probably forms from the silicon released by smectite layers in mixed-layer clays as they are converted to illite layers. While it comprises only a minor fraction of the total quartz in most Gulf Coast shales, this diagenetic quartz can constitute the major part of the clay-sized quartz of the rock.

ANALYTICAL TECHNIQUES

A small portion of each sample from Site 323 was set aside for bulk X-ray analysis. The remainder was ultrasonically disaggregated. Particle size separations, using the centrifugation techniques of Jackson (1956), were made, separating the samples into the following size fractions: 0.3 μm, 0.3-0.7 μm, and 0.7 μm (equivalent spherical diameter). Oriented mounts for X-ray diffraction were prepared by permitting dilute aqueous suspensions to dry in air on glass slides. X-ray diffractograms were made using a Norelco XRD-5 diffractometer equipped with a single-crystal monochromator and using CuK α radiation. Samples were X-rayed before and after treatment with ethylene glycol.

Quartz was isolated from the 0.3-0.7 μm size fractions and some of the greater than 0.7 μm fractions using the technique of Syers et al. (1968). The purity of the quartz thus extracted was checked by X-ray diffraction. Isotopic analyses of the untreated finer than 0.3 μm fractions and of the quartz separates were done using standard techniques (Taylor and Epstein, 1962; Savin and Epstein, 1970a). When sufficient material was available, oxygen was extracted from two aliquots of the minerals. Each sample of oxygen extracted from a mineral was analyzed twice (as CO₂) on the mass spectrometer. Isotopic results are reported in the δ -notation as per mil deviations from the SMOW standard (Craig, 1961). Average deviation from the mean value of two

analyses of the same CO₂ was almost always less than 0.10 per mil. Average deviation of the analyses of replicate CO₂ samples prepared from a mineral was usually smaller than 0.3 per mil.

MINERALOGY

Bulk Mineralogy

X-ray diffractograms were made of ethylene glycol saturated bulk samples, both randomly and nonrandomly oriented. Representative diffractograms of 5 of the 14 randomly oriented samples are shown in Figure 1. In Figure 2 are X-ray diffractograms of the same 5 samples made using nonrandomly oriented sample mounts. The diffractograms of randomly oriented samples were interpreted using the intensity factors given by Schultz (1964).

In almost all the bulk samples, the dominant mineral phase is quartz; feldspar ranks second in abundance. Clay minerals are ubiquitous, but are dominant only in Sections 15-5, 16-3, and 18-4. In these sections smectite or highly expandable mixed-layer illite/smectite is the most abundant phase. Illite, chlorite, and/or kaolinite are present in all samples except Section 16-3. (No attempt was made to differentiate between chlorite and kaolinite; the assumption is made that at least some of both minerals is present when a 7Å diffraction peak occurs.) Other minerals detected were calcite in Section 15-5 and clinoptilolite in Section 18-4.

Mineralogy of the Finer than 0.3 μm Size Fraction

The finer than 0.3 μm size fraction is dominated by highly expandable mixed-layer illite/smectite. Representative diffractograms of this size fraction are shown in Figure 3. Illite, chlorite, and kaolinite can be detected in all sections except 16-3 and 18-4. Quartz is detectable as a trace constituent and feldspar as a minor constituent in all sections except 15-5, 16-3, and 18-4 in which neither was detected.

Computer simulation studies of X-ray diffractograms by Robert Reynolds (personal communication) have demonstrated the futility of attempting to make quantitative estimates of absolute abundances of various clay minerals using X-ray diffraction data. However, a semiquantitative estimate of the *relative* amounts of clay mineral phases can be made. In this study we made semiquantitative estimates of the amounts of illite/smectite (relative to other clay minerals) in the finer than 0.3 μm fractions of all samples. These estimates were based on X-ray diffractograms made using oriented, ethylene-glycol treated samples. Conventions

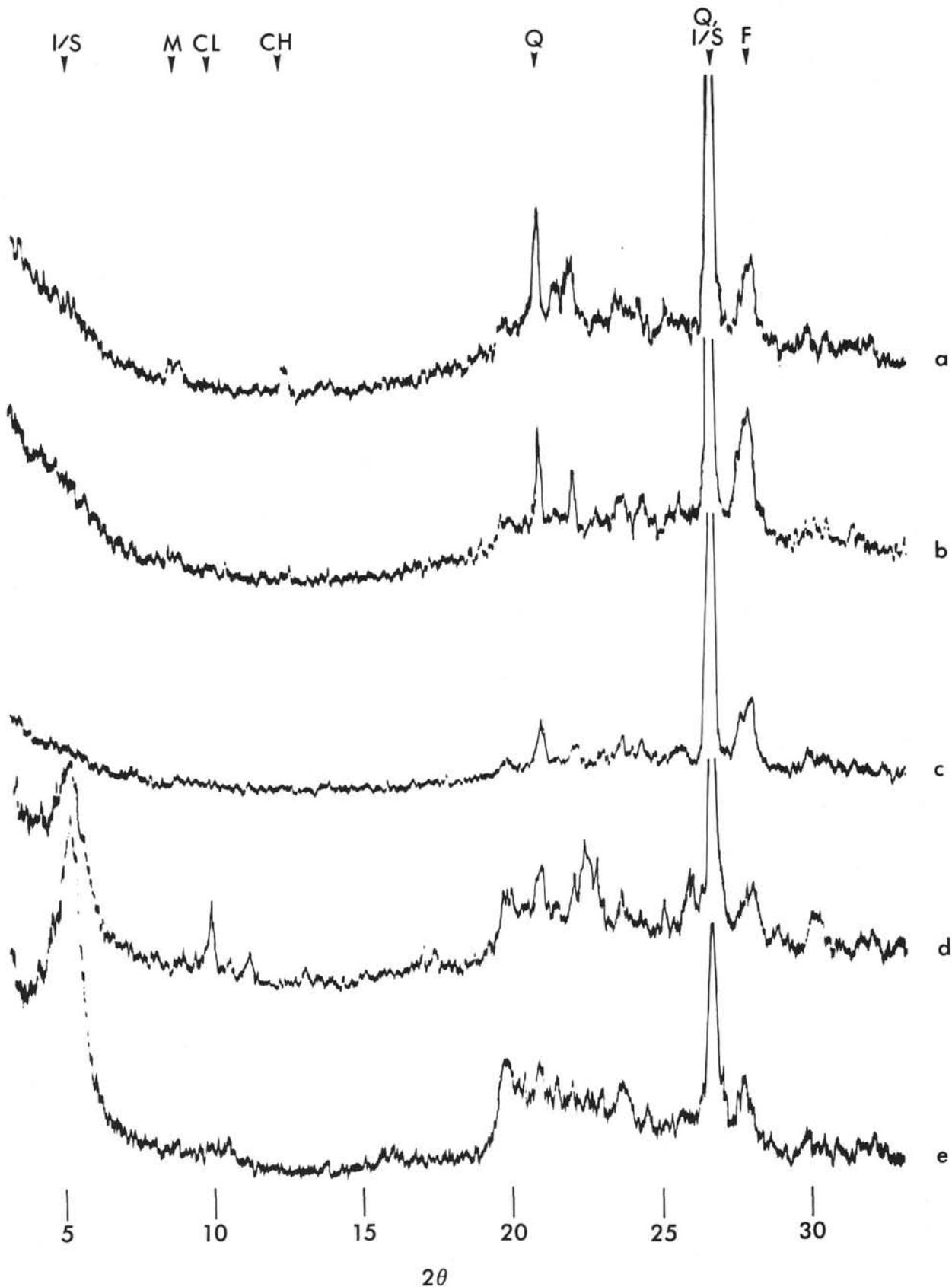


Figure 1. Representative diffractogram from Site 323 made using ethylene glycol-treated randomly oriented powders of the bulk samples. Samples are: (a) = 9, CC, (b) = 8, CC, (c) = 7-3, (d) = 18-4, and (e) = 16-3. Peaks indicated are Q = quartz, F = feldspar, M = mica (illite), Ch = chlorite and/or kaolinite, I/S = mixed layer illite/smectite, and Cl = clinoptilolite.

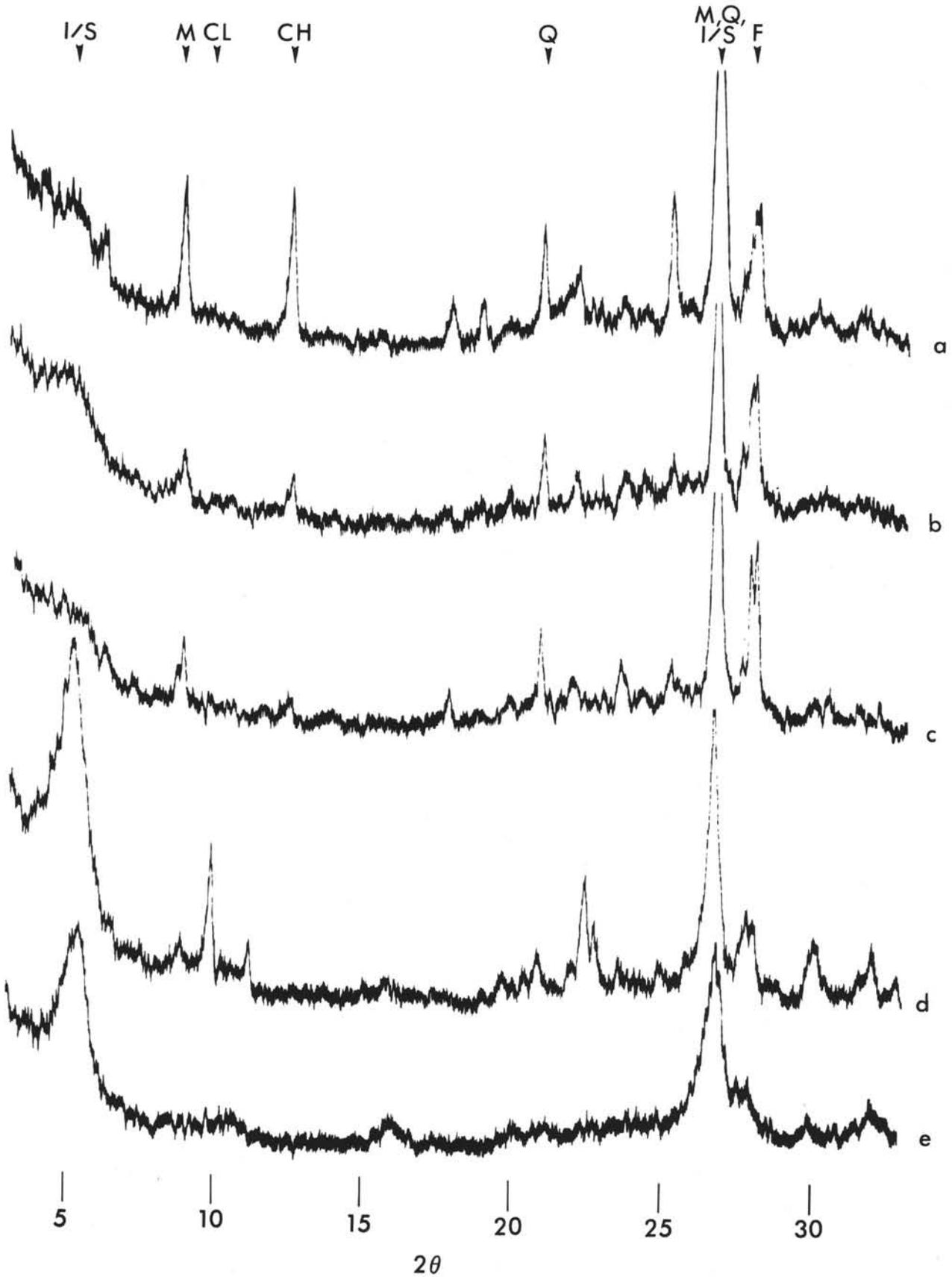


Figure 2. Representative diffractograms from Site 323 made using ethylene glycol-treated nonrandomly oriented powders of the bulk samples. Samples are: (a) = 9, CC, (b) = 8, CC, (c) = 7-3, (d) = 18.4, and (e) = 16-3. Peaks indicated are Q = quartz, F = feldspar, M = mica (illite), Ch = chlorite and/or kaolinite, I/S = mixed layer illite/smectite, and Cl = clinoptilolite.

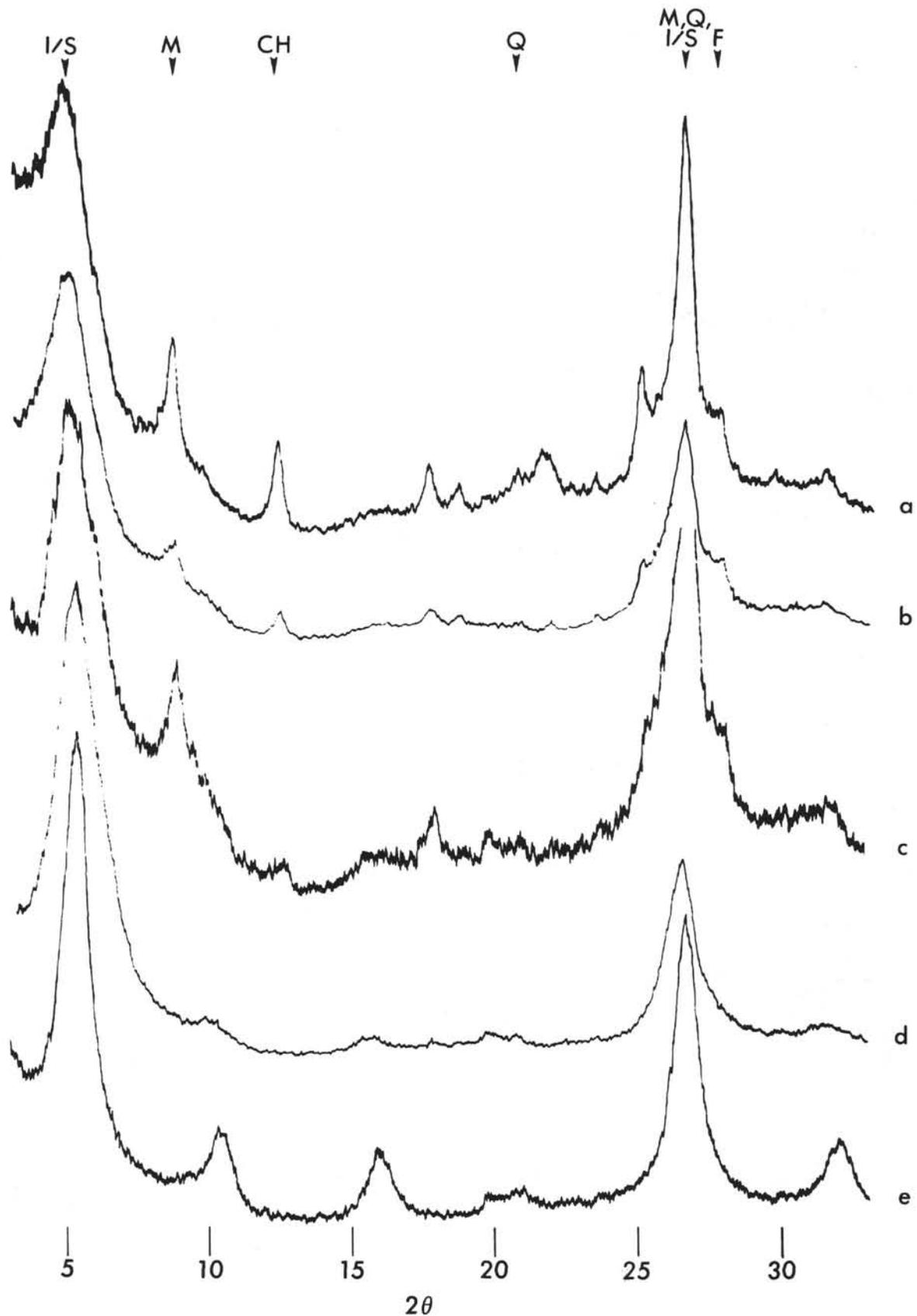


Figure 3. Representative diffractograms from Site 323 made using ethylene glycol-treated nonrandomly oriented finer than $0.3 \mu\text{m}$ fractions of the samples. Samples are: (a) = 9, CC, (b) = 8, CC, (c) = 7-3, (d) = 18-4, and (e) = 16-3. Peaks indicated are: Q = quartz, F = feldspar, M = mica (illite), Ch = chlorite and/or kaolinite, and I/S = mixed layer illite/smectite. Note the change in the nature of the 17\AA I/S reflections in diffractograms "a" through "e" indicating an increase in the average percentage of expandable layers.

were adopted to relate the intensity (I) of diffraction peaks to the abundance (A) of the phase producing the peak. The diffraction peaks and "intensity-abundance" convention used are:

Mineral	Peak(s)	Diffraction Angle (2θ°)	Intensity-Abundance Convention
illite	(001) _{10A}	8.9°	A _{illite} = I _{(003)_{10A}} = 1/2 I _{(001)_{10A}}
illite/smectite	(003/005) _{10A/17A} +	3.3°	A _{I/S} = I _{(003/005)_{10A/17A}} = I _{(003/005)_{10A/17A}} + I _{(003)_{10A}} - I _{(003)_{10A}}
	(003) _{10A}		
chlorite + kaolinite	(004) _{chl} + (002) _{kaol}	3.5°	A _{chl} + A _{kaol} = I _{(004)_{14A}} + I _{(002)_{7A}}

Using these intensity-abundance conventions, a semiquantitative ranking of illite/smectite abundance is given by the equation:

$$\text{illite/smectite abundance} = \frac{A_{I/S}}{A_{I/S} + A_{\text{illite}} + A_{\text{kaol}} + A_{\text{chl}}}$$

The abundance of illite/smectite calculated this way varies from 1.0 for a sample of pure illite/smectite to 0.0 for a sample with no illite/smectite. At all other values, the abundance should be thought of as reflecting a ranking rather than an actual abundance in weight percent, mole percent, etc. That is, in general, other factors remaining equal, samples with higher calculated illite/smectite abundances contained more of that mineral, but no significance can be attached to the absolute value of the number unless the number is 1.0 which indicates that no other phase was detected. Illite/smectite abundances calculated in this way are given in Table 1. The two deepest sections, 16-3 and 18-4, contain only illite/smectite in the finer than 0.3 μm fraction. There is no obvious trend with depth of the illite/smectite abundances in the other 12 samples.

The expandability or percentage of smectite layers of the illite/smectite component in the finer than 0.3 μm fraction has been estimated from the nature of the 17Å illite/smectite diffraction peak. Where "l" is the peak-to-trough distance on the low-angle side of the 17Å peak and "h" is the peak-to-trough distance on the high side of the peak, the parameter l/h increases as the expandability of the mixed-layer phase increases. The calculated diffraction profiles of Reynolds and Hower (1970) indicate that l/h values of 0.39 and 0.77 correspond to 60% and 80% expandable layers, respectively. l/h values are tabulated in Table 1.

The average percentage of expandable layers in the illite/smectite of a sample appears to be a clue to the origin of the illite/smectite. Close examination of the diffractograms of the finer than 0.3 μm fraction indicates that samples with a relatively small average percentage of expandable layers (small l/h values) have a broad 17Å peak indicating a heterogeneous mixture of illite/smectite and that these samples are characterized by significant amounts of coexisting illite, chlorite, kaolinite, and feldspar (Figure 3a); however, diffrac-

tograms of samples with a relatively large average percentage of expandable layers (large l/h values) have a sharp 17Å peak indicating a homogeneous illite/smectite, and these samples are characterized by little to no coexisting illite, chlorite, kaolinite, and feldspar (Figure 3e). The implication is that samples that contain illite/smectite with relatively low l/h values are largely detrital in origin, while samples that contain illite/smectite with relatively high l/h values are largely authigenic in origin. An examination of the l/h values tabulated in Table 1 shows that although there is no consistent trend with depth samples from 600 meters and deeper have l/h values of 0.68 and above while samples more shallow than 600 meters have l/h values below 0.68. Thus, samples from 600 meters and deeper contain illite/smectite having a larger authigenic component than those samples from more shallow depths. The parent material of the authigenic illite/smectite is assumed to be volcanic ash. Drever (this volume) also found an abrupt change in the mineralogy and chemistry of the clay-sized samples from Site 323 at approximately the same depth.

OXYGEN ISOTOPE DATA

Oxygen isotope data are tabulated in Table 1. δO¹⁸ values of the finer than 0.3 μm clay and 0.3-0.7 μm quartz are plotted as functions of depth in Figure 4. There are no obvious diagenetic trends with depth.

Clay Minerals

Figure 5 shows that there is a positive correlation (r = 0.81) between δO¹⁸ values of the less than 0.3 μm clay fractions and the illite/smectite abundances of these samples. δO¹⁸ values ranged from +16.82 per mil in a sample containing relatively little illite/smectite to +25.14 per mil for Section 16-3 which is essentially pure illite/smectite.

The relationship between the mineralogy and the δO¹⁸ values of the finer than 0.3 μm clay can be understood using a three component model. The fine-grained fraction can be thought of as consisting of: (1) detrital kaolinite, chlorite, illite, and to a lesser extent, feldspar; (2) detrital illite/smectite; and (3) illite/smectite formed diagenetically by the halmyrolysis of volcanic ash. Each of these components has its own characteristic range of isotopic compositions. Yeh (1974) has estimated the following δO¹⁸ values for clay minerals in isotopic equilibrium with deep ocean water (δ_{H₂O}^{O¹⁸} = -0.20 per mil; T = 1°C); smectite, +30.45 per mil; illite, +27.78 per mil; kaolinite, +26.25 per mil; chlorite, +22.95 per mil. Detrital illite/smectite is probably enriched in O¹⁸ relative to detrital illite and chlorite. Diagenetic illite/smectite would be enriched in O¹⁸ relative to detrital illite/smectite, in accord with the conclusions of Savin and Epstein (1970b). A plot (not shown) of δO¹⁸ of the finer than 0.3 μm fraction versus l/h of the illite/smectite has a positive slope, but a low correlation coefficient (r = 0.31); thus, the primary cause of the variation in δO¹⁸ values of the finer than 0.3 μm fraction is the relative abundance of illite/smectite rather than the mode of origin of the illite/smectite.

The clay, with one exception, is not in isotopic equilibrium with the pore waters. Lawrence et al. (this volume) have determined that δO¹⁸ values of pore waters

TABLE 1
Mineralogical and Isotopic Data of Samples from Site 323

Sample (Interval in cm)	Depth in Hole (m)	Relative Illite/Smectite Abundance ^a	ℓ/h of Illite/Smectite ^a	Clay (<0.1 μm) δO18	Quartz (0.1-0.5 μm) δO18	Quartz (>0.5 μm) δO18
1-5, 0-15	80	0.52	0.19	+19.02 (0.14) ^b	+10.59	-
2-2, 0-15	165	0.59	0.58	+18.94	+13.02	-
3, CC	260	0.87	0.65	+21.80	+12.56	-
7-3, 31-46	365	0.67	0.65	+20.97	+12.08	-
8, CC	410	0.74	0.52	+19.48	+11.75	-
9, CC	460	0.63	0.28	+17.94 (0.24) ^b	-	+10.48
10-3, 0-12	510	0.79	0.55	+20.71	-	-
11-1, 0-10	555	0.62	0.51	+18.76 (0.08) ^b	+11.94	-
12-1, 135-150	600	0.49	0.89	+16.82	+8.99	+12.04 (0.44) ^b
13-5, 135-150	620	0.69	0.90	+21.16	-	+11.64 (0.06) ^b
14-1, 140-150	640	0.74	0.68	+20.44	+11.28	-
15-5, 140-150	660	0.70	0.78	+20.00	-	+9.80
16-3, 135-150	670	1.00	0.77	+25.14 (0.15) ^b	+19.09	+8.64
18-4, 135-150	700	1.00	0.78	+20.56 (0.90) ^b	-	+10.36

^aSee text for definition.

^bNumbers in parentheses are average deviations from mean value of analyses of duplicate aliquots of material.

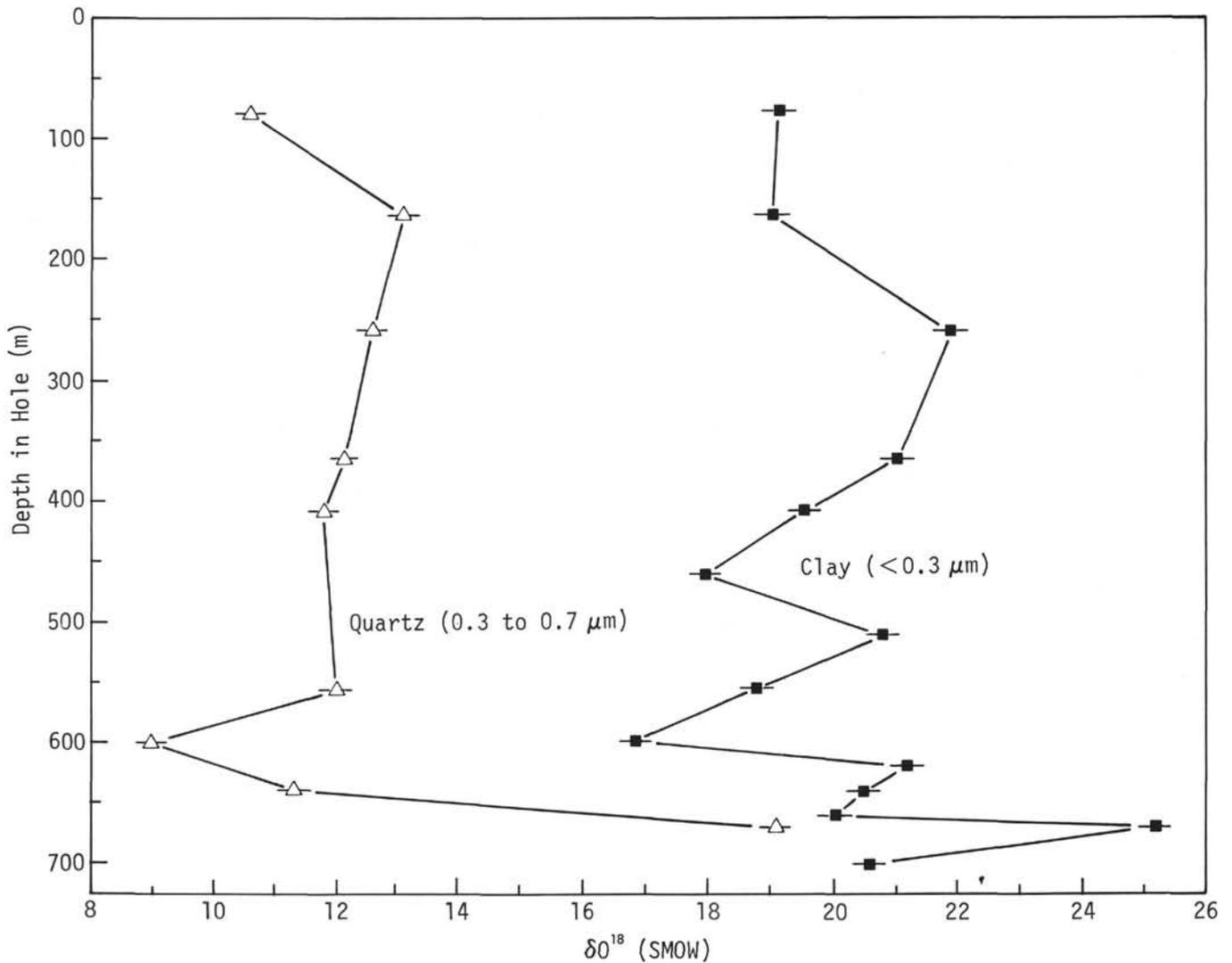


Figure 4. δO¹⁸ values (relative to SMOW standard) of the finer than 0.3 μm size fraction (predominantly clay) and of the 0.3 to 0.7 μm quartz, plotted against depth below the sediment-water interface.

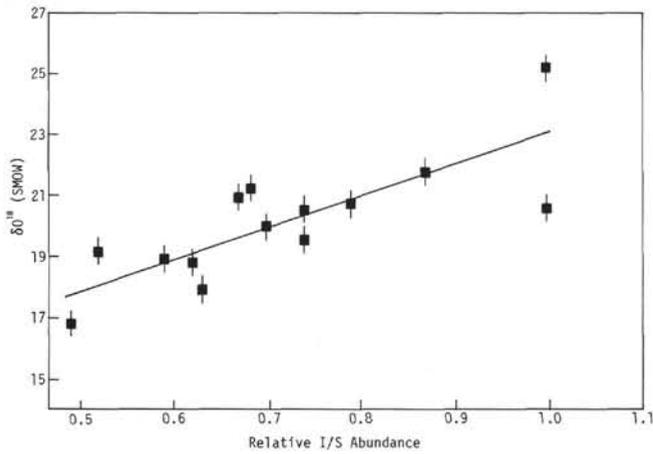


Figure 5. δO^{18} values of the finer than $0.3 \mu\text{m}$ fractions (predominantly clay) plotted against relative "abundance" of illite/smectite in the finer than $0.3 \mu\text{m}$ fractions. The "abundance" parameter is defined in the text and does not reflect absolute percentage of illite/smectite in the samples.

from Site 323 decrease with depth in the hole, becoming as negative as -3.5 per mil at the bottom of the hole. The finer than $0.3 \mu\text{m}$ size fraction of clay from Section 16-3 is essentially pure illite/smectite containing about 80% expandable layers. It has an isotopic composition of $+25.14$ per mil. If Section 16-3 were in equilibrium with pore water with a δO^{18} value of -3.5 per mil, this would correspond to an oxygen isotopic fractionation factor, $\alpha_{\text{clay-water}}$ of 1.0287. Using the equations given by Yeh (1974), this is the equilibrium fractionation factor between 80% expandable illite/smectite and water at a temperature of 8°C . Although the temperature at the sampling depth is probably about 20° warmer than this (assuming a geothermal gradient of 4°C per 100 m), the closeness of the calculated temperature to the probable actual temperature suggests that the clay-sized fraction of Section 16-3 has approached isotopic equilibrium with pore water at diagenetic temperatures. Actually, it is unlikely that all of the oxygen now in a particular illite/smectite sample was equilibrated at the same time, at the same temperature, or with pore waters having the same isotopic composition since the alteration of parent material to illite/smectite is probably a slow process. For instance, Muehlenbachs and Clayton (1972) found that submarine weathering of basalts to clays caused the δO^{18} of the whole rocks to increase at a rate of 0.25 per mil per million years.

The diffractogram of the bulk sample of 16-3 (Figure 2e) indicates that there is only a very small amount of phases other than illite/smectite present strongly suggesting that this sample is comprised largely of an alteration product of volcanic ash. The observed depletion with depth in δO^{18} of pore waters (Lawrence et al., this volume) at Site 323, as well as other sites, could be the result of isotopic exchange between volcanic ash and pore water as the ash is weathered into illite/smectite. During the weathering process, the δO^{18} of a bulk sample (unaltered volcanic ash plus the alteration product illite/smectite) would increase and the δO^{18} of the surrounding pore water would decrease in an approach

toward isotopic equilibrium as the percentage of illite/smectite in the sample increased.

The finer than $0.3 \mu\text{m}$ fraction of Section 18-4, like Section 16-3, is also composed of essentially pure illite/smectite. However, its isotopic composition is only $+20.56$. A possible explanation in the divergence of the isotopic compositions of Sections 18-4 and 16-3 is based on the nature of their diffractograms (Figure 3d and 3e). The reflections from Section 16-3 are much more well defined than those from Section 18-4, suggesting that Section 18-4 was sampled from a horizon where the extent of mineralogic alteration and isotopic exchange has not been so great as in the horizon from which Section 16-3 was taken. The correlation between δO^{18} of the finer than $0.3 \mu\text{m}$ fraction and the relative abundance of illite/smectite in the samples (Figure 5) would be better ($r = 0.90$) if Section 18-4 were ignored. Lawrence et al. (this volume) show via closed system models that the isotopic composition of diagenetic smectite (and pore water) depends on the nature of the starting material (basalt or ash), the porosity, and the extent of alteration.

Quartz

Diagenetic quartz can be distinguished from detrital quartz on the basis of its O^{18}/O^{16} ratio. δO^{18} values of detrital ocean sediment quartz are typically between $+12$ per mil and $+20$ per mil (relative to SMOW) and vary as functions of particle size and source area (Mokma et al., 1972; Clayton et al., 1972b). Diagenetic quartz in isotopic equilibrium with seawater or marine pore water would have δO^{18} values ranging from about $+40$ per mil to $+20$ per mil, corresponding to temperatures of formation between 0°C and 100°C (Clayton et al., 1972a). With other factors (e.g., provenance) remaining constant, δO^{18} values of a restricted size fraction of quartz should increase as the amount of diagenetically formed quartz in the sample increases.

The δO^{18} values of the quartz separates from Site 323 (Table 1) are similar to those of quartz extracted from core-top sediments in the southern Pacific Ocean (Mokma et al., 1972; Clayton et al., 1972b) and indicate that most of the quartz from the Site 323 samples is detrital. Only one value, that of $+18.7$ per mil obtained from the 0.3 to $0.7 \mu\text{m}$ fraction of Section 16-3, is greater than $+14$ per mil. Sufficient material was available for only one extraction of the quartz from Section 16-3; continuing work is being done on other samples near it in the section. Material balance calculations indicate that the 0.3 to $0.7 \mu\text{m}$ quartz of Section 16-3 is definitely less than 50% diagenetic and probably less than 35% diagenetic. Therefore, the quartz isotopic compositions generally do not indicate that there is a significant diagenetic component in the sediments.

CONCLUSIONS

1. The finer than $0.3 \mu\text{m}$ fractions of 14 samples from Site 323 are predominantly illite/smectite. In 10 of the samples the illite/smectite has between 50% and 80% expandable layers.

2. The asymmetry of the 17\AA illite/smectite diffractogram peak of the finer than $0.3 \mu\text{m}$ fractions of the samples indicates that samples from 600 meters and

below have a greater average percentage of expandable layers than those samples from above 600 meters. Also, the samples from 600 meters and below generally have a larger diagenetic illite/smectite component than the samples from above 600 meters.

3. δO^{18} values of the finer than $0.3 \mu m$ fractions of clay increases as the relative amounts of illite/smectite in the sample increases and also as the percentages of expandable layers in the illite/smectite increase. This increase is in the direction of increasing approach to isotopic equilibrium with the pore waters.

4. The finer than $0.3 \mu m$ fractions of samples can be approximated as simple mixtures of three components. Ranked in order of increasing δO^{18} they are: detrital clays other than illite/smectite; detrital illite/smectite, and diagenetic illite/smectite. The diagenetic component is probably a devitrification product of volcanic ash. It forms in isotopic equilibrium with the adjacent pore waters.

5. δO^{18} values of the $0.3 \mu m$ to $0.7 \mu m$ quartz generally indicate that the quartz is detrital. However, the one sample of illite/smectite (16-3) that is probably entirely diagenetic in origin also appears to contain clay-sized quartz having a small diagenetic component.

6. The diagenetic illite/smectite is an O^{18} sink. Its formation is at least partly responsible for the depletion of O^{18} in pore waters with depth that has been reported in other studies.

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