

OXYGEN ISOTOPES AND THE EXTENT OF DIAGENESIS OF CLAY MINERALS DURING SEDIMENTATION AND BURIAL IN THE SEA

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Abstract—Oxygen isotope ratios of <0.1- μm smectite in bottom sediments of the Mississippi River and the Gulf of Mexico near the mouth of the river have been determined to investigate diagenesis of land-derived clay minerals during sedimentation in the sea. No difference was detected in $\delta^{18}\text{O}$ (SMOW) between the river and the Gulf samples indicating that no smectite alteration or addition of neoformed smectite to the river samples took place during sedimentation. Thus, authigenic minerals in the river sediments cannot make up more than a few tenths of a percent of the bulk sediments.

Similar results were obtained from 3×10^6 -yr b.p. sediments buried to 80 to 600 m at Deep Sea Drilling Project site 323, Bellingshausen Abyssal Plain. No significant change with depth was noted in the $\delta^{18}\text{O}$ of the <0.3- μm size fraction, mostly smectite, of these land-derived sediments. On the basis of the $\delta^{18}\text{O}$ of the deepest sample, the maximum amount of authigenic minerals in the land-derived sediments during burial in the sea cannot be more than one or two percent of the bulk sediments. Hence, the alteration at seafloor temperatures of 25–45% of the <0.1- μm size clays in 3×10^6 yr b.p. sediments reported in a previous study is not substantiated. The data demonstrate that land-derived smectite is stable in the sea, and that oxygen isotopes can be used to investigate the modes and the temperatures of formation of authigenic smectites in marine sediments that are younger than 25×10^6 yr and that formed below 25°C.

Key Words—Diagenesis, Gulf of Mexico, Isotope, Mississippi River, Oxygen, Sedimentation, Smectite.

INTRODUCTION

Clay minerals of deep-sea bottom sediments appear to have preserved their original oxygen isotopes to the extent that most land-derived clays can be easily distinguished from clays formed in the sea by their oxygen isotope compositions (Savin and Epstein, 1970). Yeh and Savin (1976) and Yeh and Epstein (1978), however, showed that the 0.1- μm size fraction of clay minerals in deep-sea bottom and near-bottom sediments may have been isotopically altered by about 42% or more after about 3×10^6 yr. They noted that their results could also be explained as a consequence of addition of authigenic clay minerals to the samples. Such authigenic clay minerals could be products of submarine alteration of volcanic ash or crystallization of land-derived noncrystalline aluminosilicate material. The distinction between the alteration of detrital clay minerals and the addition of authigenic clay minerals was not possible from their studies.

The present study is an effort to expand our understanding of the diagenesis of clay minerals during sedi-

mentation and burial to depths where temperatures are higher than deep-sea bottom temperatures and ages are older than 3×10^6 yr. The objective of the study was to determine the constraints on the usefulness of oxygen isotopes as provenance indicators in marine sediments.

METHODOLOGY

The approach used here to determine the extent of alteration (% change) in, or addition of authigenic clay minerals to, land-derived clay minerals in the sea is adapted from Yeh and Savin (1976) as follows:

$$\% \text{ change} = \frac{\delta^{18}\text{O}_{\text{final}} - \delta^{18}\text{O}_{\text{initial}}}{\delta^{18}\text{O}_{\text{equilibrium}} - \delta^{18}\text{O}_{\text{initial}}} \times 100\%, \quad (1)$$

where $\delta^{18}\text{O}_{\text{initial}}$ is the $\delta^{18}\text{O}$ of the clays before sedimentation or burial, and $\delta^{18}\text{O}_{\text{final}}$ is the $\delta^{18}\text{O}$ of the clays after sedimentation or burial. $\delta^{18}\text{O}_{\text{equilibrium}}$ is the $\delta^{18}\text{O}$ of the authigenic counterpart. $\delta^{18}\text{O}$ is relative to Standard Mean Ocean Water (SMOW; Craig, 1961). $\delta^{18}\text{O}_{\text{final}}$ values are measured numbers, but $\delta^{18}\text{O}_{\text{initial}}$ and $\delta^{18}\text{O}_{\text{equilibrium}}$ values are estimated. The manner of estimating $\delta^{18}\text{O}_{\text{initial}}$ and $\delta^{18}\text{O}_{\text{equilibrium}}$ is discussed below. $\delta^{18}\text{O}$ values of clay minerals were determined by standard procedures (Taylor and Epstein, 1962; Yeh and Savin, 1977). The reproducibility of $\delta^{18}\text{O}$ was normally

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Table 1. $\delta^{18}\text{O}$ values and locations of samples from the Mississippi River and Gulf of Mexico.

Sample	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)	Location
1	+15.8	Head waters of the Missouri River, Three Forks, Montana.
2	+18.2	Missouri River, Williston, North Dakota.
3	+20.6	Missouri River, Sioux City, Iowa.
4	+20.8	Mississippi River, Pere Marquette State Park, Calhoun County, Illinois.
5	+20.1	Junction of Missouri and Mississippi Rivers, Madison County, Illinois.
6	+20.9	Mississippi River, 290 km upstream from Head of Pass, Louisiana.
7	+20.8	Mississippi River, 75 km upstream from Head of Pass, Louisiana.
8	+20.1	Mississippi River, 17 km upstream from Head of Pass, Louisiana.
9	+20.7	Mississippi River, Head of Pass, Louisiana.
10	+20.4	Gulf of Mexico, off Eugene Island, Louisiana.
11	+20.5	Gulf of Mexico, off Grand Isle, Louisiana.

better than 0.2‰. The value of ($\delta^{18}\text{O}_{\text{equilibrium}} - \delta^{18}\text{O}_{\text{initial}}$) in this study is about 5, so the limit of detection of the method is about 4% change.

Organic matter, carbonate, iron oxides, and manganese oxides were removed from the samples by chemical means. The purified samples were subjected to size separation to obtain clay mineral concentrates. The mineralogic compositions of the purified separates were determined by X-ray powder diffraction, and the $\delta^{18}\text{O}$ values of the separates were then measured. Details of these procedures are given elsewhere (Yeh, 1974; Eslinger and Savin, 1976; Yeh and Savin, 1977).

SAMPLES

Two sets of samples were used. The first set was bottom sediments of the Mississippi River and of the inner shelf of the Gulf of Mexico immediately off the Mississippi River. The Gulf samples were from the sea floor off Eugene Island and Grand Isle. The location of these samples is described in Table 1 and shown in Figure 1. Nine samples from the river and two sea-floor Gulf samples were used to estimate the $\delta^{18}\text{O}_{\text{initial}}$ values of the Gulf samples. Only $<0.1\text{-}\mu\text{m}$ fractions of the samples were used, because the mineralogy of this size fraction was generally simpler than that of coarser fractions and because they were more sensitive than



Figure 1. Sampling sites of Mississippi River and Gulf of Mexico samples. See Table 1 for exact locations.

coarser fractions to alteration or "contamination" by authigenic clays. The mineralogy of the $<0.1\text{-}\mu\text{m}$ fraction was mixed-layer illite/smectite (I/S) with a minor amount of illite layers. Hoffman (1979, 65–75) showed the percentage of illite layers in I/S from similar samples from the Mississippi River to be between 10 and 45.

The second set of samples was from the upper 600 m of Deep Sea Drilling Project site 323. Site 323 was drilled in 4993 m of water on the Bellingshausen Abyssal Plain about 50 km west of the Eltanin Fracture Zone and about 250 km north of the Antarctic continental rise (Hollister, Craddock *et al.*, 1976). A basal zone exists from about 630 to 700 m and is comprised largely of smectite. This zone overlies basalt (Lawrence *et al.*, 1979) and has been interpreted to have been originally mostly volcanics. The sediments from the upper 600 m are dominated by land-derived minerals and diatom debris, although minor amounts of authigenic clays may be present (Eslinger and Savin, 1976; Lawrence *et al.*, 1979). Core number, depth in the hole,

Table 2. Depth, mineralogy,¹ and isotope data of $<0.3\text{-}\mu\text{m}$ fraction of sediments from Deep Sea Drilling Project site 323.

Sample depth (m)	$\delta^{18}\text{O}$ (‰)	Estimated temperature (°C) ²	Pore water $\delta^{18}\text{O}$ ³ (‰)	$\delta^{18}\text{O}_{\text{equilibrium}}$ ⁴ (‰)
80	+19.0	3.2	-0.7	+30.0
165	+18.9	6.6	-1.1	+28.7
260	+21.8	10.4	-0.7	+28.1
365	+21.0	14.6	-1.4	+26.7
410	+19.5	16.4	-2.7	+24.8
460	+17.9	18.4	-2.5	+24.4
510	+20.7	20.4	-2.5	+23.9
555	+18.8	22.2	-2.7	+23.6
600	+16.8	24.0	-2.5	+23.2

¹ The mineralogy is mostly mixed-layer illite/smectite with trace amounts of illite, chlorite, kaolinite, quartz, and feldspar.

² Assuming: (1) Sea-floor temperature of the site is 0°C, and (2) geothermal gradient is 4°C/100 m.

³ Taken from Lawrence *et al.* (1979).

⁴ Assuming the samples are 100% smectite and using: (1) Yeh and Savin's (1977) equation, and (2) temperature and $\delta^{18}\text{O}$ of pore water of columns 3 and 4 of this table.

and mineralogy of the samples are given in Table 2. For this set of samples, $<0.3\text{-}\mu\text{m}$ fractions, instead of $<0.1\text{-}\mu\text{m}$ fractions, were used because of the small amount of sample available. As shown in Table 2, the mineralogy of these samples is more complex than that of the first set in Table 1. In addition to the highly expandable I/S, small amounts of illite, kaolinite, chlorite, feldspar, and quartz also are present. The amounts of minerals other than I/S in all the samples, however, and the differences in mineral compositions between samples are small; thus, the use of $<0.3\text{-}\mu\text{m}$ size fractions did not affect the studies. Nine samples taken from 80 to 600 m below the sea floor were used in the study. The age of the sample at 600 m depth was found to be about 25×10^6 yr (Hollister, Craddock *et al.*, 1976), and the temperature, assuming a geothermal gradient of $4^\circ\text{C}/100$ m, was estimated to be about 24°C .

RESULTS

River and Gulf samples

The $\delta^{18}\text{O}$ values of the $<0.1\text{-}\mu\text{m}$ fractions of Gulf and river samples are given in Table 1. The sample sites can be divided into four groups based on location. The Missouri River samples (1–3) had a $\delta^{18}\text{O}$ range of $+15.8$ to $+20.6\text{‰}$ and a $\delta^{18}\text{O}$ average of $+18.2\text{‰}$. The two middle Mississippi River samples (4 and 5) had values of $+20.8$ and $+20.1\text{‰}$ and a $\delta^{18}\text{O}$ average of $+20.5\text{‰}$. The lower Mississippi River samples (6–9) had a $\delta^{18}\text{O}$ range of $+20.1$ to 20.9‰ and a $\delta^{18}\text{O}$ average of $+20.6\text{‰}$. The two samples from the Gulf of Mexico (10 and 11) had, within the limits of precision, identical $\delta^{18}\text{O}$ values of $+20.4\text{--}20.5\text{‰}$. Thus, in a downstream direction and into the Gulf, the $\delta^{18}\text{O}$ values of $<0.1\text{-}\mu\text{m}$ I/S were $+18.2$, $+20.5$, $+20.6$, and $+20.5\text{‰}$.

Three conclusions are: (1) From mass balance, the upper Missouri River contributes a relatively small amount of $<0.1\text{-}\mu\text{m}$ I/S to the Mississippi River system. (2) The $\delta^{18}\text{O}$ value of $<0.1\text{-}\mu\text{m}$ I/S does not change from the middle to the lower Mississippi River area. (3) The $\delta^{18}\text{O}$ value of $<0.1\text{-}\mu\text{m}$ I/S from the Gulf of Mexico bottom sediments near the mouth of the Mississippi River (samples 10 and 11) is identical to the $\delta^{18}\text{O}$ of $<0.1\text{-}\mu\text{m}$ I/S of modern Mississippi River sediments. Thus, the current $\delta^{18}\text{O} = +20.5\text{‰}$ of the Gulf samples represents both $\delta^{18}\text{O}_{\text{initial}}$ and $\delta^{18}\text{O}_{\text{final}}$, and no measurable isotope exchange or recrystallization of $<0.1\text{-}\mu\text{m}$ I/S occurred during sedimentation onto or residence on the Gulf sea floor. Further, because $\delta^{18}\text{O}_{\text{equilibrium}} = +28.0\text{‰}$ for samples 10 and 11 (assuming the average temperature of the sampling sites to be 15°C ; Robinson, 1973), the $<0.1\text{-}\mu\text{m}$ I/S was not in isotopic equilibrium with ambient sea-bottom temperatures, but had a $\delta^{18}\text{O}$ attributable to the environment of the source areas. Assuming the I/S had an average of 30% illite layers and formed within the surface temperature range of 15° to 25°C , the equilibrium

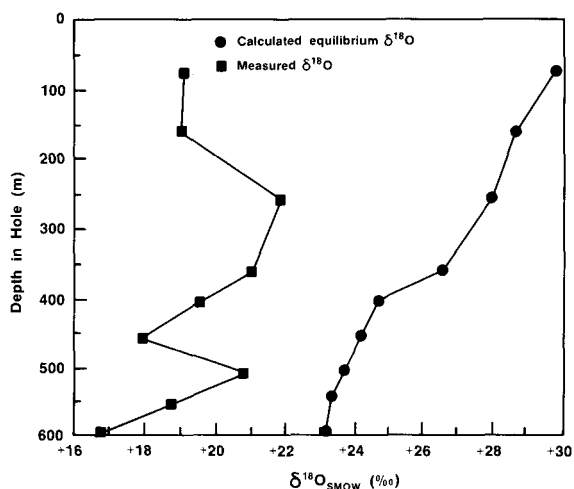


Figure 2. $\delta^{18}\text{O}$ values for samples from Deep Sea Drilling Project site 323.

isotope composition of the waters in the source area would have been about -4 to -6‰ . This $\delta^{18}\text{O}$ range is compatible with the $\delta^{18}\text{O}$ range of present-day meteoric waters in the middle Mississippi River drainage basin (Lawrence and Taylor, 1972).

Samples from Deep Sea Drilling Project site 323

The $\delta^{18}\text{O}$ values of samples from DSDP site 323 ranged from $+16.8$ to $+21.8\text{‰}$, suggesting that the sediments were mainly land-derived; in fact, most of the samples had a $\delta^{18}\text{O}$ within 1‰ of the river and Gulf samples discussed above. The $\delta^{18}\text{O}$ of the samples varied erratically with depth (Figure 2). The erratic $\delta^{18}\text{O}$ variation probably reflects variable amounts of terrigenous minerals derived from low latitudes or variable amounts of marine authigenic minerals. An increase in the amount of either of these materials would generally shift the $\delta^{18}\text{O}$ values in the positive direction because of the general increase of $\delta^{18}\text{O}$ values of meteoric water with decreasing latitude (see, e.g., Lawrence and Taylor, 1971) and because marine water generally has a higher $\delta^{18}\text{O}$ than meteoric water. Thus, the lack of a consistent trend of $\delta^{18}\text{O}$ with depth down to 600 m suggests that little diagenetic change in $\delta^{18}\text{O}$ of the detrital clays occurred during burial. Inasmuch as diagenetic alteration of terrigenous clays should have increased the $\delta^{18}\text{O}$ values during burial, it is particularly significant that the two deepest samples had smaller $\delta^{18}\text{O}$ values than the uppermost two samples.

Calculated $\delta^{18}\text{O}$ values for site 323 samples are given in Table 2 and shown in Figure 2. The values were calculated assuming that the samples were pure smectite. Correction for small amounts of nonsmectite minerals should change these values by no more than 1‰ and thus have no significant effect on the interpretations. It is obvious from Figure 2 that none of the site

323 samples was close to oxygen isotope equilibrium under the conditions of the sampling sites.

DISCUSSION

No evidence was found for alteration of detrital clays or the addition of authigenic clays in the Gulf samples inasmuch as $\delta^{18}\text{O}_{\text{initial}} = \delta^{18}\text{O}_{\text{final}} = 20.5\text{‰}$. Given that $\delta^{18}\text{O}_{\text{equilibrium}} = +28.0\text{‰}$ and that the precision of isotope analyses is 0.2‰, the detection limit is 2.7% of the total $\delta^{18}\text{O}$ "shift" necessary to bring the smectite into equilibrium with ambient conditions. Thus, the sediments cannot have acquired significant amounts of authigenic clays or undergone significant alteration during their accumulation onto the sea floor.

No evidence was found for a depth- (time-) related alteration of detrital clays or authigenic clays in the DSDP site 323 samples as deep as 600 m. Because the extent of diagenesis of detrital sediments (i.e., alteration of detrital clay minerals or formation of clay minerals from noncrystalline aluminosilicate material) should have increased with the age of and the temperature imposed on the sediments, the deepest sample should have displayed maximum diagenesis. The $\delta^{18}\text{O}$ value of the I/S fraction of the sample was about +18.0‰, probably the same value as the time of deposition because, except for hydrothermal nontronite from Red Sea metalliferous sediments, we have found no report in the literature of smectite (or highly expandable I/S) in deep-sea sediments with $\delta^{18}\text{O}$ values smaller than +18.0‰. The temperature and age of the sample at 600 m were about 25°C and 25×10^6 yr, respectively. Thus, although the possibility of a limited amount of diagenesis in this deepest sample and less in the shallower samples cannot be ruled out, it is certain that the samples could not have undergone the 20–40% of diagenetic alteration reported by Yeh and Savin (1976) for the <0.1- μm smectite in the 2–3 $\times 10^6$ yr deep-sea, near-surface sediments in North Pacific cores. In fact, the shift in isotope values with depth reported for the samples from those North Pacific cores (Yeh and Savin, 1976) must be due to factors other than diagenetic alteration of detrital sediments. Although not demonstrated, a likely cause for the shift is the addition of smectite derived from halmrolysis of volcanic ash.

The present study has not been able to define a maximum temperature or age below which sediments will not undergo significant reaction. Smectite clays may be stable at temperatures somewhat greater than 25°C or within sediments somewhat older than 25×10^6 yr.

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