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Detrital and authigenic minerals in sediments from the western part of the Indian Ocean

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ABSTRACT. Mineralogical and oxygen isotope analyses have been performed on nine western Indian Ocean core samples in order to distinguish the detrital from authigenic minerals in the sediments. Following the removal of carbonates, organic constituents and Fe and Mn oxides, the residue was separated into five size fractions, the principal minerals present being feldspar, quartz, clinoptilolite, and clay minerals.

Oxygen isotope compositions for two samples reflect an authigenic origin for clinoptilolite by the submarine alteration of volcanic material. Oxygen isotope compositions of two separates (free from feldspar and clays) suggest a detrital origin for the quartz in this area. The same mode of origin is apparent for the other components too, except possibly for some smectite which may have formed authigenically.

KEYWORDS: feldspar, quartz, clinoptilolite, clay minerals, sediments, Indian Ocean.

NINE samples of western Indian Ocean cores were analysed for mineral content and oxygen isotope composition in order to identify the modes of origin of the minerals in the sediments. The samples were obtained from depths 7.5 to 15 cm below the ocean floor by the Woods Hole Oceanographic Institution (Chain 43). They all proved to contain carbonates.

Fig. 1 presents the locations of the analysed samples and the general physiography of the region. All the samples are located west of the Carlsberg and Central Indian Ridges and lie on the same oceanic plate which moves westwards from these ridges. Sample 4 comes from the central part of the Somali Basin, while samples 5 and 6 from the eastern part of it, north of the Seychelles Bank (one of the Indian Ocean microcontinents). Sample 23 comes from the western foothills of the Carlsberg Ridge, near the oldest sector of an ancient magnetic anomaly. Sample 18 comes from the eastern part of the Mascarene Plateau, a saddle between the Seychelles and the Saya de Malha Banks. Sample 13 comes from the western foothills of the Central Indian Ridge and samples 11, 12, and 16 from the southern margin of the Mascarene Plateau.

Table I shows their latitudinal–longitudinal location, core and water depth, sediment accumulation rate, and depositional ages. These sample ages were estimated using the sedimentation rate at each site (DSDP Leg 24). The major input of terrigenous material in this region is by wind and rivers. Summer monsoons blowing from the southwest and winter monsoons blowing from the northeast constitute the normal wind system. The Indus river is the most important detrital source. The sediments of the Somali Basin have probably been transported there by turbidity currents from the adjacent continental margins.

Quartz, feldspars, and many clay minerals have been identified in recent marine sediments. Illite and chlorite are abundant components, with kaolinite commonly abundant near shore. The distribution of smectite, as well as of mixed-layer illite/smectite is irregular. These two minerals are frequently more abundant in areas where volcanic-ash debris has been an important source material. Moreover, zeolites frequently occur in high concentrations in oceanic sediments as alteration products of volcanic debris.

Oxygen isotope analyses of ocean sediments, mostly of Quaternary age, have shown that in most instances they have not reached isotopic equilibrium with the abyssal marine environment over periods of thousands of years (Savin, 1980). They therefore reflect the conditions of their formation and have potential use as indicators of provenance.

Isotopic compositions are obtained in the usual δ-notation (parts per thousand), as deviations from the isotopic composition of the SMOW standard (Craig, 1961).

Most clay minerals in the ocean basins are detrital, having been derived from the continents. However, some smectite and fine-grained quartz has been demonstrated to be of authigenic origin having been formed by the submarine alteration (halmyrolysis) of volcanic debris (Savin and Epstein, 1970*a*, *b*; Eslinger and Savin, 1976; Yeh and Savin, 1976).

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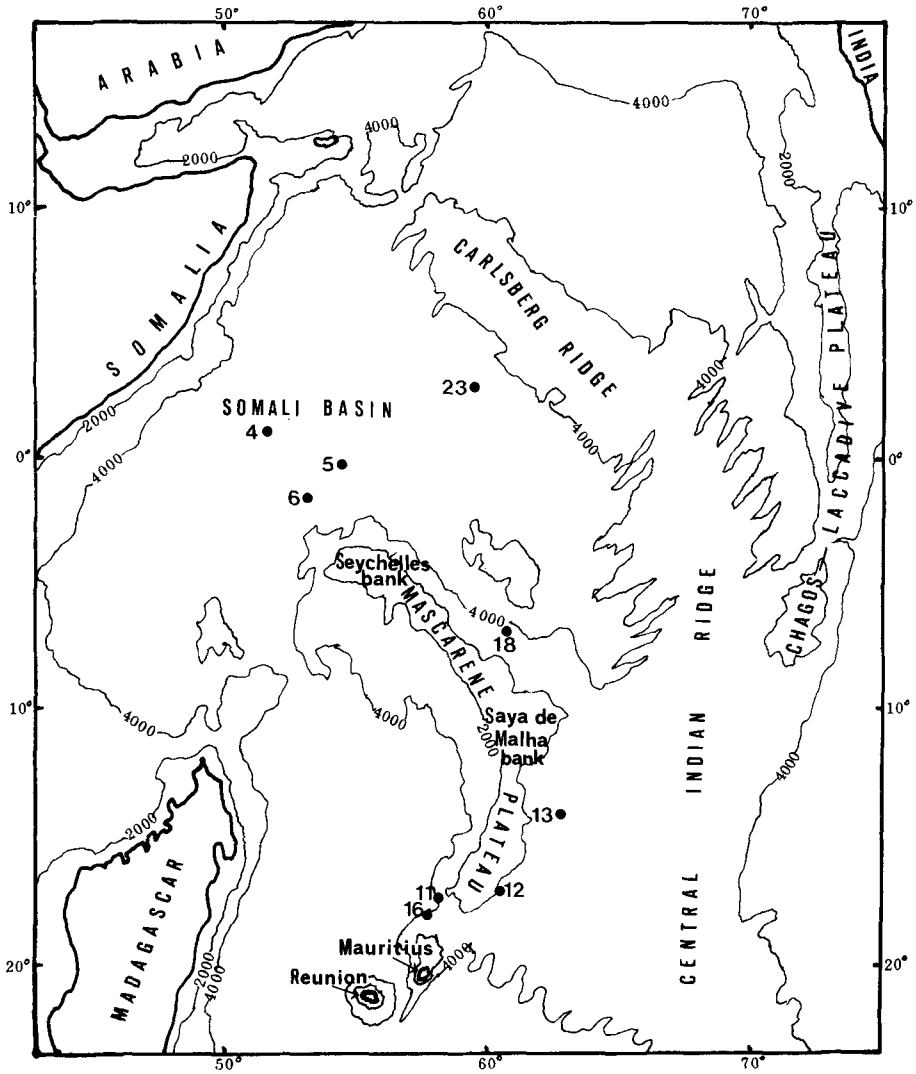

FIG. 1. Locations of samples and general physiography of the West Indian Ocean (DSDP Vol. 24).

Savin and Epstein (1970*b*) have shown that the $\delta^{18}O$ values of authigenic smectite are +10‰ higher than those of detrital smectite. Authigenic quartz in marine sediments has $\delta^{18}O$ values between +18 and +36‰ (Savin, 1973; Garlick, 1974), while quartz of igneous or metamorphic origin has values between +8 and +10‰ and +10 and +17‰ respectively (Taylor and Epstein, 1962; Garlick and Epstein, 1967; Shieh and Taylor, 1969).

Zeolite minerals in marine sediments are almost exclusively authigenic constituents. This mode of origin may be confirmed from their high $\delta^{18}O$ values. Oxygen isotope analyses of phillipsite have given $\delta^{18}O$ values as high as +34‰ (Degens and Epstein, 1962).

Biscaye (1965) made many deep-sea sediment analyses from the Atlantic, Antarctic, and western Indian Oceans. He concluded that the formation of minerals *in situ* on the ocean bottoms may be significant in parts of the southwestern Indian Ocean.

Analytical techniques. The core samples were subjected to the following chemical treatments (Jackson, 1974) to remove non-silicate phases: 1N sodium acetate buffer solution (pH 5) for carbonate removal; 30% H_2O_2 for organic matter and Mn-oxides removal; and a 1M

Table I. Locations, core & water depths, sedimentation rates and depositional ages

Sample	Latitude	Longitude	Core depth (cm)	Water depth (m)	Sedim.rate (cm/10^3yrs)	Depos.age (yrs)
CH-23	2°53'N	59°39'E	12.5	4099	1.0	12,500
CH- 4	0°55'N	51°38'E	10.0	4956	1.0	10,000
CH- 5	0°22'S	54°33'E	12.5	4721	1.0	12,000
CH- 6	1°38'S	53°20'E	15.0	4646	1.0	15,000
CH-18	7°17'S	60°32'E	12.5	3704	1.1	11,400
CH-13	14°14'S	62°51'E	10.0	3722	2.1	4,700
CH-12	17°23'S	60°24'E	12.5	3784	2.1	5,900
CH-11	17°26'S	58°05'E	7.5	3929	2.1	3,600
CH-16	18°04'S	57°40'E	10.0	3773	2.1	4,700

$NaHCO_3$-0.3M Na-citrate solution, with periodic addition of 1 g increments (up to 3 g) of $Na_2S_2O_4$ during digestion in a water-bath at 75–80 °C (removal of free Fe-oxides and interlayer Fe and Al hydroxides). The above treatments have no effect on the oxygen isotope composition of clays and other silicate minerals (Eslinger, 1971; Yeh, 1974).

The residues were separated into five size fractions by centrifuging (Table II) and stored in an oven overnight at about 100 °C. Subsequently, oriented glass-slides of each size fraction were prepared for mineralogical analysis by X-ray diffraction. However, as most of the initial untreated samples comprised more than 83% carbonate (Table II), the applied chemical treatments frequently left insufficient residue for both mineralogical and isotopic analysis. Consequently the mineral data are incomplete (Table III). All the oriented mounts were reanalysed following ethylene-glycolation to distinguish the expandable clay minerals and four samples were treated with DMSO (dimethyl sulphoxide) (Gonzalez and Sanchez, 1968) to resolve kaolinite and chlorite diffraction peaks.

The oxygen isotope composition of each of the separated fractions was determined using approximately 20 mg splits of sample material. Prior to analysis the sample splits were stored for 24 h in a dry box over P_2O_5. During the first two hours the dry box was flushed with N_2-gas as a preliminary step towards removal of the adsorbed and interlayer water from the clays. When a relative humidity close to 0% was obtained, the samples were loaded into Ni reaction vessels and linked up to a vacuum line where they were outgassed at about 250 °C for 2 h to complete the removal of the adsorbed and interlayer water. The structural oxygen was then displaced from the samples by fluorination (Taylor and Epstein, 1962). The oxygen liberated was isolated from other volatile by-products by passing through a KBr furnace and four liquid-N_2 traps on the vacuum line. Ultimately, the O_2 was converted to CO_2 for collection by interaction with a carbon rod. The CO_2 was collected, after manometric measurement of its volume and purification by circulating over hot Hg to remove any excess of F_2 or Br.

The isotopic composition of the CO_2 was measured in a double collecting mass spectrometer (Nier, 1947; McKinney *et al.*, 1950). All samples were analysed in duplicate with very good reproducibility (average deviation generally within ± 0.04‰). The measured δ-values were related to SMOW through a secondary standard,

Table II. Weight percent of the different sample size fractions

Sample	Weight (g)	Weight* (g)	COI (%)	Q + F + Clays(%)	Grain size (μm) >2	2-1	1-0.5	0.5-0.1	<0.1
CH-23	2.87	0.47	83.6	16.4	22.1	26.6	8.4	13.3	29.6
CH- 4	2.09	1.19	42.9	57.1	23.3	9.6	10.2	14.3	42.6
CH- 5	3.48	2.15	38.2	61.8	22.0	13.2	8.3	17.2	39.3
CH- 6	2.37	1.30	45.2	54.8	14.5	12.9	9.5	11.1	52.0
CH-18	1.98	0.22	88.9	11.1	26.4	19.0	14.6	11.7	28.3
CH-13	2.29	0.12	94.6	5.4	20.9	54.6	11.8	9.1	3.6
CH-12	3.86	0.15	96.1	3.9	36.3	10.5	3.2	4.0	46.0
CH-11	6.80	0.48	93.0	7.0	59.0	7.9	6.3	3.1	23.7
CH-16	4.38	0.33	92.5	7.5	42.9	17.6	7.3	8.6	23.6

Weight* = Weight after chemical treatments

COI = Carbonates + Organics + Iron & manganese oxides

Q = quartz, F = feldspar

NBS No. 28, a specimen of which was analysed with each set of five samples. Corrections for the contribution of quartz and feldspar have been applied to the $\delta^{18}O$ values of those samples where suitable information was available.

Mineralogical results and discussion. Most of the samples were so calcareous (oozes and chalks) that insufficient residue remained after the chemical treatments for a complete mineralogical analysis of all the separated size fractions. In six samples, 83% or more of the bulk sediment comprised carbonate material minor amounts of organic matter, Fe and Mn oxides, and Fe and Al hydroxides (Table II). The high clay content of samples 1, 5, and 6 suggests that they represent pelagic deep-water sediments.

The residues, whose grain size distributions are presented in Table II, were composed of quartz, feldspar (orthoclase plus plagioclase), illite, smectite, mixed-layer illite/smectite, kaolinite, chlorite, and clinoptilolite in varying proportions (Table III). Insufficient sample material was available for preparation of random mounts for X-ray diffraction analysis. Estimates of quartz and feldspar contents were therefore determined not from random mounts, but from the oriented-glycolated samples. Moreover, the percentages of quartz and feldspar in the different size fractions of samples 4 and 5 were determined following isolation of the quartz and feldspar using the pyrosulphate technique of Syers *et al.* (1968). The purity of the quartz and feldspar thus extracted was checked by X-ray

Table III. Mineralogical and oxygen isotope results

Sample	Size (μm)	Expand. layers(%)	I (%)	I/S (%)	K (%)	Ch (%)	Q (%)	Or (%)	Pl (%)	Cl	δO^{18} (‰)	Aver. dev.
CH-23	>2	0	55	0	5	5	18	8	9		+18.91	0.02
	2-1	0	59	tr	4	4	21	5	7		+18.64	0.04
	1-0.5	0	91	tr	3	6	tr	0	0		+18.83	0.06
	0.5-0.1	20	72	13	5	10	0	0	0		+19.98	0.02
	<0.1	50	25	59	5	11	0	0	0		+25.07	0.01
CH- 4	>2	0	57	0	6	3	8	26*			+18.26	0.05
	2-1	0	70	0	11	6	4	9			+19.99	0.06
	1-0.5	0	73	tr	15	8	4	tr			+21.74	0.02
	0.5-0.1	20	64	8	18	10	0	0			+19.18	0.01
	<0.1	50	34	35	20	11	0	0			+21.56	0.02
CH- 5	>2	0	61	0	5	5	8	11	10		+22.68	0.02
	2-1	0	68	tr	7	7	7	5	6		+19.31	0.01
	1-0.5	10	75	7	9	7	2	tr	tr		+16.12	0.04
	0.5-0.1	30	70	10	11	9	tr	0	0		+16.13	0.01
	<0.1	50	37	38	14	11	0	0	0		+19.82	0.00
CH- 6	>2	0	53	0	3	4	9	18	13		+20.43	0.04
	2-1	0	56	0	4	4	12	16	8		+18.21	0.03
	1-0.5	0	86	0	9	5	0	tr	0		+16.86	0.02
	0.5-0.1	30	46	22	32**		0	0	0		+17.13	0.05
	<0.1	40	45	28	27		0	0	0		+15.72	0.00
CH-18	>2	0	52	0	10		25	6	7		+38.21	0.02
	2-1	0	85	0	15		tr	tr	tr		+30.67	0.00
	1-0.5	10	76	9	15		0	0	0		+31.70	0.04
	0.5-0.1										+29.52	0.00
	<0.1	50	38	46	16		0	0	0		+26.08	0.04
CH-13	>2										+36.96	0.06
	2-1	0	44	0	16		40		tr		+34.35	0.02
	1-0.5										+29.20	0.02
	0.5-0.1										+23.96	0.00
	<0.1										+23.42	0.05
CH-12	>2	30	49	10	11		0		30	Maj.@	+35.93	0.01
	2-1										+25.53	0.03
	1-0.5										+18.00	0.06
	0.5-0.1										+15.76	0.00
	<0.1	55	32	45	23		0		0	0	+21.96	0.00
CH-11	>2	25	46	19	6		0		29	Imp.@	+34.56	0.06
	2-1										+23.30	0.02
	1-0.5										+18.76	0.08
	0.5-0.1										+17.70	0.04
	<0.1	55	41	41	18		0		0	0	+16.74	0.02
CH-16	>2	20	34	20	6	4	tr		36		+16.48	0.04
	2-1	60	41	22	10	6	0		21		+14.55	0.03
	1-0.5	65	46	25	18	11	0		tr		+10.54	0.02
	0.5-0.1										+15.54	0.04
	<0.1	50	25	54	13	8	0		0		+26.30	0.04

I = illite, I/S = mixed-layer illite/smectite, K = kaolinite, Ch = chlorite
Q = quartz, Or = orthoclase, Pl = plagioclase, Cl = clinoptilolite
* Or + Pl, ** K + Ch
@ Major: Diffraction peaks of clinoptilolite dominate the diffraction pattern.
Important: A number of peaks of clinoptilolite are visible on the diffraction pattern.

diffraction. Clay mineral percentages were determined from the X-ray diffractograms of ethylene-glycol saturated samples obtained in a GE Diffractometer using Cu-$K\alpha$ radiation (methods of Schultz, 1964; Reynolds and Hower, 1970).

Clinoptilolite, although present as a major constituent in sample 12 and in significant quantity in sample 11, was not included in the total percentage of the remaining components. In the case of four samples the DMSO treatment was applied to differentiate between kaolinite and chlorite which could then be summed separately. For the rest of the samples, kaolinite and chlorite were summed either separately, when the kaolinite (002) and chlorite (004) peaks appeared resolved, or together, when there was only one peak at this angle (about 24.8° 2θ). However, all the mineral estimates are semiquantitative with a $\pm 10\%$ error (Schultz, 1964; Reynolds and Hower, 1970). The mineral data are presented in Table III.

In the north, quartz and feldspar are the dominant components of the > 2 μm non-clay mineral fraction, decreasing in abundance with decreasing grain size. In the south, orthoclase is absent while plagioclase is the sole mineral in the non-clay mineral fraction.

In samples 11, 12, and 16 plagioclase is the dominant mineral in the coarser fractions while quartz is absent from samples 11 and 12, and only traces exist in sample 16 (> 2 μm). Additionally, clinoptilolite is a major component in sample 12 (> 2 μm) and important in sample 11 (> 2 μm). The > 2 μm fraction of samples 11 and 12 consists respectively of 25% and 30% expandable layers while in their < 0.1 μm size fraction the content of expandable minerals increases in both samples to 55%. This behaviour is also evident in sample 16 where a more complete mineralogical analysis is available.

The dominant clay mineral in all samples is illite, whose percentage in any given sample is relatively consistent throughout all grain sizes except in the < 0.1 μm. In the latter size fractions the dominant clay mineral is mixed-layer illite/smectite. Expandable minerals are more evident in the southern samples and especially in sample 16 where even in the > 2 μm fraction there are 20% expandable layers. Generally, I/S mixed-layers are more abundant in the smaller two grain size fractions. In sample 16 the expandable layers are as high as 65%. The rest of clay minerals comprise kaolinite and chlorite.

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 (Eslinger and Savin, 1976). The implication, according to the same authors, is that samples that contain illite/smectite with a relatively broad 17 Å peak are largely detrital in origin, while samples that contain illite/smectite with relatively sharp 17 Å peak are largely authigenic in origin. Close examination of the diffractograms of the < 0.5 μm fractions indicated that samples with a relatively small average percentage of expandable layers had a broader 17 Å peak, indicating a heterogeneous mixture of illite/smectite. These samples are characterized by significant amounts of coexisting illite, kaolinite, and chlorite. However, diffractograms of some samples with a relatively large average percentage of expandable layers showed a sharp 17 Å peak indicating a homogeneous illite/smectite with a large authigenic percentage. These samples are characterized by lower percentages of illite, kaolinite, and chlorite.

The parent material of the authigenic illite/smectite is assumed to be volcanic ash.

Oxygen isotope results and discussion. The oxygen isotope results of the analysed samples are presented in Table III. The $\delta^{18}O$ values obtained range from $+10.54$ to $+38.21$ ‰. In general, they gave low $\delta^{18}O$ values reflecting a detrital origin for most of their components. An authigenic origin of at least some of the smectite in association with clinoptilolite in the southern samples must not be ruled out for those samples with $\delta^{18}O$ values higher than $+25$ ‰.

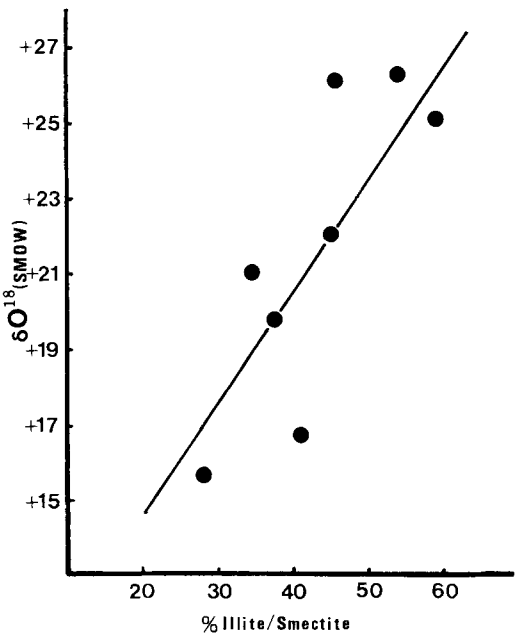

FIG. 2. $\delta^{18}O$ values *vs.* percentage of illite/smectite in the $< 0{\cdot}1$ μm fractions.

The dominant clay mineral phase in the < 0.1 μm fraction is illite/smectite containing 40–55% expandable layers. This fraction has an isotopic composition that varies from +16.74 to +26.30‰ depending on the I/S percentage (fig. 2). During the weathering process the $\delta^{18}O$ of the bulk rock (unaltered volcanic ash plus the alteration product illite/smectite) has increased and the $\delta^{18}O$ of the surrounding sea water has decreased in an approach toward isotopic equilibrium as the percentage of illite/smectite in the sample increases.

Lawrence *et al.* (1975) have shown that the isotopic composition of diagenetic smectite depends on the nature of the source material (basalt or ash), the porosity, and the extent of alteration.

The clinoptilolite probably formed *in situ* from the alteration of volcanic debris. Intense volcanic activity prevailed in this region (Saya de Malha, Mauritius, Réunion) during the Late-Tertiary–Early-Quaternary period. Moreover, abundant volcanic fragments and ash occur among the sedimentary layers that lie below the horizon from which the samples of this study were extracted. The higher (above +34‰) $\delta^{18}O$ values obtained for the > 2 μm fraction of samples 11 and 12 suggest the authigenic formation of clinoptilolite.

Table IV. Isotopic compositions of quartz and feldspar separates

Sample	Size (μ)	δO^{18}_{total}	δO^{18}_{q}	δO^{18}_{f}	δO^{18}_{q+f}	$\delta O^{18}_{corr.}$	Aver. dev.
CH- 4	>2	+18.26	+17.92			+18.29	0.03
CH- 5	>2	+22.68	+19.09			+23.04	0.36
CH- 5	2-1	+19.31		+17.39	+17.84	+19.63	0.32

In contrast, all of the quartz present is detrital in origin. Two quartz separates of the > 2 μm fraction (Table IV) gave $\delta^{18}O$ values of +19.09 and +17.92‰, very close to the average of +18‰ for detrital quartz of ocean sediments obtained by Clayton *et al.* (1968).

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REFERENCES

Biscaye, P. E. (1965) *Bull. Geol. Soc. Am.* **76,** 803–32.
Clayton, R. N., Muffler, L. J. P., and White, D. E. (1968) *Am. J. Sci.* **266,** 968–79.
Craig, H. (1961) *Science,* **133,** 1833–4.
Degens, E. T., and Epstein, S. (1962) *Bull. Am. Assoc. Petrol. Geol.* **46,** 534–42.
Eslinger, E. V. (1971) *Mineralogy and oxygen isotope ratios of hydrothermal and low-grade metamorphic argillaceous rocks.* Ph.D. thesis, Dept. of Geology, CWRU, Ohio, USA.
——and Savin, S. M. (1976) In *Initial Reports of the DSDP,* **35,** 489–96.
Garlick, G. D. (1974) In *The Sea,* **5** (E. D. Goldberg, ed.). Wiley, New York, 393–425.
——and Epstein, S. (1967) *Geochim. Cosmochim. Acta,* **31,** 181–214.
Gonzalez, G. S., and Sanchez, C. M. (1968) *Clay Minerals,* **7,** 445–50.
Jackson, M. L. (1974) *Soil chemical analysis—Advanced course.* 2nd edn. Madison, Wis. Published by the author.
Lawrence, J. R., Gieskes, J. M., and Broecker, W. S. (1975) *Earth Planet. Sci. Lett.* **27,** 1–10.
McKinney, C. R., McCrea, J. M., Epstein, S., Allen, H. A., and Urey, H. C. (1950). *Rev. Sci. Instrum.* **21,** 427–30.
Nier, A. O. (1947) Ibid. **18,** 398–411.
Reynolds, R. C., and Hower, J. (1970) *Clays and Clay Minerals,* **18,** 25–36.
Savin, S. M. (1973) In *Proceedings of Symp. on Hydroch. Bioch.,* Tokyo, 372–91.
——(1980) Contr. No. 121, Dept. of Earth Sciences, C.W.R.U., Ohio, USA.
——and Epstein, S. (1970*a*) *Geochim. Cosmochim. Acta,* **34,** 25–42.
————(1970*b*) Ibid. **34,** 43–63.
Schultz, L. G. (1964) *U.S.G.S. Spec. Paper,* 391-C.
Shieh, Y. N., and Taylor, H. P. (1969) *Contrib. Mineral. Petrol.* **20,** 306–56.
Syers, J. K., Chapman, S. L., Jackson, M. L., Rex, R. W., and Clayton, R. N. (1968) *Geochim. Cosmochim. Acta,* **32,** 1022–5.
Taylor, H. P., and Epstein, S. (1962) *Geol. Soc. Am. Bull.* **73,** 461–80.
Yeh, H. W. (1974) *Oxygen isotope studies of ocean sediments during sedimentation and burial diagenesis.* Ph.D. thesis, Dept. of Geology, CWRU, Ohio, USA.
——and Savin, S. M. (1976) *Geochim. Cosmochim Acta,* **40,** 743–8.

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