

## IV. GEOCHEMISTRY OF CARBON AND SULFUR: DSDP LEG 29

J. G. Erdman, K. S. Schorno, and R. S. Scalan, Phillips Petroleum Company, Bartlesville, Oklahoma

### INTRODUCTION

A total of 11 samples from core sections and one core chip were received from a sample distribution from the JOIDES Organic Geochemistry Subcommittee. Locations of the holes from which these samples came are shown in Figure 1. Six-cm samples had been obtained onboard ship. The samples in their plastic core liners were frozen onboard ship and maintained frozen thereafter. Later, 5-cm sections were removed from the frozen core for determination of volatile hydrocarbons. The remainder of the sample was then split, the authors receiving half for description, for photographing, and for carrying out the determinations discussed below.

### SAMPLING AND STUDY PROCEDURES

A channel was cut down each side of the plastic liner using a circular saw. Cuttings were removed with a brush, and the final cut was made with a sharp knife. The sample was split using a piece of steel wire.

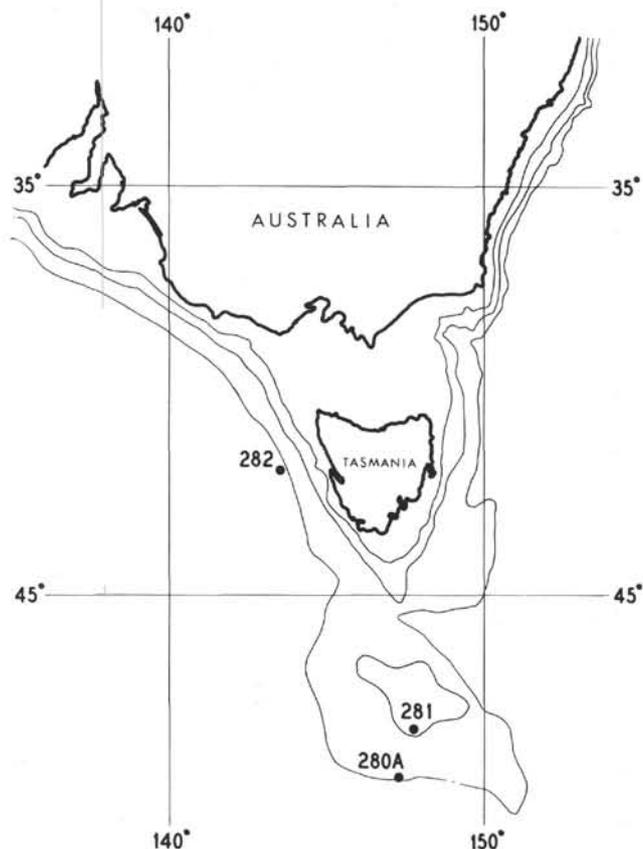


Figure 1. Location of holes from which samples for geochemical study were procured.

The flat surfaces of the samples were smoothed for description and photographing, using a milling machine and flycutter. Photographs of the samples are provided in Figures 2-12 along with overlay diagrams of textural or color patterns and brief lithological descriptions. Sample chips of each textural type or color were removed to determine carbonate carbon and organic carbon values (Table 1). The vertical (top-bottom) orientation of the samples was not recorded onboard ship. The remaining determinations described herein were made on linear strips of the sample.

The flow diagram for separating and determining carbon species is shown in Figure 13. The solvents were distilled in glass immediately before use. Each analytical determination was performed in duplicate. The flow diagram for separation and isotopic characterization of "solid" sulfate is shown in Figure 14. The extracted sulfate was converted to silver sulfide, which was then burned to sulfur dioxide for determination of isotopic composition.

### RESULTS AND DISCUSSION

Tables 2 and 3 list the data representative of the bulk sample, i.e., the average for the entire core sample in order of reported increasing geological age. Within each age group the listing is given according to increasing depth into the sediment. The calcium carbonate values are calculated from the carbonate carbon values.

TABLE 1  
Carbonate and Organic Carbon Values for  
Inclusions Noted in Figures 2-12

Figure	Inclusion	Carbonates		Organic Carbon (wt. %)
		Carbon (wt. %)	Calcium (wt. %)	
2	1	11.26	93.8	0.05
3	1	4.27	35.6	0.12
	2	1.92	16.0	0.49
	3	3.88	32.3	0.10
	4	3.73	31.1	0.16
	5	3.64	30.3	0.14
	6	3.78	31.5	0.17
4	1	1.30	10.8	0.36
5	1	0.01	0.08	0.26
6	1	0.02	0.1	0.25
	2	0.02	0.1	0.31
7	1	0.02	0.2	0.34
	2	0.17	1.4	0.42
	3	0.05	0.4	0.36
8	1	0.01	0.08	0.45
	2	0.02	0.1	0.55
9	1	0.04	0.3	1.42
10	1	0.11	1.0	0.78
11	1	0.19	1.6	0.63
	2	0.18	1.5	0.60
12	1	3.87	32.3	0.67

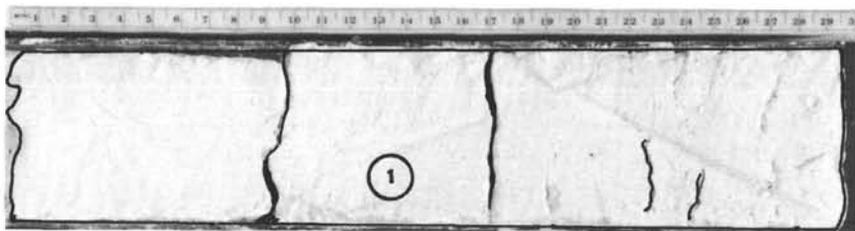


Figure 2. Site 281, Core 11, Section 0. Lime ooze, white (N9) to very light gray (N8) very soft and plastic, sandy, massive.

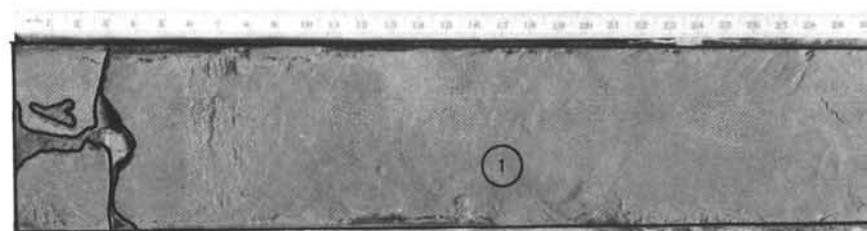


Figure 4. Site 281, Core 14, Section 0. Sandy clay, olive-gray (5Y 4/1) medium firm and only slightly plastic, fine grained and homogeneous throughout vertical extent, but contains 4.5-cm silicified siltstone pebble at base.

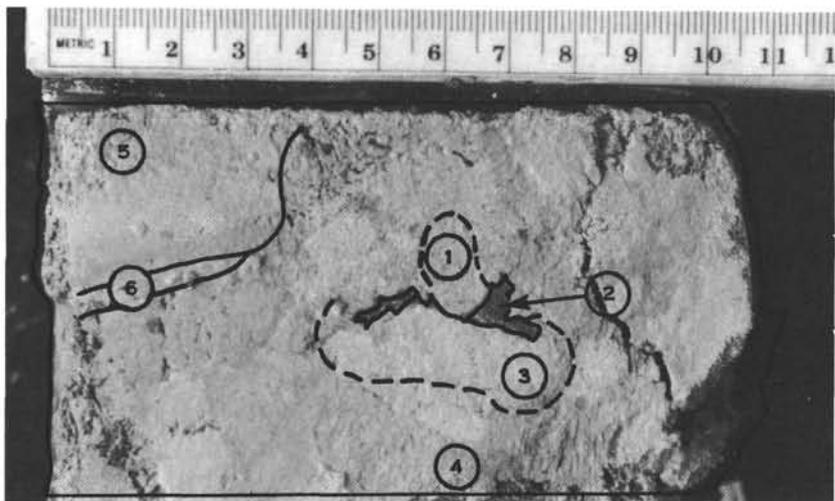


Figure 3. Site 282, Core 4, Section 0. Clay ooze very calcareous light greenish-gray (5G 8/1) to greenish-gray (5GY 6/1) (deformed due to coring process). Very soft and wet stocky, plastic nonsilty.

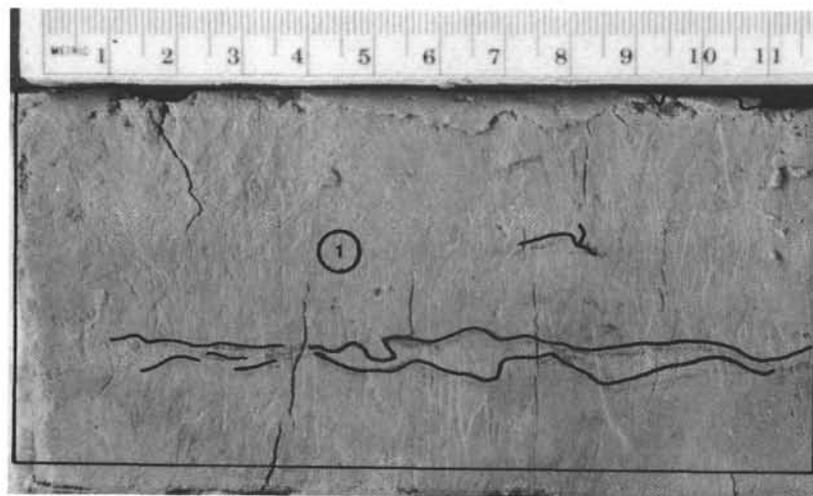


Figure 5. Site 280 (Hole 280A), Core 6, Section 2. Clay, grayish-olive-green (5GY 3/2) to olive-gray (5Y 4/1), soft, very plastic, massive.

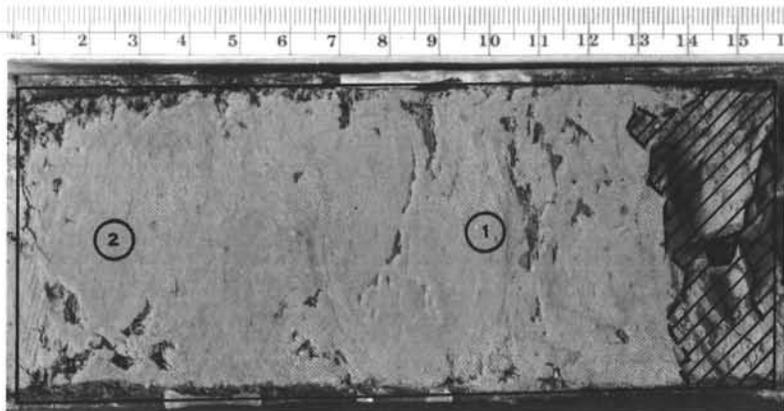


Figure 6. Site 280 (Hole 280A), Core 10, Section 4. Clay, olive-gray (5Y 4/1), to dark greenish-gray (5GY 4/1), silty, massive bedded, appears to have subconchoidal fractures, soft and plastic. Core is homogenous throughout vertical extent.

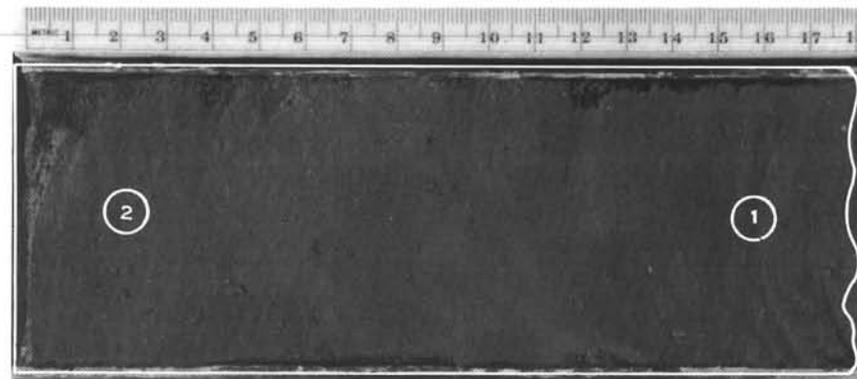


Figure 8. Site 280 (Hole 280A), Core 13, Section 3. Clay, dark greenish-gray (5GY 4/1) soft, somewhat plastic massive and homogeneous throughout vertical extent.

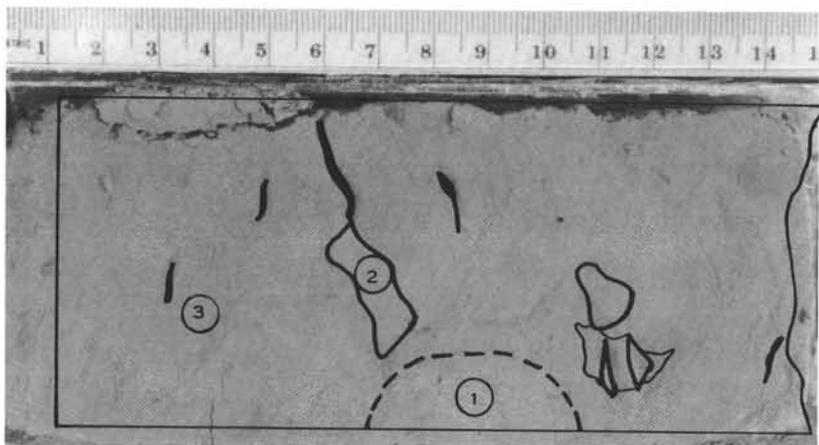


Figure 7. Site 280 (Hole 280A), Core 11, Section 1. Clay, greenish-gray (5G 6/1), plastic, medium hard and contains interspersed dark laminae (dark gray - N3) throughout core; laminae contacts are sharp and also gradational. Overall core appears to resemble a breccia and consists of angular fragments.

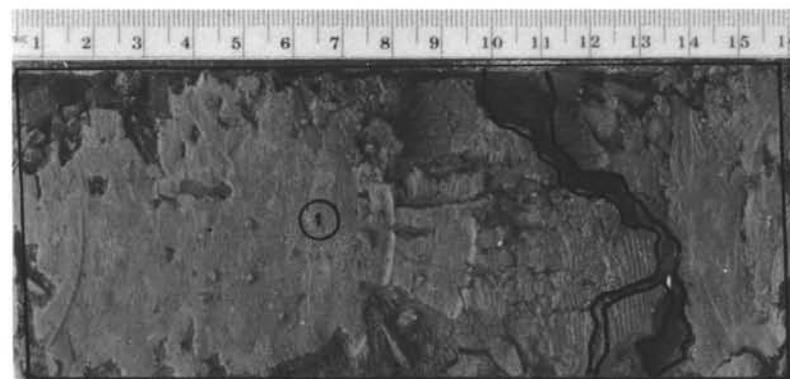


Figure 9. Site 280 (Hole 280A), Core 19, Section 0. Clay, olive-gray (5Y 4/1) medium hard, nonplastic, slightly silty, and massive. Core recovery poor and sample badly fractured. Core appears homogeneous throughout vertical extent.

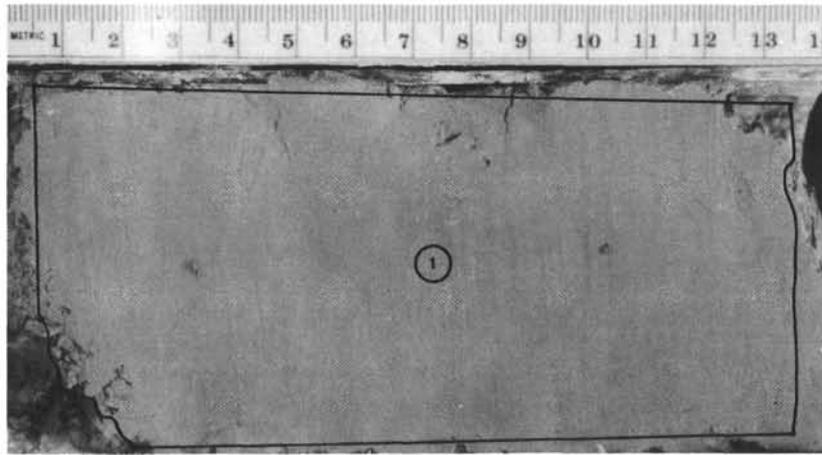


Figure 10. Site 280 (Hole 280A), Core 20, Section 2. Clay, light olive-gray (5Y 6/1) soft, only slightly plastic, massive bedded.

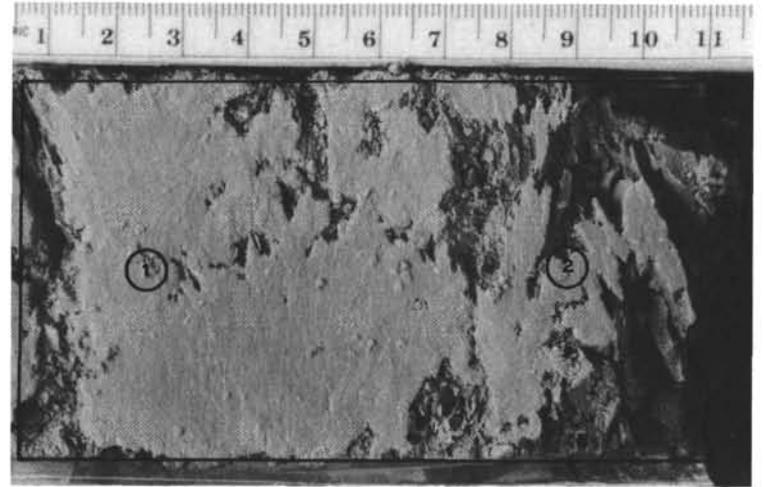


Figure 11. Site 280 (Hole 280A), Core 21, Section 1. Clay, olive-gray (5Y 4/1), medium soft, plastic, slightly silty, massive bedding homogeneous.

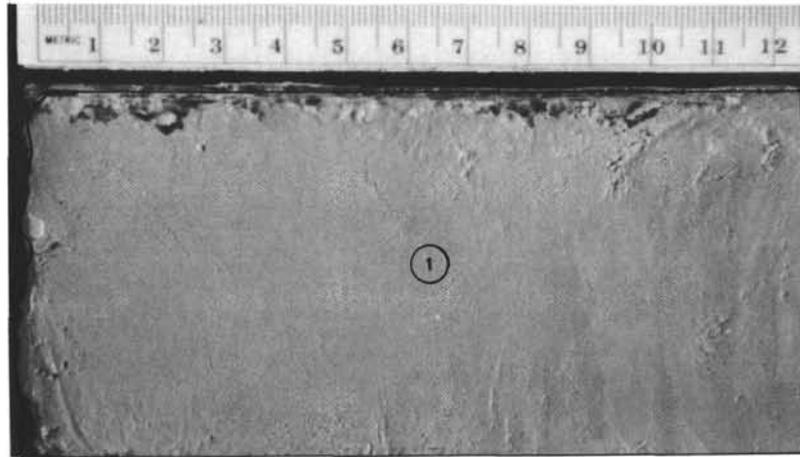


Figure 12. Site 281, Core 16, Section 0. Clay, yellowish-gray (5Y 7/2) to grayish-yellow (5Y 8/4) very soft, plastic, water wet and silty, calcareous clay is homogeneous throughout vertical extent with exception of lower 5 cm which is slightly mottled.

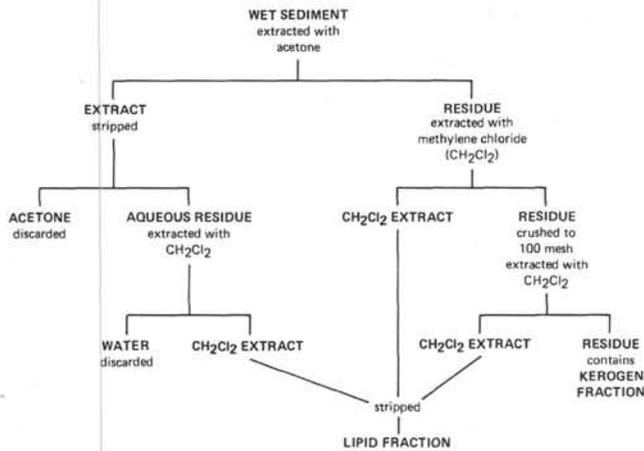


Figure 13. Flow diagram for separation and determination of carbon species.

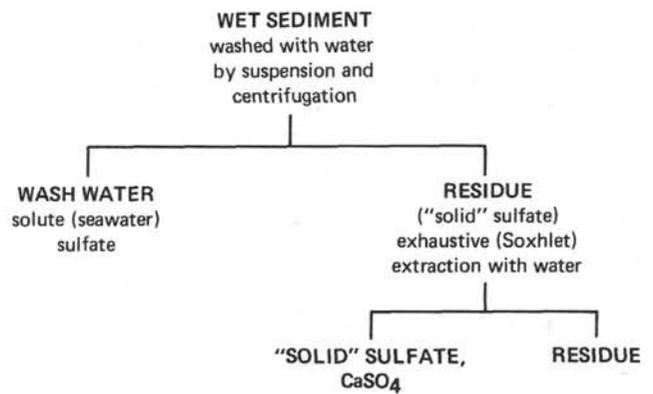


Figure 14. Flow diagram for separation and isotopic determination of "solid" sulfate.

TABLE 2  
Carbonate Content and Concentrations of Organic Fractions in  
Geochemical Samples from DSDP Leg 29

Site-Core-Section	Age <sup>a</sup>	Subbottom Depth (m)	Carbonate		Organic Carbon			Total Lipid
			Carbon	CaCO <sub>3</sub>	Total	Lipid	Kerogen	
281-11-0	Middle Miocene	93.2-93.5	11.34	94.5	0.06	0.004	0.06	0.073
282-4-0	Early Miocene	28.3-28.5	3.63	30.3	0.29	0.001	0.29	0.003
281-14-0	Early Miocene	121.5-122.0	1.13	9.42	0.34	0.019	0.32	0.054
280A-6-2	Late to middle Eocene	121.5-122.0	0.06	0.50	0.40	0.024	0.38	0.059
280A-10-4	Late to middle Eocene	196.1-197.5	0.11	0.92	0.32	0.017	0.34	0.047
280A-11-1	Late to middle Eocene	216.3-216.5	0.09	0.75	0.39	0.013	0.38	0.042
280A-13-3	Late to middle Eocene	262.5-262.7	0.15	1.3	0.69	0.024	0.67	0.038
280A-19-0	Late to middle Eocene	443.0-443.2	0.17	1.4	1.47	0.076	1.39	0.052
280A-20-2	Late to middle Eocene	482.3-482.5	0.15	1.3	0.87	0.056	0.81	0.064
280A-21-1	Late to middle Eocene	510.8-511.0	0.30	2.5	0.60	0.042	0.56	0.071
281-16-0	Early Eocene	140.8-141.0	3.98	33.2	0.61	0.023	0.59	0.038
282-17-25	Early Eocene	256.5 <sup>b</sup>	1.72	14.3	3.34	0.075	3.27	0.023

<sup>a</sup>DSDP Shipboard Summary Report, Leg 29.

<sup>b</sup>Core chip (not photographed or spot sampled).

TABLE 3  
Carbon Isotopic Composition of Lipid and Kerogen  
Fractions in Geochemical Samples from DSDP Leg 29

Site-Core-Section	Carbon Isotopic Composition, $\delta C_{PDB}^{13}$		
	Lipid	Kerogen	Difference L-K
281-11-0	-27.4	-23.7	-3.7
282-4-0	-26.2	-21.3	-4.9
281-14-0	-28.1	-28.7	0.6
280A-6-2	-26.9	-24.9	-2.0
280A-10-4	-26.4	-27.4	1.0
280A-11-1	-27.6	-24.5	-3.1
280A-13-3	-27.3	-25.5	-1.8
280A-19-0	-25.9	-23.5	-2.4
280A-20-2	-25.7	-29.7	4.0
280A-21-1	-27.4	-26.8	-0.6
281-16-0	-27.5	-27.5	0.0
282-17-25	-26.5	-24.5	-2.0

Assuming that a single characteristic sample extends over an area encompassing the three drilling sites, the data suggest several trends. The carbonate content drops from high values in the middle to early Miocene, reaches a low in the late to middle Eocene, and then appears to rise again in the lower Eocene. This transition is abrupt ranging from approximately 95% calcium carbonate to an average of 1% or at most several percent. As shown by the photographs and the core descriptions (Figures 2-12), the color trends from near white in the middle Miocene and the more calcareous of the two early Miocene cores to dark greenish-gray in the shallower late to middle Eocene cores. In the deeper, presumably older late to middle Eocene cores of Hole 280A, the color becomes progressively more brown. This trend continues to the late Eocene cores.

Red bed sections on land and red deep marine oozes usually are extremely low in organic matter, but in the present sequence the concentration of total organic

matter increases from less than 0.1% in the near white middle Miocene lime ooze, to values of 0.6% or higher in those late to middle, and lower Eocene samples showing brown shades. As organic-rich sediments age under anaerobic conditions, the ratio of lipid to total organic carbon usually increases. Under aerobic conditions this trend is reversed. In these cores, the ratio of lipid to total carbon is average to high for such geochemically young, i.e., shallowly buried sediments, and there does not seem to be any significant trend with geologic age, sediment depth, or sediment color.

The carbon isotopic values of the lipid fractions vary by  $2.4^{\circ}/_{\infty}$  and for the kerogen fraction by  $8.4^{\circ}/_{\infty}$ . Usually as organic diagenesis proceeds, particularly under anaerobic conditions, the spread between the values for the lipid and kerogen values increases, with the values for the lipid fractions being the more negative. For the 12 samples, the lipid fraction of 9 samples is isotopically lighter, i.e., more negative than the corresponding kerogen. There is no apparent trend, however, with increasing geological age or depth.

A preliminary isotopic investigation has been made of the sulfate fractions of Site 281, Core 14, Section 0 and Site 281, Core 11, Section 0. The first sample consisted of sandy clay with only 9.42% calcium carbonate and 0.34% total organic matter. A large difference was observed in sulfur isotopic composition between the

seawater sulfate and the solid sulfate. The initial water extract gave a value of  $+22.8^{\circ}/_{\infty}$  typical of that observed for seawater and sedimentary sulfates (Holser and Kaplan, 1966). Sulfates removed by exhaustive extraction of the same sample, i.e., solid sulfate, gave a value of  $-14.4^{\circ}/_{\infty}$ . This value is unusual for sulfates and lies in the range of values of sedimentary sulfides, and free sulfur of biogenic origin (Ault and Kulp, 1959). It may represent reoxidation of sulfur previously fractionated by microbiotic reduction of sulfates. Results are preliminary, and this value will be checked.

Site 281, Core 11, Section 0 is a lime ooze averaging 94.5% calcium carbonate and 0.06% organic matter. The solid sulfate fraction, presumably gypsum, gave a sulfur isotopic value of  $+22.4^{\circ}/_{\infty}$ . This value is typical of the reported ranges of sedimentary sulfates.

The large difference reported here for the sulfate sulfur isotopic compositions is difficult to explain in terms of other core properties, and on the basis of so little data further explanation would be unwarranted.

#### REFERENCES

- Ault, W. U. and Kulp, J. L., 1959. Isotope geochemistry of sulfur: *Geochim. Cosmochim. Acta*, v. 16, p. 201-235.  
 Holser, W. T. and Kaplan, I. R., 1966. Isotope geochemistry of sedimentary sulfates: *Chem. Geol.*, v. 1, p. 93-135.