35. SECULAR VARIATIONS IN SEDIMENTARY ORGANIC δ^{13}C DURING THE LAST 35 M.Y. IN THE TROPICAL ATLANTIC, SITE 925[1]

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ABSTRACT

We present the sedimentary organic carbon isotope (δ^{13}C) record at Site 925 (Ceara Rise) for the last 35 m.y. The δ^{13}C values increase from −24‰ in the Oligocene to −21‰ in the middle Quaternary. At the Oligocene/Miocene boundary, values shift about +1‰, and during the latest Miocene to late Pliocene, values again shift by nearly +2‰. Sedimentary aluminum and titanium contents suggest that the secular variations of the organic δ^{13}C are mainly controlled by the marine δ^{13}C value. The isotopic composition of total dissolved CO_2 in the Oligocene was probably slightly heavier than the present value. We suggest three mechanisms to explain the secular variations of $\delta^{13}C_{org}$ during the last 35 m.y.: changes in (1) surface water CO_2(aq) concentration, (2) activity of carbon fixation process, and (3) relative abundance of organic compounds.

INTRODUCTION

Until recently, the organic carbon isotope composition ($\delta^{13}C_{org}$) of pelagic sediments had been neglected compared to the inorganic carbon isotopes mainly because of the complexity of the mechanisms controlling organic carbon isotopes (e.g., Fontugne and Duplessy, 1986; Macko, 1989; Galimov, 1995). However, recent progresses in plant physiology revealed the mechanism of carbon isotope fractionation during photosynthesis (e.g., O'Leary, 1981; Farquhar, 1983; Hayes, 1993), which allows the analysis of the potential environmental information recorded in the carbon isotope composition of organisms. By applying this knowledge to the δ^{13}C of organic matter preserved in deep-sea sediments, several authors have obtained paleoenvironmental information in recent years (e.g., Popp et al., 1989; Jasper and Hayes, 1990; Rau et al., 1991).

In this study we report analytical results of $\delta^{13}C_{org}$ from Site 925 covering the last 35 m.y. and discuss the cause of its secular variations during this time span. In addition, we measured aluminum and titanium contents of these sediments to estimate the input of terrigenous material.

METHODS

The dried sediments were ground to a fine powder using an agate pestle. Pulverized samples were treated with excess 3M HCl overnight to remove carbonate carbon. After checking that the pH of the solution was less than 2, the residue was washed with distilled water twice to remove salts. Organic carbon contents for these decarbonate samples were measured using a Yanagimoto MT-3 CHN analyzer.

Aluminum and titanium concentrations were determined by an X-ray fluorescence spectrometer. The $CaCO_3$ content was calculated from the Ca concentration after subtracting an aluminosilicate Ca component. The Ca/Al value of aluminosilicate is assumed to be the average crustal value of 0.345 (Turekian and Wedepohl, 1961).

Organic carbon isotopic compositions were determined by the standard technique described in Wada and Matsubara (1995). We

placed 300 mg of dry sediment in a quartz tube with CuO (1 g), Cu (0.5 g), and a piece of Ag foil. It was evacuated to 10^{-3} mmHg. The sealed tube was heated at 850°C for 2 hr and cooled down overnight. The carbon dioxide produced was cryogenically isolated from other combustion products. Isotopic measurements were performed using a Finnigan-MAT 252 mass spectrometer. Isotopic compositions are expressed in the conventional δ notation:

$$\delta^{13}C = (R_{sample} / R_{standard} - 1) \times 1000 \ (‰),$$

where R denotes the $^{13}C/^{12}C$ ratio of samples and standards (Peedee belemnite). The analytical error is within 0.1‰.

RESULTS AND DISCUSSION

The $CaCO_3$ contents range between 20% and 80% and are generally higher than 50% (Fig. 1; Table 1). The total organic carbon (TOC) content is quite low (<0.4%) and the C/N molar ratio ranges between 2.6 and 8.1 (Fig. 1; Table 1). The sedimentary organic δ^{13}C increased from −24‰ in the Oligocene to −21‰ in the Quaternary (Fig. 2; Table 1). At the Oligocene/Miocene boundary, $\delta^{13}C_{org}$ rapidly increased by 1‰. The middle Miocene sediments (15−16 Ma) yielded values that are similar to those from Oligocene sediments of about −24‰. From the latest Miocene to the late Pliocene, isotopic compositions rapidly increased once again by nearly 2‰. The $\delta^{13}C_{org}$ values in the Quaternary were about −21‰, which is nearly the same as the modern sedimentary $\delta^{13}C_{org}$ values (Dean et al., 1986). The sedimentary $\delta^{13}C_{org}$ values are controlled by the relative contributions of marine and terrestrial materials because isotopic compositions of terrestrially derived organic matters are significantly lighter than those of marine organic matter (Sackett, 1989).

$$\delta^{13}C_{org} = f_{marine} \ \delta^{13}C_{marine} + f_{terrestrial} \ \delta^{13}C_{terrestrial},$$

and

$$f_{marine} + f_{terrestrial} = 1,$$

where f_{marine} and $f_{terrestrial}$ denote relative abundances of marine-derived and terrestrially derived organic carbon, respectively. The C/N value of most sediments from Site 925 is substantially lower than Redfield ratio (about 7). The mechanisms by which carbon was se-
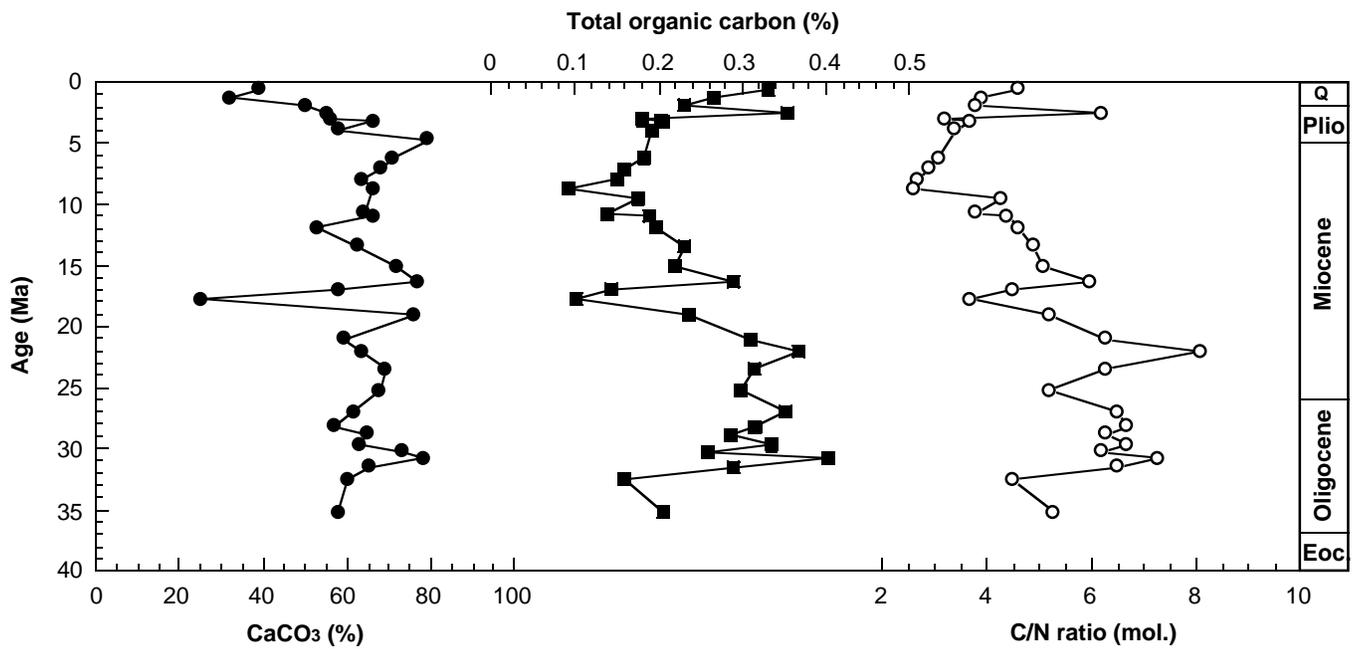
Figure 1. CaCO$_3$, total organic carbon, and C/N molar ratios for Site 925 samples during the last 35 m.y. Q = Quaternary, Plio = Pliocene, and Eoc = Eocene.

Table 1. Summary of analytical results of samples from Site 925.

Sample	Depth (mbsf)	Age (Ma)	TOC (%)	TN (%)	C/N (mol)	CaCO$_3$ (%)	Al$_2$O$_3$ (%)	TiO$_2$ (%)	δ^{13}C$_{org}$ (‰)
154-925B-									
3H-5	20.55	0.64	0.337	0.086	4.6	39.4	16.2	0.655	−21.20
5H-5	39.55	1.29	0.271	0.082	3.9	32.4	16.2	0.692	−21.57
7H-5	58.55	1.97	0.236	0.073	3.8	50.2	14.7	0.609	−21.32
9H-5	77.55	2.62	0.359	0.067	6.2	55.2	10.7	0.449	−21.30
11H-2	92.05	3.12	0.185	0.067	3.2	56.5	11.7	0.486	−22.23
11H-5	96.75	3.28	0.210	0.067	3.7	66.5	8.38	0.351	NA
13H-5	115.53	3.96	0.197	0.067	3.4	58.2	10.3	0.442	−21.83
15H-5	134.55	4.72	NA	NA	NA	79.6	4.71	0.203	−22.20
19H-5	172.55	6.30	0.187	0.070	3.1	71.3	7.33	0.311	−22.94
21H-5	191.55	7.13	0.165	0.067	2.9	68.3	8.17	0.347	NA
23H-5	210.55	7.96	0.156	0.068	2.7	63.8	10.8	0.432	−22.79
25H-5	229.55	8.78	0.097	0.043	2.6	66.5	6.92	0.274	−22.50
27H-4	247.05	9.62	0.182	0.049	4.3	NA	7.91	0.316	−22.47
29H-5	267.55	10.76	0.145	0.044	3.8	64.3	10.9	0.441	−22.38
30H-2	272.55	11.04	0.195	0.051	4.4	66.4	9.87	0.379	−22.46
31H-5	286.55	11.98	0.203	0.052	4.6	52.9	14.9	0.570	−22.90
33H-5	305.55	13.44	0.237	0.057	4.9	62.8	10.8	0.398	−22.74
154-925A-									
5R-2	325.45	15.15	0.226	0.052	5.1	72.0	6.56	0.250	−23.39
7R-5	349.25	16.36	0.294	0.057	6.0	77.0	5.43	0.197	−23.92
9R-5	368.55	17.01	0.149	0.038	4.5	58.1	11.4	0.434	−22.62
12R-2	392.85	17.82	0.107	0.034	3.7	25.4	20.1	1.08	−22.81
15R-1	420.26	19.06	0.241	0.054	5.2	76.3	5.43	0.202	−22.93
18R-2	450.65	21.08	0.315	0.058	6.3	59.4	9.50	0.354	−22.59
20R-2	469.85	22.12	0.373	0.054	8.1	63.7	8.82	0.326	−23.11
23R-2	498.75	23.57	0.320	0.059	6.3	69.5	8.06	0.301	NA
26R-5	531.05	25.26	0.304	0.068	5.2	68.1	8.42	0.312	−23.02
30R-2	566.25	27.02	0.358	0.064	6.5	61.7	9.77	0.376	−24.00
32R-5	590.05	28.21	0.321	0.056	6.7	57.2	11.6	0.413	−23.94
34R-4	607.85	28.86	0.292	0.054	6.3	65.1	9.18	0.347	−23.96
38R-2	643.47	29.76	0.340	0.059	6.7	63.1	9.70	0.358	−24.39
40R-2	662.85	30.27	0.265	0.050	6.2	73.6	6.71	0.254	−24.37
43R-2	685.12	30.85	0.408	0.065	7.3	78.5	4.09	0.142	−23.79
46R-2	711.05	31.53	0.294	0.053	5.5	65.5	7.77	0.278	−23.91
51H-2	748.78	32.53	0.164	0.042	4.5	60.4	7.73	0.280	−23.92
57H-2	807.23	35.30	0.211	0.046	5.3	58.1	8.33	0.308	−24.16

Note: NA = not analyzed.
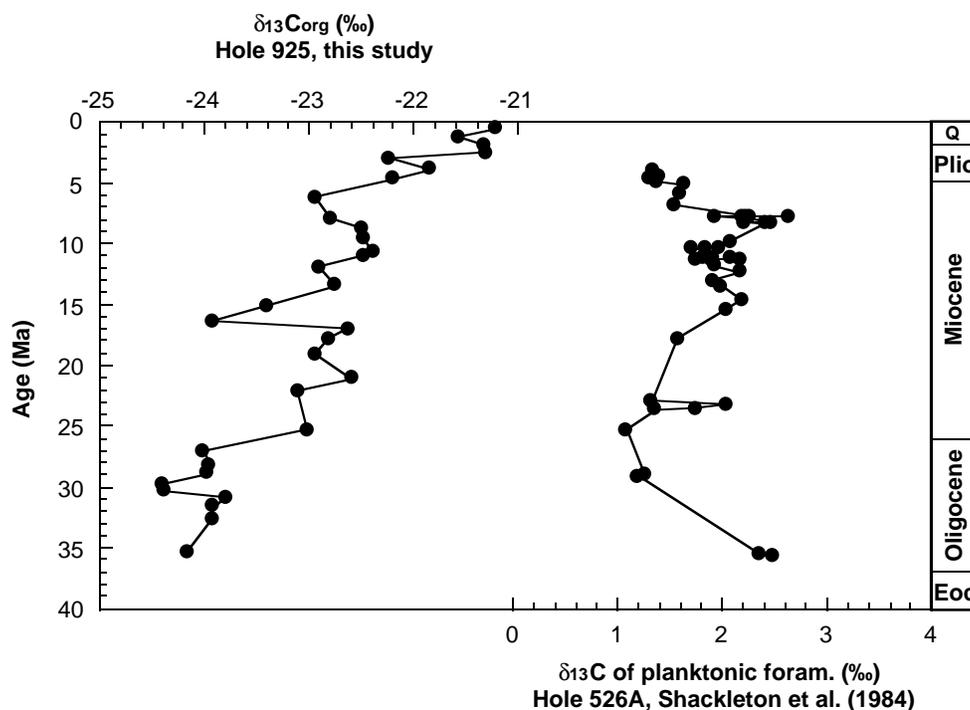
Figure 2. Sedimentary organic $\delta^{13}C$ at Site 925 (left: $\delta^{13}C_{org}$ [‰]) and inorganic $\delta^{13}C$ of Hole 526A (right: $\delta^{13}C$ of planktonic foraminifers [‰]) during the last 35 m.y. The definition of δ notation is provided in the text. Q = Quaternary, Plio = Pliocene, and Eoc = Eocene.

lectively lost and/or nitrogen was added as clay-bound ammonium during the diagenesis would explain why C/N values are anomalously low. In any case, the C/N value of these sediments cannot be used to estimate f_{marine} and $f_{terrestrial}$. The concentrations of terrestrial elements, aluminum (as Al_2O_3) and titanium (as TiO_2), are inversely correlated to the calcium content (as CaO) (Fig. 3), suggesting that the sediments are composed of two major components; one is biogenic carbonate, which mainly controls the calcium content in the sediments, and the other is lithogenic material. As suggested by the good correlations between CaO and Al_2O_3, and CaO and TiO_2 (Fig. 3; Table 1), biogenic opal has only a minor influence on the relative abundance of these elements. The organic carbon may be mainly derived from marine organic matter because the total organic carbon (TOC) content shows no correlation to either Al_2O_3 or TiO_2 contents (Fig. 4). In addition, $\delta^{13}C_{org}$ also shows no correlation with these element concentrations (Fig. 5). Although Al and Ti may not be necessarily correlated with terrestrial organic matter, we consider that the sedimentary organic matter is mostly composed of marine-derived organic matter. This implies that the secular variation of $\delta^{13}C_{marine}$ is the main factor controlling $\delta^{13}C_{org}$:

$$f_{marine} \approx 1, f_{terrestrial} \approx 0$$

and

$$\delta^{13}C_{org} \approx \delta^{13}C_{marine}.$$

The $\delta^{13}C_{marine}$ depends on the $\delta^{13}C$ of total dissolved CO_2 (TCO₂), fractionation at the time of photosynthesis (ϵ), and secondary effects caused by diagenetic changes (Δ):

$$\delta^{13}C_{org} \approx \delta^{13}C_{marine} = \delta^{13}C_{TCO2} + \epsilon + \Delta.$$

The isotopic composition of TCO₂ ($\delta^{13}C_{TCO2}$), as deduced from carbonate carbon, shows a stable or a slightly decreasing trend rather than an increase during the last 35 m.y. (Fig. 2; Shackleton et al., 1984). Therefore, the difference between $\delta^{13}C_{TCO2}$ and $\delta^{13}C_{marine}$, ($\epsilon + \Delta$) in the early Oligocene was 4‰–5‰ greater than today (Fig. 2). This phenomenon has been pointed out by several authors (Hoefs, 1980; Dean et al., 1986; Galimov, 1995).

Isotopic fractionations accompanying ϵ of C_3 plants comprise two processes: mass transport across cell membrane by diffusion and carbon dioxide fixation by riburose 1,5-bisphosphate carboxylase (RuBPCase) (e.g., O'Leary, 1981). Carbon isotope fractionation during the former process can be ascribed to the change in $CO_2(aq)$ concentration in ambient seawater, whereas that in the latter process can be attributed to light intensity, the intracellular $CO_2(aq)$ concentration, and RuBPCase activity, as factors to controlling the speed of the Calvin cycle. Several investigations suggest that $CO_2(aq)$ mainly affects the degree of carbon isotopic fractionation in the modern ocean (Freeman and Hayes, 1992; Fogel and Cifuentes, 1993; Rau, 1994; Hinga et al., 1994), although some others doubt this (Goericke and Fry, 1994). These investigators determined empirical relationships between $CO_2(aq)$ and $\delta^{13}C$ of particulate organic matter (McCabe, 1985; Hollander and McKenzie, 1991; Freeman and Hayes, 1992; Rau, 1994). However, other authors have suggested that the activity of carbon-fixation process mainly controls the isotopic fractionation. Takahashi et al. (1991) report that the algal $\delta^{13}C$ value increases with the specific growth rate as a result of nutrient availability or light intensity in a culture experiment of green alga *Chlamydomonas reinhardtii*. They concluded that the isotopic fractionation is mainly controlled by the rate of carboxylation reaction rather than $CO_2(aq)$ in case of relatively low $CO_2(aq)$. On the other hand, Hinga et al. (1994) reported that no growth rate effect was found for the diatom *Skeletonema costatum*. Whether or not algal growth rate affects the carbon isotopic composition may depend on the species. Not only growth rates but other parameters such as cell size were reported to be related to isotopic fractionation (Fry and Wainright, 1992). Sea-surface tem-
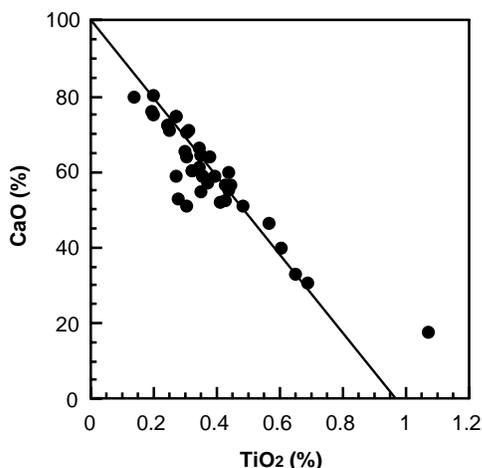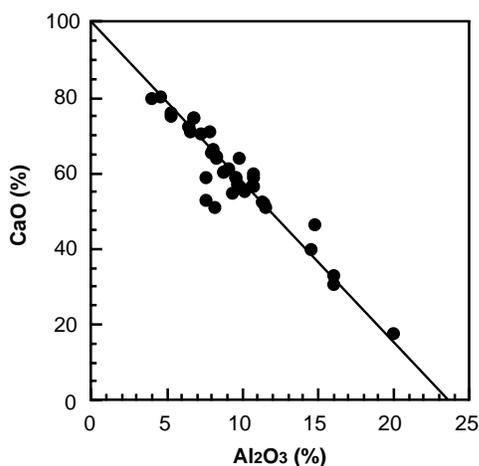
Figure 3. CaO vs. Al_2O_3 and TiO_2, Site 925.
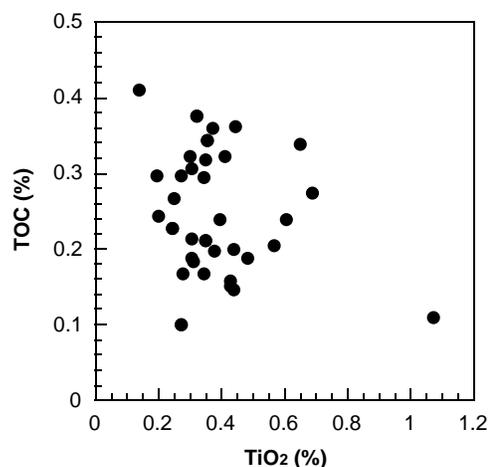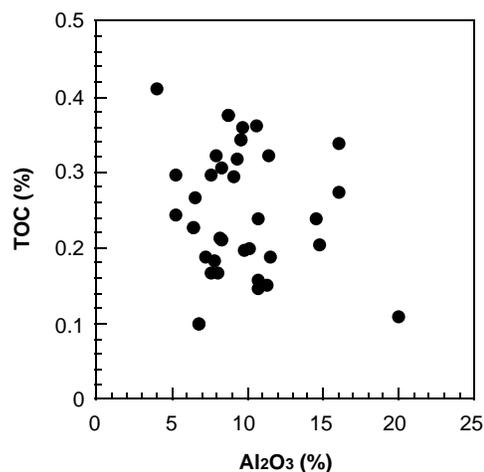
Figure 4. Total organic carbon (TOC) vs. Al_2O_3 and TiO_2, Site 925.

perature as a factor controlling the activity of RuBPCase was estimated to have not changed much during the last 35 m.y. in the tropical Atlantic (Adams et al., 1990). Identifying whether the processes that control the distribution of carbon isotopic fractionation in the modern ocean are mass transport or carbon fixation is an important goal.

Problematic for the application of the photosynthetic model to the sedimentary $\delta^{13}C_{org}$ is the fact that the sedimentary organic matter is a mixture of numerous organic components. Carbohydrates, hemicellulose, proteins, and pectine show a relative depletion of ^{12}C compared to cellulose, lignin, and lipids (Degens et al., 1968). Moreover, most compounds composing these groups originate from different biochemical pathways and, thus, have different isotope compositions. Therefore, the changes in relative abundances of these organic compounds can change the isotope composition of the bulk organic carbon. Secular variations of plankton community and/or evolution of plankton species may cause the changes in the combination of organic compounds produced. Currently, we have no information about the secular variation of relative abundances of organic compounds in our sediment samples.

Diagenetic degradation of organic matter can also change the sedimentary organic $\delta^{13}C$ record. The isotope shifts occurring during the deposition and burial of organic matter (Δ) are primarily linked to preferential loss of biogenically labile organic compounds such as amino acids or lipids and functional groups. If organic compounds and/or functional groups that have heavier carbon isotope compositions than the bulk $\delta^{13}C_{org}$ selectively degrade during diagenesis, then the carbon isotope composition of the remaining organic matter would become lighter as diagenesis proceeds. Several authors have empirically demonstrated that the diagenetic degradation of sedimentary organic matter tends to make the isotopic composition of remaining organic carbon nearly the same or somewhat heavier (e.g., Sackett, 1989; Schidlowski et al., 1983). Galimov (1995) concluded, on the other hand, that there is a slight trend toward the accumulation of the light isotope in C_{org} with depth. However, he concluded that this effect may not exceed 1.5‰. Therefore, it is unlikely that a 3‰ decrease of $\delta^{13}C_{org}$ can be explained only by the diagenetic degradation of organic matter.

If our observations are supported by additional analyses at other sites, secular changes in carbon isotope fractionation at the time of photosynthesis should be an important knowledge when constructing the model of the past global carbon cycle. Culture experiments of the algae in question is also highly required.

CONCLUSIONS

Here, we report that the difference between sedimentary organic and carbonate $\delta^{13}C$ during the early Oligocene in Ceara Rise was 4‰−5‰ larger than present day. This may reflect any one (or a mix) of the following reasons: (1) the surface-water CO_2(aq) concentration was substantially high, (2) the activity of carbon fixation process was low, or (3) the relative abundance of organic compounds was different.
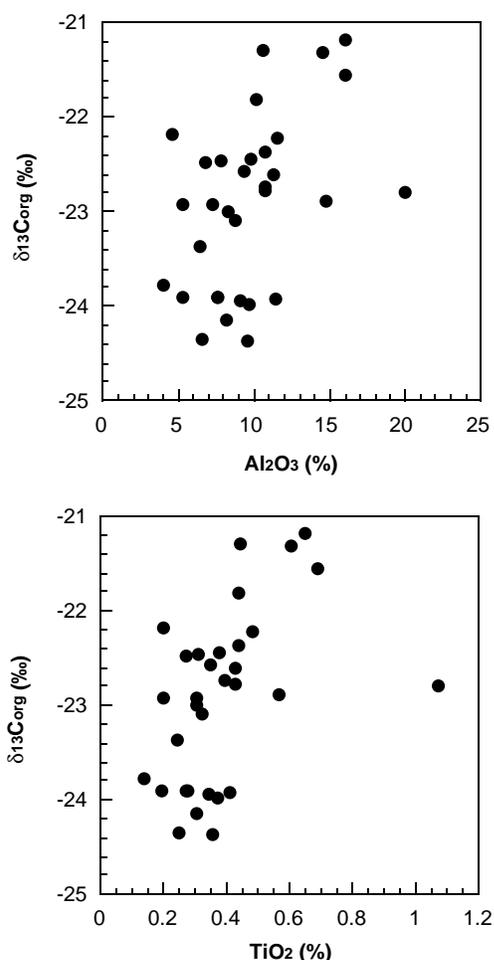
Figure 5. Sedimentary $\delta^{13}C_{org}$ vs. Al_2O_3 and TiO_2, Site 925.

ACKNOWLEDGMENTS

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