

### 63. DIAGENETIC ALTERATION OF ORGANIC MATTER IN LEG 57 SEDIMENTS, DEEP SEA DRILLING PROJECT

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#### ABSTRACT

I analyzed Leg 57 sediments organogeochimically and spectroscopically. Organic carbon and extractable organic matter prevail from the Pliocene to the Miocene. Humic acids occur widely from the Pleistocene to the lower Miocene and one portion of the Oligocene. The absence of humic acids in Oligocene and Cretaceous samples suggests that humic acids had changed to kerogen. Visible spectroscopic data reveal that humic acids in this study have a low degree of condensed aromatic-ring system, which is a feature of anaerobic conditions during deposition, and that chlorophyll derivatives that had at first combined with humic acids moved to the solvent-soluble fraction during diagenesis. The elemental compositions of humic acids show high H/C and O/C ratios, which seem appropriate to a stage before transformation to kerogen. The relation between the linewidths and g-values on the electron spin resonance data indicates that the free radicals in humic acids are quite different from those in kerogen. The low spin concentrations of kerogen and the yields of humic acids up to the lower Miocene demonstrate that organic matter in these sediments is immature. The foregoing indicate the necessity to isolate humic acids even in ancient rocks in the study of kerogen.

#### INTRODUCTION

Several DSDP samples contained humic acids (Nissembaum and Kaplan, 1972; Aizenshtat et al., 1973; Stuermer et al., 1978). Humic acids seem to convert to kerogen during diagenesis and catagenesis (Nissembaum and Kaplan, 1972; Welte, 1973). Recently, Stuermer and coworkers (1978) isolated humic acids and protokerogen (insoluble organic residue in unlithified sediments) and reported the relation between two substances. However, few workers have studied the relation between humic acids and kerogen by separating both materials.

In this study I isolated humic acids and kerogen from the sediments. In the category "kerogen" I include the protokerogen, because the samples range from Recent sediments to ancient rocks.

The objective of this chapter is to evaluate the diagenetic alteration of organic matter from three sites along the Japan Trench transect through chemical and physical analyses. The study methods include electron spin resonance (ESR) spectroscopy of humic acids and kerogen; visible spectroscopy and elemental analyses of humic acids; and organogeochimical measurements of organic carbon and extractable organic matter.

Sites 438 and 439 are on the seaward edge of the deep sea terrace of the Japan Trench, and Site 440 is on the flat sea floor of the midslope terrace. The sediments from Sites 438 and 439 are terrigenous diatomaceous claystone (Pleistocene to lower Miocene), turbidites and claystone (base of lower Miocene), massive sandstone

and breccia-conglomerate (Oligocene), and black silicified claystone (Cretaceous). The sediments from Site 440 are largely claystones (Pleistocene to upper Miocene).

#### METHODS

##### Preparation and Extraction

I divided the dried and ground samples into two fractions and provided a portion of one fraction (about 0.6 g) for organic carbon analysis. I extracted the other fraction for 80 hours in a Soxhlet apparatus with benzene:methanol 7:3; added copper to extracts in the boiling flask to remove sulfur; filtrated the extracts; and weighed the dried extracts as extractable organic matter. I treated the residue of the Soxhlet extraction for 10 hours in a shaker with 0.1 N NaOH; centrifuged the alkaline suspension; acidified the supernatant solution with 6 N HCl; washed the resultant precipitates with distilled water; and weighed the dried precipitates as humic acids. I treated the centrifuged residue with 6 N HCl and 48 per cent HF to remove carbonates and silicates; centrifuged the suspension; washed the resultant residue with distilled water; and obtained kerogen.

##### Instrumentation

I measured the ESR spectra of humic acids and kerogen on a JEOL electron spin resonance spectrometer PE-3X, employing a modulation frequency of 100 kHz

and an operating frequency of about 9.4 GHz. I determined the spin concentration with reference to that of artificial coal with a known value ( $5.8 \times 10^{14}$  spins); the linewidth with reference to that of the  $Mn^{2+}$  marker fixed in the sample cavity; and the *g*-value with reference to that of diphenylpicrylhydrazyl (*g*-value = 2.0036). Because kerogen in this preparation contained large amounts of impurities, I expressed the value of the spin concentration as the ratio to carbon of kerogen and humic acids.

I observed the visible spectra of humic acids with 1 mg in 10 ml of 0.1 N NaOH solution on a Shimadzu multipurpose spectrometer MPS 5000.

According to the method of Heistand and Humphries (1976), I analyzed organic carbon in sediments by combustion at 460 °C for 13 minutes in an oxygen atmosphere on a Perkin-Elmer 240 elemental analyzer. For elemental analyses of humic acids and carbon analysis of kerogen for the ESR, I measured samples by combustion at 950 °C for 3 minutes in an oxygen atmosphere on the same analyzer.

## RESULTS AND DISCUSSION

Table 1 lists the organic carbon, extractable organic matter, and humic acid content. Figure 1 illustrates the variation of these values with depth.

The sediments in Sites 438 and 439 contain 0.35 to 1.44 per cent organic carbon, 0.024 to 0.210 per cent extractable organic matter, and 0 to 0.287 per cent humic acids. The Oligocene sediments contain small amounts of organic matter because these lithofacies are sandstone and breccia-conglomerate. At Site 440, organic carbon, extractable organic matter, and humic acid content ranges from 0.50 to 2.21 per cent, 0.070 to 0.183 per cent, and 0.062 to 0.875 per cent, respectively. The values of organic carbon and extractable organic matter from the Pliocene to the lower Miocene samples in Sites 438 and 439 and from all samples in Site 440 are almost identical to those of the presumed source rocks from the Neogene Tertiary in the Japan Sea side, where we find the majority of hydrocarbon accumulations in Japan. Organic carbon ranges from 0.86 to 2.04 per cent and extractable organic matter from 0.066 to 0.212 per cent in the Akita and Niigata oilfields of the Japan Sea side (Yagishita, 1962; Kudo et al., 1965; Sato et al., 1972; Taguchi and Sasaki, 1973). Generally, organic carbon content reflects organic richness, and a relation between organic carbon and extractable organic matter (Figure 2) can be a criterion for petroleum generation. Because most samples in this study include more than 0.5 per cent organic carbon and more than 0.05 per cent extractable organic matter, they are good prospects for oil formation.

Humic acids occur widely but are absent in the Oligocene (except for Sample 439-24-3) and Cretaceous samples. This suggests that humic acids below the Oligocene had changed to kerogen, as described by Nissembaum and Kaplan (1972) and Welte (1973). Samples from Site 440 indicate higher amounts of organic carbon, extractable organic matter, and humic acids than those from

TABLE 1  
Organic Carbon, Extractable Organic Matter, and Humic Acid Content in Sediments at Sites 438, 439, and 440

Sample	Sub-bottom Depth (m)	Organic Carbon (%)	Extractable Organic Matter (%)	Humic Acids (%)
438-1-2	3	0.68	0.081	0.070
438-5-3	37	0.52	0.059	0.114
438-9-3	76	1.01	0.147	0.116
438-11-3	94	1.21	0.068	0.059
438A-7-4	122	1.21	0.101	0.260
438A-10-2	147	1.44	0.113	0.193
438A-13-2	175	1.19	0.122	0.147
438A-16-3	205	1.29	0.116	0.102
438A-20-3	243	0.80	0.102	0.096
438A-24-3	281	0.82	0.114	0.057
438A-27-3	309	0.70	0.142	0.173
438A-31-3	348	0.95	0.089	0.038
438A-34-2	375	1.06	0.089	0.033
438A-37-3	405	1.15	0.074	0.073
438A-42-3	452	0.55	0.092	0.026
438A-44-3	473	0.84	0.098	0.072
438A-48-3	520	1.10	0.210	0.046
438A-52-3	549	0.72	0.142	0.042
438A-56-3	587	0.61	0.076	0.116
438A-60-2	624	0.88	0.087	0.127
438A-65-5	676	0.91	0.089	0.084
438A-68-5	704	0.68	0.084	0.095
438A-71-3	729	0.48	0.106	0.200
438A-73-3	749	0.77	0.111	0.287
438A-78-2	795	1.04	0.067	0.150
438A-82-2	833	0.59	0.068	0.262
438A-84-3	853	0.81	0.083	0.088
439-7-3	872	0.79	0.142	0.110
439-11-3	910	0.75	0.102	0.074
439-14-2	934	0.79	0.072	0.079
439-18-3	967	0.58	0.106	0.050
439-21-3	996	0.54	0.084	0.026
439-22-3	1004	0.36	0.083	0
439-24-3	1024	0.66	0.052	0.022
439-26-3	1044	0.40	0.039	0
439-30-3	1081	0.35	0.024	0
439-38-1	1149	0.44	0.052	0
439-39-1	1154	0.51	0.097	0
440-1-2	2	1.29	0.106	0.146
440-5-5	42	1.54	0.183	0.223
440A-2-3	87	1.15	0.140	0.220
440A-5-4	116	0.87	0.105	0.200
440A-7-3	134	0.91	0.160	0.875
440B-4-3	172	1.38	0.131	0.084
440B-7-3	200	0.94	0.081	0.303
440B-11-3	239	0.95	0.165	0.838
440B-14-5	270	2.21	0.105	0.072
440B-18-2	303	1.89	0.077	0.300
440B-21-3	333	0.93	0.086	0.067
440B-24-3	362	1.00	0.092	0.216
440B-31-3	428	0.78	0.108	0.151
440B-35-3	466	0.81	0.113	0.062
440B-39-3	504	1.26	0.136	0.066
440B-43-3	542	0.68	0.090	0.036
440B-47-1	578	1.01	0.134	0.076
440B-51-1	616	0.67	0.116	0.087
440B-54-3	647	0.84	0.070	0.063
440B-58-2	683	0.92	0.115	0.108
440B-61-1	710	0.88	0.066	0.076
440B-66-3	761	0.50	0.088	0.064
440B-71-1	806	0.63	0.080	0.106

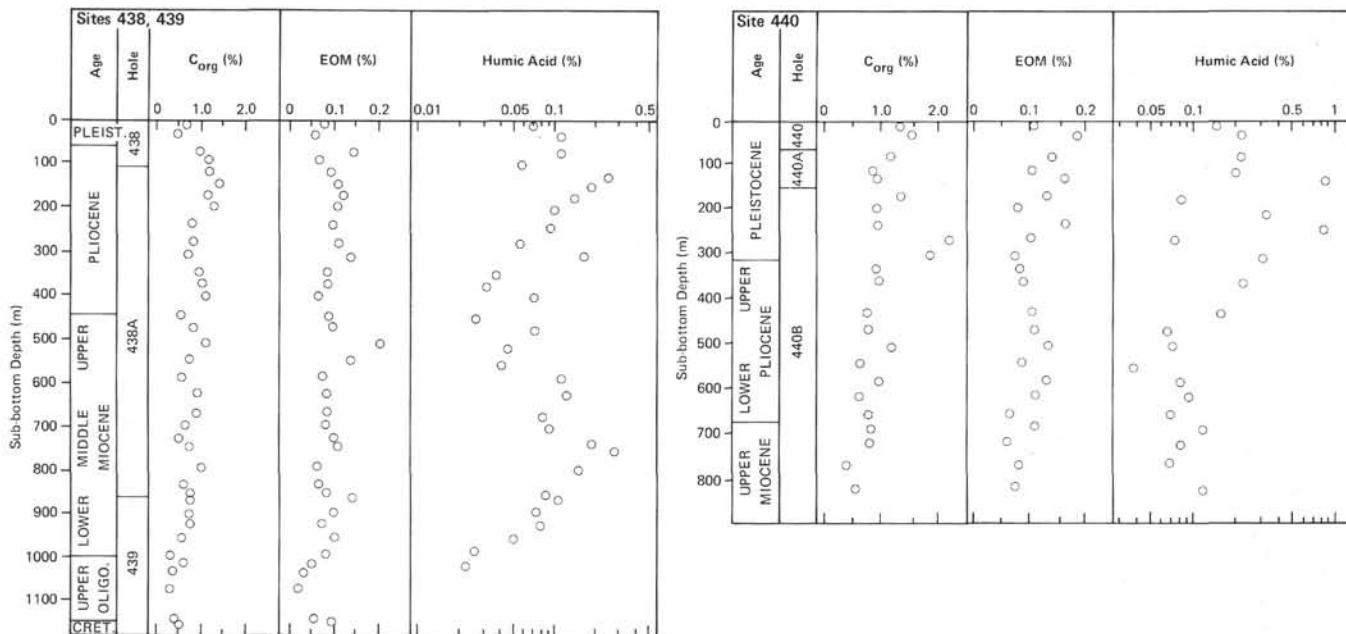


Figure 1. Variations of organic carbon, extractable organic matter, and humic acids content with depth at Sites 438, 439, and 440.

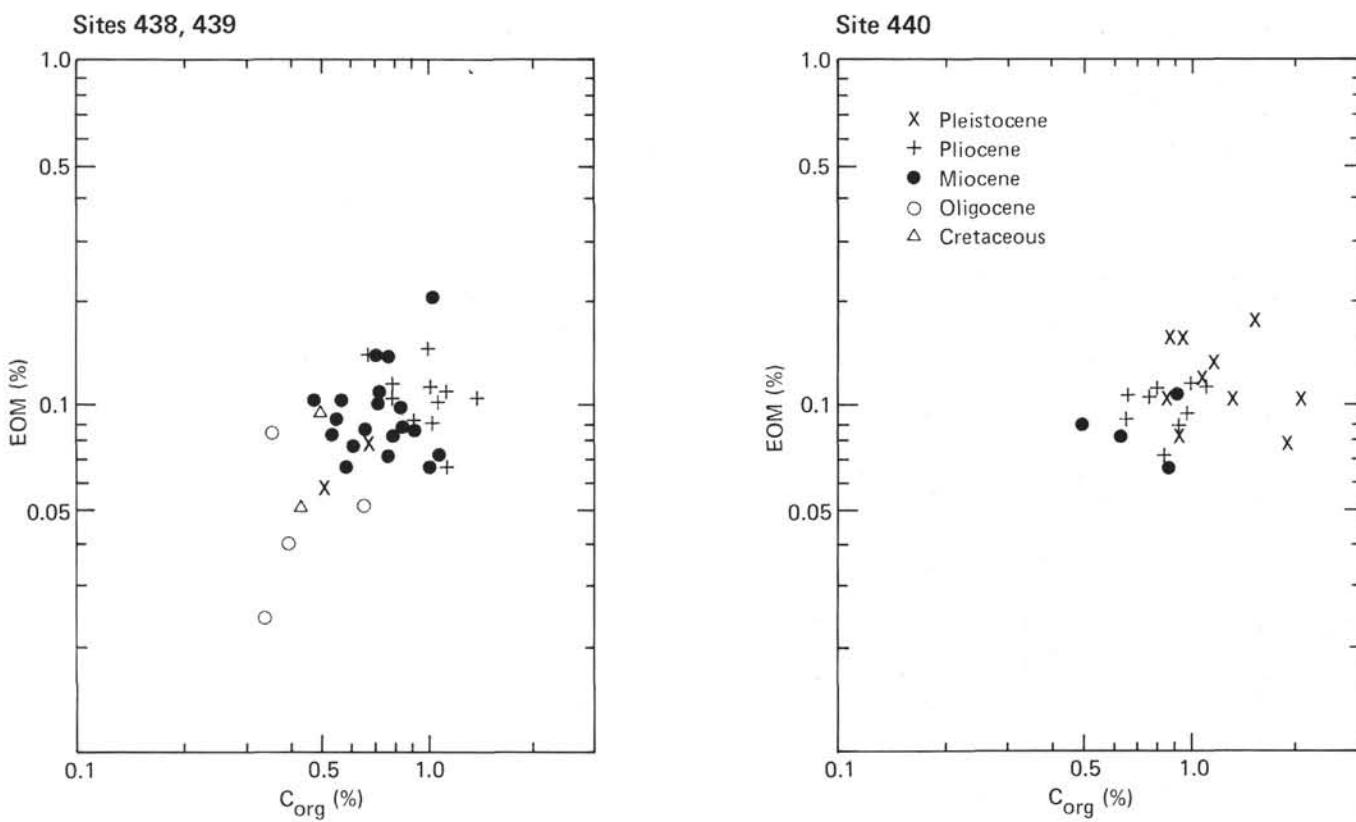


Figure 2. Relationship between organic carbon and extractable organic matter at Sites 438, 439, and 440.

Sites 438 and 439, because at Site 440 fine sediments were deposited at a faster rate.

Most workers have neglected humic acids in ancient rocks because they believed that humic acids converted to kerogen in the early stages of diagenesis. It is there-

fore important in this study to confirm that humic acids occur from the Pleistocene to the lower Miocene and in one of the Oligocene samples (439-24-3). Although the transformation of humic acids to kerogen has not occurred in this area because of low heat flow (Uyeda,

1972) and low thermal gradient, humic acid yields in ancient rocks do provide significant clues for future studies of humic acids and kerogen.

Table 2 shows the ratio of extinction at 465 nm to that at 665 nm (*E*-value), peak height at 405 nm ( $H_{405}$ ) on visible spectroscopy, and elemental composition of humic acids. Figure 3 indicates the change of the *E*-value and the  $H_{405}$  value with depth.

The *E*-value is lower with increased aromatic condensation of humic acids (Schnitzer and Skinner, 1969; Rashid and Vilks, 1975), and a low degree of condensed aromatic-ring system is a characteristic feature of humic acids developing in anaerobic environments (Rashid and Vilks, 1975). The *E*-values vary from 1.76 to 6.44 at Sites 438 and 439 and from 4.70 to 6.32 at Site 440. Except for Sample 439-21-3, the sediments exhibit fairly constant *E*-values between 4.22 and 6.44 which are higher than the values between 3.7 and 4.7 determined by Rashid and Vilks (1975). This suggests that humic acids in the present study contain a low degree of aromatic condensation and that sedimentary deposition occurred in anaerobic conditions. The lowest value of Sample 439-21-3 may indicate a transitional stage in the transformation of humic acid to kerogen.

The 405-nm peak is the Soret peak of the chlorophyll derivatives and occurs commonly in marine humic substances (Watanabe, 1972).  $H_{405}$ -values range from 0 to 0.074 at Sites 438 and 439 and from 0.022 to 0.186 at Site 440. The samples from Site 440 have higher  $H_{405}$ -values than those from Sites 438 and 439, which indicates that at the former marine humic substances were preserved.

As Figure 3 shows,  $H_{405}$ -values decrease with depth, especially in Samples 438A-65-5 to 438A-82-2. These results indicate that the chlorophyll derivatives moved from the humic fraction to the solvent-soluble fraction during diagenesis.

The elemental composition of humic acids shows high amounts of oxygen in comparison with that of coal (van Kleveln, 1961) and kerogen (Forsman and Hunt, 1958; Forsman, 1963; McIver, 1967; Tissot et al., 1974; Sato, 1976; Stuermer et al., 1978). The N/C atomic ratios are fairly constant, but the others fluctuate with depth.

Figure 4 indicates the relation between H/C and O/C atomic ratios of humic acids. The samples studied fall in positions similar to those of Stuermer and coworkers (1978). The high H/C and O/C ratios in this study, as well as the results of the *E*-values, may provide evidence for the low degree of aromatic condensation of humic acids.

Table 3 lists the linewidth, *g*-value, and spin concentration on the ESR spectroscopy of humic acids and kerogen. Figure 5 shows the variation of ESR data with depth.

Humic acids from Sites 438 and 439 show linewidth from 3.14 to 7.15 G, *g*-value from 2.0027<sub>7</sub> to 2.0035<sub>9</sub>, and spin concentration from  $0.19 \times 10^{18}$  to  $2.17 \times 10^{18}$  spins/gC. At Site 440 humic acids range in linewidth

from 2.93 to 9.36 G, in *g*-value from 2.0028<sub>3</sub> to 2.0035<sub>5</sub>, and in spin concentration from  $0.18 \times 10^{18}$  to  $1.12 \times 10^{18}$  spins/gC. The linewidth and *g*-value decrease gradually with increasing depth except for a rapid decrease in Samples 438A-71-3 to 438A-82-3. The spin concentrations increase in Samples 438-1-2 to 438A-52-3, decrease rapidly at the Sample 438A-52-3/438A-56-3 boundary; and then increase in Samples 438A-56-3 to 438A-84-3 and from 439-7-3 to 439-21-3. The values of linewidth at Site 440 increase with depth, but *g*-values decrease in wide ranges except for Sample 440A-7-4. The spin concentrations increase irregularly in Site 440.

The ESR signals of kerogen at Sites 438 and 439 vary from 2.88 to 5.77 G in the linewidth, from 2.0027<sub>1</sub> to 2.0031<sub>2</sub> in *g*-value, and from  $0.26 \times 10^{18}$  to  $2.55 \times 10^{18}$  spins/gC in the spin concentration. At Site 440 they vary from 2.93 to 5.02 G in linewidth, from 2.0028<sub>0</sub> to 2.0031<sub>3</sub> in *g*-value, and from  $0.18 \times 10^{18}$  to  $1.22 \times 10^{18}$  spins/gC in the spin concentration. At Sites 438 and 439, the linewidth and *g*-value of kerogen decrease with depth; in Samples 438A-56-3 to 438A-82-2, linewidth decreases rapidly. The spin concentrations of humic acids change in a manner similar to that of kerogen. The Oligocene and Cretaceous kerogens have slightly high spin concentrations. The ESR signals of kerogen from Site 440 increase dispersedly with depth. It is a characteristic feature of kerogen in this study to have lower spin concentrations than that in the Japanese source rocks analyzed by Sato (1976) and by Morishima and Matsubayashi (1978). This indicates that organic matter in our study is still immature.

Figure 6 shows the relation between linewidths and *g*-values of humic acids and kerogens. It indicates a close relation between linewidth and *g*-value, in contrast to the report by Stuermer and coworkers (1978), who found no relation between them. In this study, kerogens fall in a quite different zone from humic acids; the kerogen zone is low both in linewidth and *g*-value in comparison with that of humic acids. This seems to be due to the fact that kerogens and humic acids produce different types of free radicals: the free radicals in humic acids are mainly semiquinone (Steelink, 1964; Ishiwatari et al., 1976), whereas in kerogen they are mainly pure aromatic. Therefore the ESR profiles of humic acids and kerogen exhibit different depth trends. Morishima and Matsubayashi (1978) reported that *g*-values and linewidth of carbonaceous materials decrease with increasing coalification or maturation. In this study, the fact that *g*-values and linewidth of humic acids are higher than those of kerogen suggests that humic acids are the precursor of kerogens.

Since the report by Abelson (1967), who included insoluble organic residue in Recent sediments in the term "kerogen," most workers have been measuring the ESR spectra of kerogen without separating out humic acids. Kerogen itself is the mixture of higher molecular compounds, and the composition of the precursor affects the ESR spectra, as pointed out by Sato (1976) and by Morishima and Matsubayashi (1978). Thus the results in

**TABLE 2**  
Visible Spectroscopy and Elemental Analyses of Humic Acids at Sites 438, 439, and 440

Sample	Sub-bottom Depth (m)	Visible Spectroscopy		Elemental Composition (%)						Atomic Ratio		
		E-Value	H <sub>405</sub> -Value	Ca	Ha	Na <sup>a</sup>	Ob	Ash	H/C	N/C	O/C	
438-1-2	3	5.40	0.061	38.0	4.5	3.9	53.6	19.1	1.43	0.087	1.06	
438-5-3	37	5.24	0.042	39.5	4.5	3.7	52.3	17.6	1.38	0.081	0.99	
438-9-3	76	5.29	0.074	44.5	4.8	3.8	46.9	13.6	1.29	0.072	0.79	
438-11-3	94	5.05	0.032	36.2	5.2	3.4	55.6	15.7	1.72	0.082	1.15	
438A-7-4	122	5.72	0.029	43.1	6.1	3.4	47.4	14.9	1.68	0.068	0.83	
438A-10-2	147	5.05	0.029	40.4	6.2	3.2	50.2	14.6	1.83	0.068	0.93	
438A-13-2	175	5.45	0.068	44.8	4.7	4.1	46.4	9.1	1.27	0.078	0.78	
438A-16-3	205	5.56	0.056	50.2	5.1	4.4	40.4	7.5	1.21	0.074	0.60	
438A-20-3	243	5.56	0.070	51.9	5.3	4.4	38.4	8.4	1.23	0.073	0.56	
438A-24-3	281	5.31	0.070	56.7	5.9	4.8	32.7	8.7	1.24	0.073	0.43	
438A-27-3	309	5.36	0.038	51.8	5.6	4.1	38.6	10.3	1.29	0.068	0.56	
438A-31-3	348	5.38	0.069	52.3	5.5	4.2	38.0	7.7	1.27	0.069	0.54	
438A-34-2	375	4.84	0.048	48.0	5.7	4.3	41.9	12.6	1.42	0.077	0.65	
438A-37-3	405	4.89	0.053	60.2	6.3	5.1	28.4	2.9	1.25	0.073	0.35	
438A-42-3	452	5.35	0.050	44.6	5.0	3.9	46.6	8.0	1.35	0.074	0.78	
438A-44-3	473	5.13	0.054	48.0	4.9	3.8	43.3	10.0	1.22	0.068	0.68	
438A-48-3	520	5.40	0.036	46.4	5.9	3.5	44.2	12.1	1.54	0.064	0.61	
438A-52-3	549	5.60	0.038	39.3	4.3	3.1	53.4	15.7	1.30	0.068	1.02	
438A-56-3	587	5.38	0.015	42.3	5.6	5.5	46.7	16.4	1.58	0.111	0.83	
438A-60-2	624	5.40	0.011	44.7	6.0	5.5	43.9	11.3	1.60	0.105	0.74	
438A-65-5	676	5.19	0.007	45.8	6.3	5.6	42.4	9.7	1.64	0.104	0.69	
438A-68-5	704	4.22	0.001	43.4	6.5	3.3	46.8	8.9	1.80	0.065	0.81	
438A-71-3	729	6.14	0.001	41.4	5.0	3.9	49.8	10.7	1.45	0.080	1.03	
438A-73-3	749	6.00	0.001	42.6	4.5	2.5	50.4	15.8	1.28	0.050	0.89	
438A-78-2	795	5.20	0.002	40.2	5.3	3.7	50.8	18.1	1.59	0.078	0.95	
438A-82-2	833	5.35	0.002	38.4	5.3	1.5	54.9	23.5	1.65	0.034	1.07	
438A-84-3	853	4.97	0.019	44.8	4.9	3.2	47.1	16.6	1.32	0.060	0.79	
439-7-3	872	6.46	0.019	39.8	4.5	3.4	52.4	23.1	1.34	0.072	0.99	
439-11-3	910	6.00	0.028	43.1	4.6	3.4	48.9	13.3	1.29	0.067	0.85	
439-14-2	934	6.29	0.001	44.2	6.7	2.7	46.4	11.3	1.82	0.052	0.79	
439-18-3	967	6.44	0	40.5	4.6	3.0	51.9	16.2	1.38	0.064	0.96	
439-21-3	996	1.76	0	43.4	4.9	3.7	48.0	12.0	1.36	0.073	0.83	
439-24-3	1024	5.82	0	42.3	3.6	1.9	52.2	13.4	1.03	0.038	0.93	
440-1-2	2	5.43	0.144	45.8	5.2	4.4	44.6	8.3	1.37	0.083	0.73	
440-5-5	42	5.30	0.056	42.7	5.0	4.2	48.0	12.2	1.42	0.094	0.84	
440A-2-3	87	5.61	0.090	55.7	6.2	4.7	33.5	2.3	1.33	0.072	0.45	
440A-5-4	116	5.40	0.186	54.4	5.9	4.6	35.1	3.3	1.30	0.073	0.48	
440A-7-3	134	5.82	0.022	40.6	5.4	3.2	50.8	8.8	1.59	0.079	0.94	
440B-4-3	172	6.00	0.102	49.4	5.9	4.3	40.5	8.2	1.43	0.074	0.62	
440B-7-3	200	5.62	0.054	42.0	6.6	3.7	47.6	9.1	1.88	0.076	0.85	
440B-11-3	239	6.23	0.050	41.9	6.4	3.9	47.8	10.9	1.82	0.080	0.86	
440B-14-5	270	6.27	0.065	47.6	6.0	4.4	42.0	11.5	1.51	0.079	0.66	
440B-18-2	303	5.47	0.120	44.1	6.0	3.9	46.0	14.7	1.63	0.075	0.78	
440B-21-3	333	4.77	0.080	49.0	6.2	4.5	40.3	7.2	1.52	0.079	0.62	
440B-24-3	362	5.48	0.079	49.6	6.0	4.1	40.3	6.4	1.46	0.070	0.61	
440B-31-3	428	5.31	0.090	43.5	5.3	3.6	47.8	7.8	1.48	0.071	0.83	
440B-35-3	466	5.74	0.067	46.9	6.4	4.2	42.5	8.8	1.64	0.076	0.68	
440B-39-3	504	4.70	0.114	45.9	6.1	4.1	43.9	9.3	1.60	0.076	0.72	
440B-43-3	542	5.44	0.083	48.0	6.3	3.8	41.9	11.4	1.57	0.068	0.65	
440B-47-1	578	5.85	0.059	46.0	6.2	3.8	44.0	4.6	1.62	0.071	0.72	
440B-51-1	616	5.30	0.064	38.5	4.6	3.1	53.8	19.1	1.44	0.070	1.05	
440B-54-3	647	5.87	0.055	35.9	4.9	3.1	56.2	22.8	1.62	0.074	1.17	
440B-58-2	683	5.29	0.050	36.6	5.0	3.2	55.3	16.4	1.65	0.074	1.13	
440B-61-1	710	4.97	0.049	37.8	5.2	3.1	53.9	25.0	1.64	0.071	1.07	
440B-66-3	761	5.67	0.030	43.7	5.5	3.4	47.4	8.1	1.53	0.067	0.81	
440B-71-1	806	6.32	0.037	43.4	5.7	3.3	47.6	6.6	1.59	0.066	0.82	

<sup>a</sup>Dry-ash-free.<sup>b</sup>By difference.

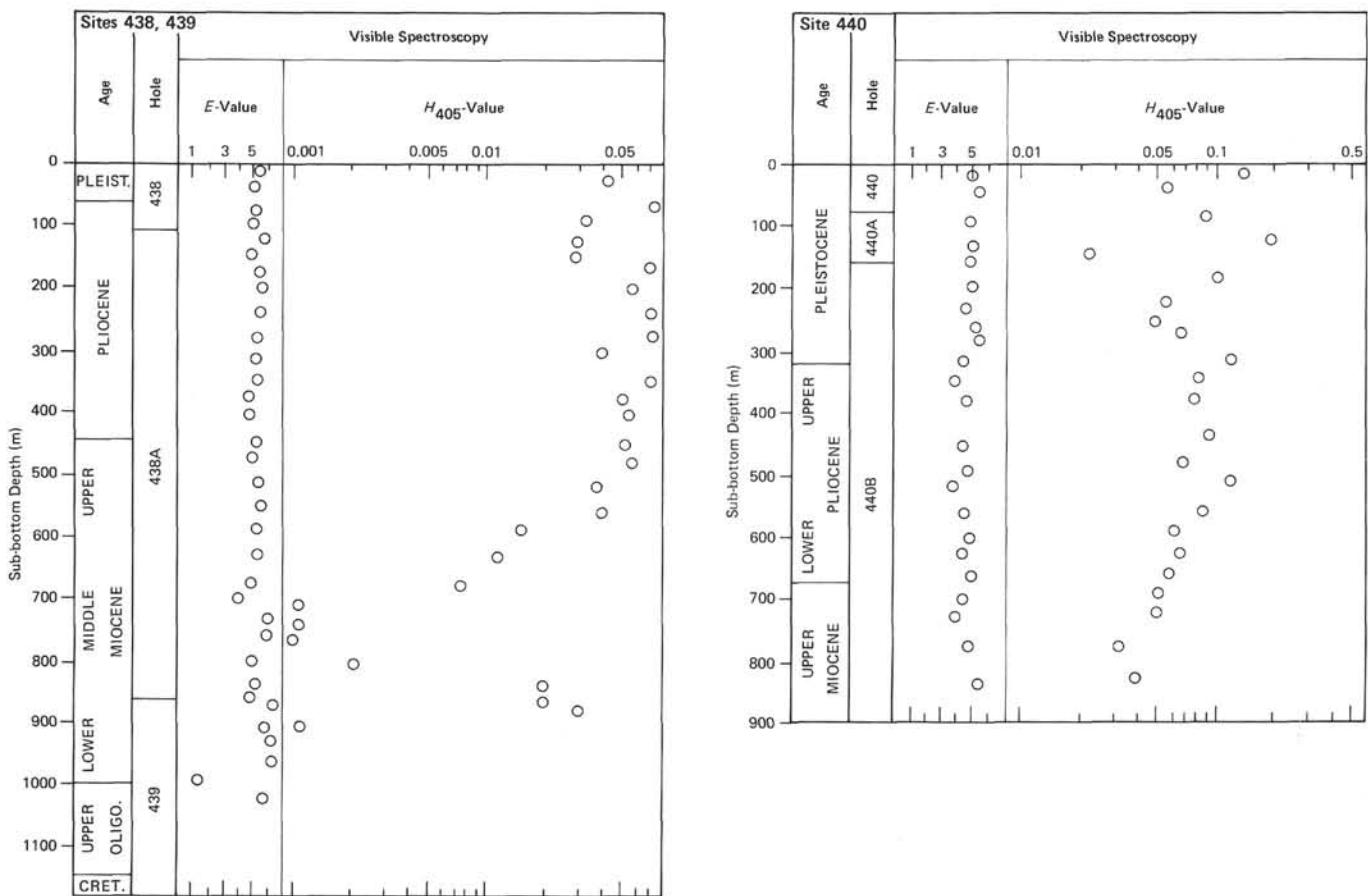


Figure 3. Variations with depth of the E-value and  $H_{405}$ -value in visible spectra of humic acids at Sites 438, 439, and 440.

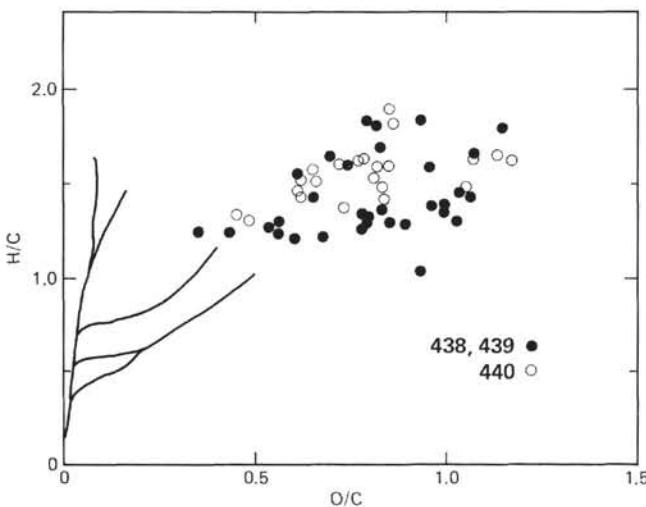


Figure 4. Relationship between H/C and O/C atomic ratios of humic acids at Sites 438, 439, and 440 on the basis of the diagram of van Klevlen (1961).

this study show that it is necessary to separate out humic acids in addition to measuring each kerogen type in the ESR study.

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TABLE 3  
ESR Data of Kerogen and Humic Acids at Sites 438, 439, and 440

Sample	Sub-bottom Depth (m)	Kerogen			Humic Acids		
		Linewidth (G)	g-value	Ns (spins/gC) $\times 10^{18}$	Linewidth (G)	g-value	Ns (spins/gC) $\times 10^{18}$
438-1-2	3	4.88	2.00303	0.60	7.04	2.00331	0.19
438-5-3	37	4.93	2.00309	0.92	7.65	2.00333	0.28
438-9-3	76	5.08	2.00312	0.82	6.56	2.00328	0.56
438-11-3	94	5.77	2.00309	0.63	6.06	2.00337	0.44
438A-7-4	122	5.06	2.00293	0.63	6.55	2.00346	0.76
438A-10-2	147	5.01	2.00302	0.56	6.35	2.00361	0.75
438A-13-2	175	4.67	2.00301	0.66	5.66	2.00363	0.34
438A-16-3	205	4.92	2.00304	0.39	6.05	2.00354	0.36
438A-20-3	243	4.92	2.00298	0.24	5.81	2.00346	0.47
438A-24-3	281	4.72	2.00301	1.45	6.56	2.00351	0.40
328A-27-3	309	4.82	2.00301	2.39	7.15	2.00346	0.55
438A-31-3	348	4.82	2.00304	0.47	6.26	2.00345	0.64
438A-34-2	375	4.62	2.00307	1.83	6.07	2.00339	0.71
438A-37-3	405	4.27	2.00301	2.79	6.96	2.00351	0.84
438A-42-3	452	4.57	2.00301	1.37	5.88	2.00359	1.17
438A-44-3	473	4.07	2.00289	1.56	5.33	2.00348	0.79
438A-48-3	520	4.47	2.00292	2.39	6.57	2.00333	0.75
438A-52-3	549	4.57	2.00301	0.87	6.47	2.00336	1.56
438A-56-3	587	2.97	2.00284	0.26	5.81	2.00327	0.41
438A-60-2	624	2.87	2.00284	0.28	5.51	2.00345	0.27
438A-65-5	676	2.78	2.00286	0.73	5.52	2.00330	0.49
438A-68-5	704	4.27	2.00298	0.97	6.57	2.00313	0.29
438A-71-3	729	3.13	2.00283	0.27	3.14	2.00279	0.66
438A-73-3	749	3.28	2.00289	0.47	3.38	2.00277	0.34
438A-78-2	795	3.52	2.00283	0.16	3.43	2.00289	0.95
438A-82-2	833	2.88	2.00280	0.61	3.13	2.00289	0.64
438A-84-3	853	4.77	2.00298	0.87	6.17	2.00357	0.53
439-7-3	872	4.47	2.00295	0.62	6.23	2.00343	0.52
439-11-3	910	4.22	2.00292	0.64	5.72	2.00354	0.59
439-14-2	934	3.88	2.00289	0.91	7.01	2.00333	0.45
439-18-3	967	4.81	2.00307	0.53	5.57	2.00342	1.07
439-21-3	996	4.32	2.00295	0.54	5.38	2.00348	2.17
439-22-3	1004	3.73	2.00283	0.40	—	—	—
439-24-3	1024	4.78	2.00300	1.00	5.26	2.00346	0.78
439-26-3	1044	3.93	2.00292	1.47	—	—	—
439-30-3	1081	4.43	2.00280	0.61	—	—	—
439-38-1	1149	4.62	2.00271	1.88	—	—	—
439-39-1	1154	4.52	2.00271	2.55	—	—	—
440-1-2	2	3.73	2.00286	0.18	6.06	2.00349	0.44
440-5-5	42	4.92	2.00310	0.22	6.55	2.00341	0.46
440A-2-3	87	4.07	2.00292	0.41	5.82	2.00339	1.12
440A-5-4	116	3.23	2.00280	0.66	6.02	2.00336	0.45
440A-7-3	134	2.93	2.00283	0.38	2.93	2.00283	0.74
440B-4-3	172	4.43	2.00294	0.36	7.65	2.00335	0.82
440B-7-3	200	4.28	2.00286	1.02	7.36	2.00323	0.20
440B-11-3	239	4.17	2.00289	0.33	6.86	2.00313	0.36
440B-14-5	270	4.37	2.00298	0.49	7.16	2.00331	0.38
440B-18-2	303	3.48	2.00286	1.22	8.55	2.00313	0.21
440B-21-3	333	4.51	2.00295	0.33	7.56	2.00309	0.39
440B-24-3	362	4.32	2.00289	0.65	8.39	2.00319	0.27
440B-31-3	428	4.67	2.00292	0.27	8.54	2.00333	0.32
440B-35-3	466	4.87	2.00310	0.81	8.67	2.00342	0.39
440B-39-3	504	5.02	2.00313	0.47	7.55	2.00355	0.50
440B-43-3	542	5.02	2.00304	0.61	8.83	2.00339	0.78
440B-47-1	578	4.92	2.00301	0.62	9.36	2.00333	0.29
440B-51-1	616	4.37	2.00289	0.39	8.76	2.00329	0.34
440B-54-3	647	4.91	2.00301	0.65	6.77	2.00315	0.25
440B-58-2	683	4.96	2.00304	0.47	8.46	2.00325	0.52
440B-61-1	710	4.67	2.00292	0.64	9.35	2.00311	0.24
440B-66-3	761	4.47	2.00292	0.79	7.86	2.00327	0.18
440B-71-1	806	4.47	2.00295	0.52	6.05	2.00335	0.65

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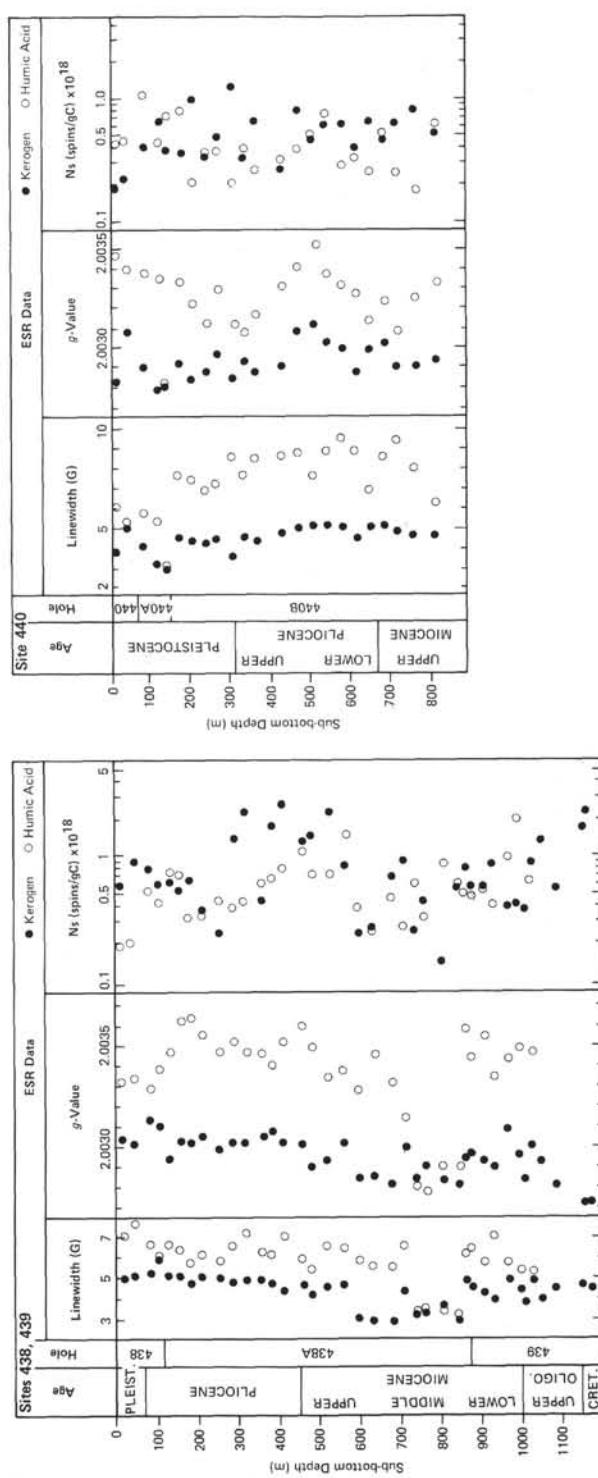


Figure 5. Variations with depth of ESR signals of kerogen and humic acids at Sites 438, 439, and 440.

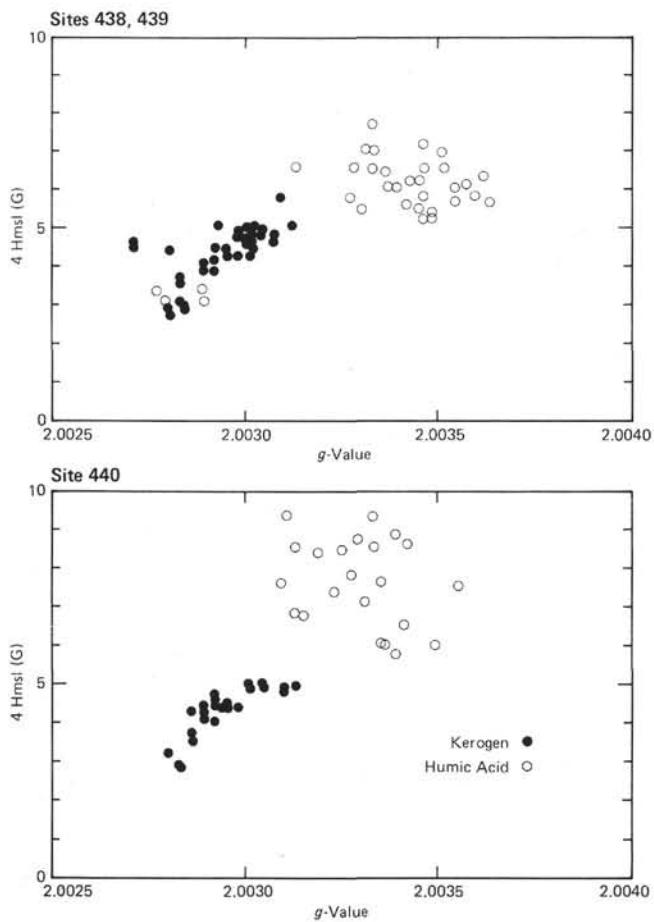


Figure 6. Relationship between linewidth and g-value on ESR spectra of kerogen and humic acids at Sites 438, 439, and 440.

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