

### 13. GEOCHEMICAL COMPARISONS OF ORGANIC MATTER IN CRETACEOUS BLACK SHALES FROM SITE 897, IBERIA ABYSSAL PLAIN, SITES 638 AND 641, GALICIA MARGIN, AND SITE 398, VIGO SEAMOUNT<sup>1</sup>

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#### ABSTRACT

Three episodes of accumulation of organic-carbon-rich "black shales" occurred on the Iberia Margin of the North Atlantic during the Early-middle Cretaceous. The origins of the organic matter contents of these deposits have been investigated using elemental, isotopic, Rock-Eval, and biomarker analyses. The organic matter in Berriasian-Barremian turbiditic marlstones contains major proportions of continental plant material. Aptian-Albian turbiditic shale sequences include black layers similarly dominated by land-derived organic matter but also having important amounts of marine material. A thin layer of Cenomanian-Turonian black shale contains over 11% organic carbon, most of which is derived from marine sources. Downslope transport and rapid reburial of shelf-edge sediments within predominantly oxygenated deep-water settings contributed to deposition of the Early Cretaceous black shales. The Cenomanian-Turonian black shales evidently record a brief episode of intensified mid-water oxygen minimum zone and consequent improved preservation of marine organic matter during the middle Cretaceous.

#### INTRODUCTION

Scientific ocean drilling has documented the existence of organic-carbon-rich Cretaceous strata at many locations in the North Atlantic Ocean. Although lithologically heterogeneous, these "black shales" are uniformly darker in color and notably richer in organic matter than typical deep-sea sediments and sedimentary rocks. The amounts and types of organic matter contained within sediments are generally influenced by the oceanographic and depositional conditions that existed at the time of their accumulation. Study of the organic constituents of black shales consequently provides insights into the special conditions that permitted their deposition.

The seafloor at several locations on and near the Galicia Margin has yielded black shale sequences. Drilling during Ocean Drilling Program (ODP) Leg 149 encountered black shales at Site 897 on the Iberia Abyssal Plain. Earlier drilling at sites 638 and 641 of ODP Leg 103 on the Galicia Bank recovered several sequences of black shales. The earliest discovery of black shales on this margin was at Site 398 on the Vigo Seamount, which was drilled during Deep Sea Drilling Project (DSDP) Leg 47 in 1976. This report compares the organic matter contents of the black shales newly discovered at Site 897 to those from earlier discoveries from this region and presents a synthesis of organic matter delivery and deposition to this part of the eastern North Atlantic Ocean during the Early to middle Cretaceous.

#### LITHOLOGIC SETTINGS

##### Site 897

Site 897 is located on the eastern edge of the Iberia Abyssal Plain at a water depth of 5330 m (Fig. 1). The site was positioned on a sediment-covered basement ridge so that drilling could easily reach oceanic crust. Parts of the Lower Cretaceous to Pleistocene sedimentary sequence at this site are consequently condensed or missing. Creta-

ceous sediments, in particular, consist of only a 40-m-thick Hauterivian to lower Aptian debris-flow sequence containing fragments of peridotite and continental basement rocks; Upper Cretaceous sediments are incomplete (Shipboard Scientific Party, 1994). Black shales are present in the lower Aptian debris-flow deposit.

##### Sites 638 and 641

Sites 638 and 641 are situated at depths of 4661 m and 4640 m, respectively, on the continental rise southwest of the Galicia Bank (Fig. 1). Drilling done during Leg 103 provides a composite lithostratigraphic column of Cretaceous sedimentation on this rise (Shipboard Scientific Party, 1987). A thick limestone, marlstone, and sandstone sequence was deposited from Tithonian to Barremian times. This was followed by accumulation of debris flows and turbidites and then by bioturbated claystones in which Berriasian-Barremian, Aptian-Albian, and Cenomanian-Turonian black shales are interspersed.

##### Site 398

Site 398 is located in 3910 m water depth on the southern slope of the Vigo Seamount (Fig. 1). A Hauterivian sequence consisting of fine-grained nannofossil limestone with interbedded brown mudstones is overlain by Barremian to Cenomanian dark-colored laminated claystones (Shipboard Scientific Party, 1979). Paleo-water depths at this location evidently were below the calcite compensation depth during the Barremian to Cenomanian. Thin layers of turbiditic sandstones and siltstones are frequently interspersed throughout the claystone sequence and indicate inputs of continental sediments from coastal regions. Black shales accumulated at this location during Hauterivian-Barremian, Aptian-Albian, and Cenomanian times.

#### METHODS

##### Organic Carbon Measurements

The total organic carbon contents (TOC) of Site 897 samples were determined by the difference between total carbon concentrations as measured by a Carlo Erba NA 1500 NCS analyzer (Verardo et al.,

<sup>1</sup>Whitmarsh, R.B., Sawyer, D.S., Klaus, A., and Masson, D.G. (Eds.), 1996. *Proc. ODP, Sci. Results*, 149: College Station, TX (Ocean Drilling Program).

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1990) and the carbonate carbon concentrations as measured by a Coulometrics 5011 inorganic carbon analyzer (Engleman et al., 1985). Freeze-dried samples were combusted at 1000°C in an oxygen atmosphere in the NCS analyzer, and the resulting combustion products were chromatographically separated and quantified to yield the concentrations of total carbon and nitrogen. The TOC and total nitrogen values were used to calculate atomic C/N ratios of the samples. These C/N ratios are assumed to represent those of sediment organic matter in this report.

### Organic Carbon Isotope Ratios

Organic carbon isotope ratios of Site 897 samples were measured in the Stable Isotope Laboratory at The University of Michigan. Organic  $^{13}\text{C}/^{12}\text{C}$  ratios of samples that had been treated with 3N HCl to destroy carbonate minerals were measured after reacting the samples with CuO in evacuated and sealed quartz tubes for 3 hr at 800°C. The  $\text{CO}_2$  produced by oxidation of the total organic matter was analyzed with a Finnigan Delta S mass spectrometer. National Bureau of Standards carbon isotope standards were routinely used to calibrate the instrument. Results are reported relative to the PDB standard.

### Rock-Eval Pyrolysis

Rock-Eval pyrolysis of organic matter consists of heating samples at a rate of 25°C/min between 300°C to 600°C to yield the amount of volatile hydrocarbons ( $S_1$ ), the amount of thermogenic hydrocarbons ( $S_2$ ), and the amount of  $\text{CO}_2$  released during pyrolysis to 390°C ( $S_3$ ). These values are combined with TOC values to provide the information necessary to calculate the hydrogen index ( $\text{HI} = 100 \times S_2 / \text{TOC}$ , or milligrams hydrocarbons / gram organic carbon) and the oxygen index ( $\text{OI} = 100 \times S_3 / \text{TOC}$ , or milligrams  $\text{CO}_2$  / gram organic carbon). The temperature of maximum hydrocarbon release during pyrolysis ( $T_{\text{max}}$ ) is also obtained and provides a measure of organic matter thermal maturity (Espitalié et al., 1977).

## RESULTS AND DISCUSSION

The definition of a "black shale" includes three principal requirements—it must be a fine-grained sedimentary rock, have a dark color, and contain at least 0.5% organic carbon (Arthur, 1979; Huyck, 1990). Drilling at Site 897 discovered black shales in a lower Aptian debris flow sequence deposited on the landward edge of the Iberia Abyssal Plain. These shales appear to represent the sedimentary matrix in which the debris flow material settled; they do not appear to be redeposited clasts (Shipboard Scientific Party, 1994). Black shales of neither older nor younger ages were found at this site, probably as a consequence of the abbreviated and incomplete Cretaceous sequence found here. The origins of the organic matter contents of black shales from Holes 897C and 897D were investigated using elemental, isotopic, and Rock-Eval source indicators, and the results were compared to earlier studies of black shales from the Galicia Margin and Vigo Seamount.

### Organic Carbon Concentrations

The concentrations of organic carbon in the black shale samples from Holes 897C and 897D average  $1.03 \pm 0.34\%$  and have a maximum of 1.77% (Table 1). These values are significantly higher than the average organic carbon content of 0.2% of deep-sea sediments and rocks from DSDP Legs 1 through 33 compiled by McIver (1975). They are, however, relatively low in comparison to the organic carbon concentrations reported for black shales from the Galicia Margin and Vigo Seamount. Most of these values are between 1 and 2%, and those of the Cenomanian-Turonian boundary samples reach nearly 13% (Fig. 2).

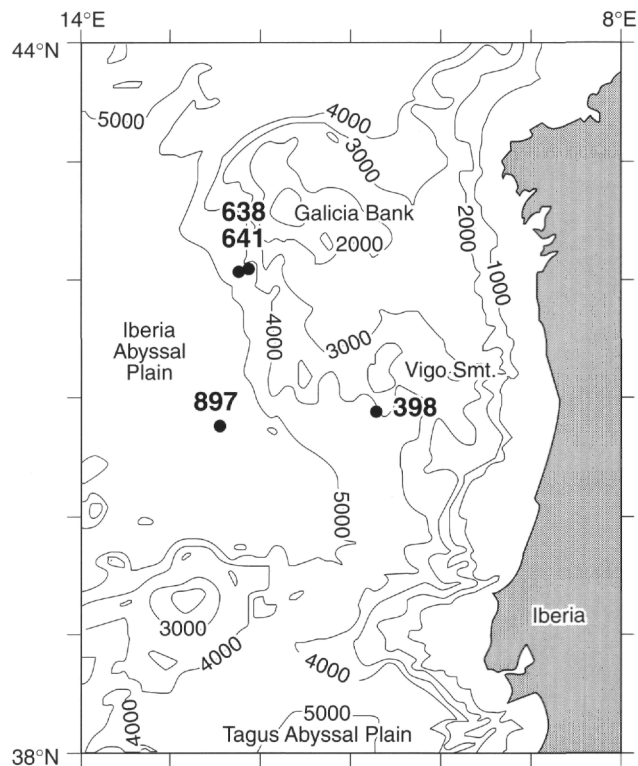


Figure 1. Locations of Site 398 of DSDP Leg 47 on the Vigo Seamount, Sites 638 and 641 of ODP Leg 103 on the Galicia Margin, and Site 897 of ODP Leg 149 on the Iberia Abyssal Plain of the eastern North Atlantic Ocean. Depth contours given in meters.

### Organic Matter C/N Ratios

C/N ratios help to distinguish between algal and land-plant origins of sedimentary organic matter. Algae typically have atomic C/N ratios between 4 and 10, whereas vascular land plants have C/N ratios of 20 and greater (Premuzic et al., 1982; Jasper and Gagosian, 1990; Meyers, 1994; Prahl et al., 1994). This distinction arises from the absence of cellulose in algae and its abundance in vascular plants and is largely preserved in sedimentary organic matter. Identification of the proportions of marine and continental organic matter in ocean sediments is needed to estimate rates of marine paleoproduction and to determine the importance of delivery of allochthonous material in the past. Furthermore, terrigenous organic matter is less susceptible to oxidative destruction in sediments (Waples, 1983) and consequently has an important role in elevating organic carbon concentrations in times of unexceptional productivity.

The C/N ratios of organic matter in the Site 897 black shales are high, averaging 39 and ranging widely between 5.6 and 69.8 (Table 1). Most of these values are greater than 20, indicating that land-derived material dominates the organic matter contents of these black shales. This dominance is consistently seen in the rocks from Hole 897C and is less consistent in the Hole 897D samples. A similar dominance in land-derived organic matter contributions was reported for Galicia Margin black shales of Hauterivian-Barremian age from Site 638 and of Aptian-Albian age from Site 641 (Meyers et al., 1988).

### Carbon Isotope Ratios

Organic carbon isotopic ratios are useful to distinguish between marine and continental plant sources of sedimentary organic matter. Most photosynthetic plants incorporate carbon into organic matter using the  $\text{C}_3$  Calvin pathway which biochemically discriminates

**Table 1. Bulk organic matter characteristics of lower Aptain black shales from Site 897 on the Iberia Abyssal Plain.**

Core, section, interval (cm)	Depth (mbsf)	Org. C (%)	C/N (atomic)	T <sub>max</sub> (°C)	HI	OI
149-897C-						
63R-1, 94-95	649.64	1.24	24.4	nd	nd	nd
63R-2, 17-25	649.89	1.08	43.4	416	26	82
63R-2, 28-30	650.00	0.75	64.9	nd	nd	nd
64R-1, 13-14	658.53	0.78	54.6	nd	nd	nd
64R-1, 56-57	658.96	1.00	62.0	nd	nd	nd
64R-1, 96-97	659.36	0.67	61.2	nd	nd	nd
64R-2, 3-4	659.48	1.21	69.8	nd	nd	nd
64R-2, 31-35	659.74	1.05	39.5	413	44	106
64R-2, 35-40	659.78	0.83	31.2	415	28	154
65R-2, 110-114	670.56	1.12	24.6	415	81	145
149-897D-						
7R-1, 39-40	655.59	0.60	62.1	nd	nd	nd
7R-1, 107-113	656.27	0.59	19.1	—	0	122
7R-1, 124-125	656.44	1.14	66.4	nd	nd	nd
7R-2, 8-9	656.78	0.47	5.6	nd	nd	nd
7R-2, 20-26	656.90	0.68	29.4	—	0	132
7R-2, 76-77	657.46	1.28	45.6	nd	nd	nd
7R-3, 60-61	658.30	1.48	14.7	nd	nd	nd
7R-CC, 2-8	658.61	1.45	20.1	446	62	33
8R-1, 30-31	665.10	1.30	16.3	nd	nd	nd
8R-1, 109-113	665.89	1.58	25.2	443	69	48
8R-2, 38-42	666.68	1.77	28.3	443	73	42
8R-2, 55-56	666.85	0.74	55.1	nd	nd	nd
8R-3, 34-38	667.64	1.21	23.5	445	77	72
8R-CC, 3-4	667.93	1.10	14.1	nd	nd	nd
10R-3, 68-69	687.00	0.68	56.6	nd	nd	nd
10R-4, 90-91	688.72	0.95	57.5	nd	nd	nd

Note: HI = Rock-Eval hydrogen index (mg hydrocarbons/g TOC), OI = Rock-Eval oxygen index (mg CO<sub>2</sub>/g TOC), dashes = pyrograms having immeasurable T<sub>max</sub> values, nd = not determined.

against <sup>13</sup>C to produce a δ<sup>13</sup>C shift of about -20‰ from the isotope ratio of the inorganic carbon source. Organic matter produced from atmospheric CO<sub>2</sub> (δ<sup>13</sup>C of about -7‰) by land plants using the C<sub>3</sub> pathway consequently has δ<sup>13</sup>C (PDB) values that average roughly -27‰ (cf. O'Leary, 1988). The source of inorganic carbon for marine algae is dissolved bicarbonate, which has a δ<sup>13</sup>C value of about 0‰. Marine organic matter consequently typically has δ<sup>13</sup>C values between -20‰ and -22‰. The approximately 7‰ difference between organic matter produced by C<sub>3</sub> land plants and marine algae has been used to trace the delivery and distribution of organic matter to sediments of ocean margins (Newman et al., 1973; Prah et al., 1994). Carbon isotope ratios can be affected, however, by photosynthetic dynamics and by postdepositional diagenesis (Dean et al., 1986; McArthur et al., 1992) and consequently must be interpreted cautiously.

Dunham et al. (1988) and Erdman and Schorno (1979) provide the results of organic δ<sup>13</sup>C determinations of black shales from the Galicia Margin and Vigo Seamount, respectively. The values range widely between -21.5‰ to -28.5‰ (Fig. 2). Neocomian and Aptian-Albian black shales, in particular, are variable in their isotopic compositions. In contrast, samples from the especially organic-carbon-rich thin layer of Cenomanian-Turonian black shale found at Hole 641A on the Galicia Margin have δ<sup>13</sup>C values that group tightly around -24‰ (Fig. 2).

If interpreted strictly on the basis of isotopic source signatures, the isotopic variability evident in the black shales suggests that the delivery of organic matter to the Iberia Margin locations varied widely between land-plant and marine dominance. Other factors, however, impact the isotopic composition of organic matter. Prominent among these are the availability of CO<sub>2</sub> during photosynthesis and the possibility of selective diagenesis of organic matter fractions that are isotopically heavy or light. Any diagenetic isotope shift appears to be small, less than 2‰ (Dean et al., 1986; Fontugne and Calvert, 1992; McArthur et al., 1992; Meyers, 1994). Increased availability of dissolved CO<sub>2</sub> to algae, however, would enhance their isotopic discrim-

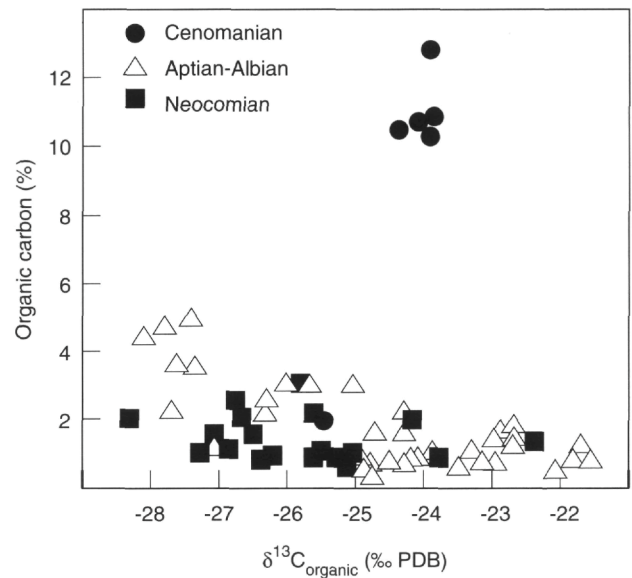


Figure 2. Compilation of organic carbon concentrations and δ<sup>13</sup>C values of black shales from the Iberia Margin. Data are from Erdman and Schorno (1979) and Dunham et al. (1988).

ination and produce marine organic matter that is isotopically light (Dean et al., 1986), as would increased delivery of isotopically light fluvial dissolved inorganic carbon (Fontugne and Calvert, 1992). The variability of organic δ<sup>13</sup>C values of these black shales suggests that they represent accumulation of organic matter during periods of environmental perturbation that includes both a variety of biosynthetic conditions and a variety of depositional conditions. Such conditions would likely accompany the early rifting settings that existed on the Iberia Margin of the North Atlantic in the Early Cretaceous (Shipboard Scientific Party, 1987, 1994).

### Rock-Eval Analyses

Rock-Eval pyrolysis was originally developed to characterize the organic matter present in oil source rocks. Such organic matter typically is more thermally mature and is present at higher concentrations than commonly found during scientific ocean drilling. Rock-Eval analyses have nonetheless proved valuable in helping to determine organic matter sources in DSDP and ODP samples. Land-plant organic matter is usually rich in woody components and consequently has lower hydrogen indices and higher oxygen indices than found in lipid-rich and cellulose-poor algal organic matter. This distinction between organic matter from continental and marine sources becomes blurred by diagenesis as marine matter either is oxidized to gradually take on HI and OI values similar to those of land-plant material or is degraded to detrital, type IV organic matter.

A Van Krevelen-type plot of the HI and OI values indicates that the Site 897 black shales contain type III (land-derived) organic matter (Fig. 3). This source indication for the organic matter in these Aptian rocks is consistent with the high C/N ratios listed in Table 1. The T<sub>max</sub> values of the Hole 897C samples are ~415°C (Table 1), which is typical of organic matter that is thermally immature with respect to petroleum generation (Espitalié et al., 1977). Vitrinite reflectance analyses show that the organic matter at Sites 398, 638, and 641 is similarly thermally immature (Cornford, 1979; Stein et al., 1988). The Hole 897D samples, in contrast, have T<sub>max</sub> values of ~445°C, which indicates that the organic matter in these black shales has reached thermal maturity. A possible explanation for the elevated thermal maturity is that hydrothermal activity may have altered the

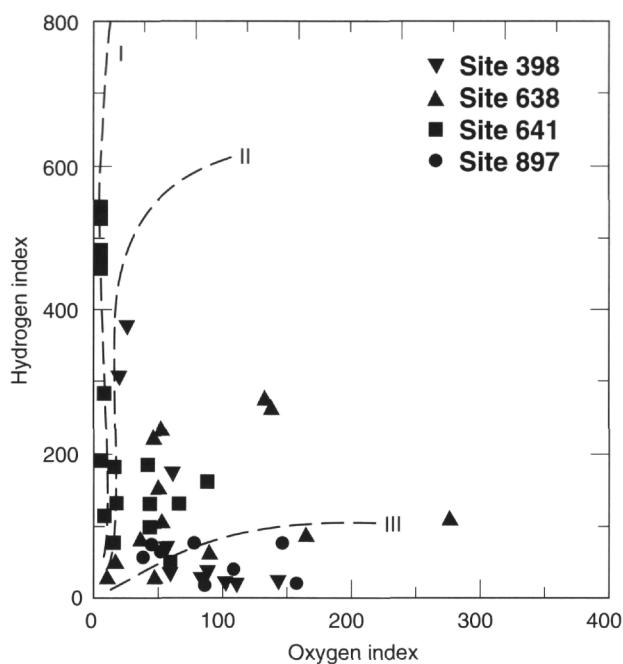


Figure 3. Results of Rock-Eval analyses of Aptian-Albian black shale samples from Site 897. Units for hydrogen index are milligrams of hydrocarbons per gram TOC and for oxygen index are milligrams of CO<sub>2</sub> per gram TOC. Diagenetic pathways of kerogen types I, II, and III are shown.

organic matter in Hole 897D, whereas absence of this activity in nearby Hole 897C, as well as at other sites on the Iberia Margin, left the organic matter unaltered. This explanation is hypothetical, inasmuch as evidence for hydrothermal activity is sparse at this site, consisting only of slightly elevated heat-flows and low-temperature alteration of basement rock (Shipboard Scientific Party, 1994). An alternate possibility is that the Hole 897D black shales contain mostly recycled organic matter eroded from thermally mature sedimentary rocks on the Iberia Peninsula.

Comparison of the HI and OI values of the Site 897 black shales to those from Sites 398, 638, and 641 shows that most of the black shales on the Iberia Margin are hydrocarbon-poor (Fig. 4). Their organic matter is made up of varying mixtures of continental material and oxidized marine material. Cornford (1979) and Stein et al., (1988) note that the vitrinite contents of the Lower Cretaceous black shales have a broad range of reflectance values, indicating that the organic matter is indeed a mixture of primary and recycled material. Some black shales, particularly the Cenomanian samples from Site 641, have relatively high HI values (Dunham et al., 1988). These samples show that deposition of black shales rich in marine organic matter occurred on this margin during the Cenomanian-Turonian Boundary Event (CTBE) (Thurow et al, 1988).

### Biomarker Analyses

The molecular composition of the extractable lipid fraction of sediment organic matter provides particularly useful information about the sources and diagenetic alterations of organic matter. Many of these compounds have specific biological origins; all of them reflect enzymatic control on their molecular structures. Retention of their biological heritage earns the name "biological marker," commonly abbreviated to "biomarker," for many of these compounds. This characteristic makes the biomarker fraction especially important to studies of black shales, even though it typically constitutes at most a few percent of the total organic matter.

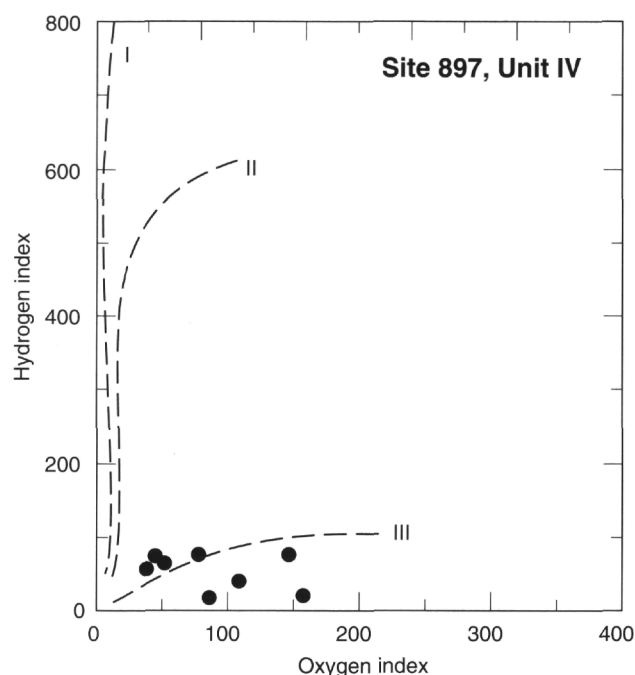


Figure 4. Compilation of Rock-Eval results from black shales from DSDP Site 398 on the Vigo Seamount, ODP Sites 638 and 641 on the Galicia Margin, and ODP Site 897 on the Iberia Abyssal Plain. Units for hydrogen index are milligrams of hydrocarbons per gram TOC and for oxygen index are milligrams of CO<sub>2</sub> per gram TOC. Diagenetic pathways of kerogen types I, II, and III are shown. Data are from Deroo et al. (1979), Dunham et al. (1988), Stein and Rullkötter (1988), and this study.

The biomarker compositions extracted from the black shales from the Iberia Margin reflect the transition through time from land-source dominance to marine dominance of organic matter evident from the bulk determinations. Biomarker distributions in the Neocomian and the Aptian-Albian black shales from Sites 398, 638, and 641 are dominated by the C<sub>27</sub>, C<sub>29</sub>, and C<sub>31</sub> *n*-alkanes and C<sub>29</sub> steroids characteristic of land-plant organic matter (Simoneit and Mazurek, 1979; Dunham et al., 1988; Stein et al., 1988). A series of cyclic diterpenoid hydrocarbons diagnostic of land plants is present in the Valanginian-Hauterivian sequence but not in younger sediments at this location (Stein et al., 1988). The shift to marine dominance is evident in the biomarker distributions present in the Cenomanian-Turonian black shales from Site 641 (Dunham et al., 1988; Stein et al., 1988). Shales of this age continue to contain important contributions of land-derived components, but they have larger proportions of algal components than present in black shales from the older depositional episodes. Distributions of *n*-alkanes, for example, are dominated by the algal C<sub>17</sub> component (Dunham et al., 1988).

Important contributions of bacterial biomarkers are found in all of the distributions and indicate that the organic matter in the black shales has been extensively reworked by microbes. Dunham et al. (1988) observe that the pristane/phytane ratios of the Iberia Margin black shales, particularly the Cenomanian ones, are low. Low pristane/phytane ratios have been variously interpreted to indicate anoxic depositional conditions, low thermal maturity of organic matter, or evidence of methanogenic bacterial activity. All of these possibilities could be valid for the black shales from the Iberia Margin locations. The presence of series of hopanes, hopenes, and ferenes in the hydrocarbon fractions extracted from the shales (Stein et al., 1988), all of which can be attributed to microbial activity, however, suggests that microbial activity is probably the major factor in depressing the pristane/phytane ratios at these locations. The biomarker evidence of

microbial reworking supports the contention that the low HI values shown in Figure 4 similarly derive from microbial alteration of organic matter.

### Paleoceanographic Implications

The dominance of land-derived organic matter in the Aptian-Albian black shales discovered at Site 897 strengthens existing reconstructions of the paleoceanographic conditions that led to deposition of black shales in the eastern North Atlantic Ocean during the Cretaceous (Arthur, 1979; Cornford et al., 1980; Summerhayes, 1981; de Graciansky et al., 1987; Stein et al., 1986, 1989). Changes in continental weathering rates, eustatic sea level, and basin circulation as the North Atlantic rifted and expanded created episodes when organic-carbon-rich sediments accumulated offshore of Iberia.

Redeposition of sediments from shallow-water to deep-water sites by turbidity flows and slumping is a major element in most of the black shale occurrences on the Iberia Margin. A combination of humid climate in southwestern Europe (Hallam, 1984) and lowered sea level (Vail et al., 1980) in the Berriasian-early Hauterivian resulted in relatively high accumulation rates of land-derived organic matter on the Iberia Margin (Stein et al., 1988). A higher sea level during the mid-Hauterivian-Barremian decreased the delivery of terrigenous organic matter as fluvial sediments were trapped on the expanded continental shelves. A short-lived drop in sea level in the early Aptian (Vail et al., 1980) is accompanied by an elevated accumulation of continental organic matter (Stein et al., 1988). This was followed by a high sea-stand and diminished accumulations of terrigenous sediments for most of the Aptian-Albian. Black shales from this period typically contain 1%-2% organic carbon, which is mostly from land plants, and little or no diluting calcium carbonate. The Site 897 black shales are of this type.

The globally well-developed Cenomanian-Turonian Boundary Event (CTBE) is represented on the Iberia Margin by black shales at Sites 398 and 641; drilling at other sites did not recover sediments of this age. The organic matter in the CTBE Site 641 samples is ~90% marine (Stein et al., 1988) and consequently was deposited under very different conditions than the terrigenous material that dominates older black shales. Black shales at Site 641 exhibit the carbon isotopic excursion to heavier values that is globally common at the Cenomanian-Turonian boundary (Thurrow et al., 1988). This excursion has been attributed to burial of large amounts of  $^{12}\text{C}$ -rich marine organic matter with consequent drawdown of the global reservoir of  $^{12}\text{C}$  available to marine algae, rather than being a product of elevated productivity (Pratt and Threlkeld, 1984). Indeed, the paleoproductivity on the Galicia Plateau during the time when these black shales were being deposited has been estimated to be as low as  $10 \text{ g/m}^2/\text{yr}$  (Stein and Rullkötter, 1988). Sedimentation rates on the Iberia Margin in the late Cenomanian also were low (Shipboard Scientific Party, 1979, 1987), probably as a consequence of elevated sea level. The important factor in creating these organic-carbon-rich sediments is believed to be an expanded and intensified oxygen minimum zone (Herbin et al., 1986; de Graciansky et al., 1987; Farrimond et al., 1990; Thurrow et al., 1992). Circulation rates of deep ocean waters improved after the seaway between the North Atlantic and the South Atlantic opened, and the ensuing disappearance of oxygen-poor conditions terminated the burial of marine organic matter in bottom sediments that typified the CTBE.

Emplacement of lower Aptian black shales on the basement high that was the drilling objective of Site 897 is curious because they are part of a debris flow-slump deposit. This location was probably a topographic high in the Early Cretaceous, yet it received slumped continental sediments. How these sediments traveled uphill remains problematic.

### SUMMARY

The principal factors that contributed to deposition of organic-carbon-rich black shales on the Iberia Margin during the Cretaceous are (1) supply of continental organic matter, (2) supply of marine organic matter, (3) preservation of organic matter, and (4) dilution of organic matter by other sediment components. All of these factors varied during the early stages of rifting of the proto-North Atlantic.

The elemental, isotopic, and biomarker compositions of three episodes of accumulation of organic-carbon-rich black shales on the Iberia Margin of the North Atlantic during the Early-middle Cretaceous are compared. C/N ratios and organic  $\delta^{13}\text{C}$  values indicate a progressive change in the proportions of continental and marine organic matter over time. Berriasian-Barremian turbiditic marlstones contain major proportions of continental organic matter. Aptian-Albian turbiditic shale sequences include black layers similarly enriched in land-derived organic matter but with enhanced amounts of marine material. A thin layer of Cenomanian-Turonian black shale contains up to 13% organic carbon, 90% of which is derived from marine sources. Distributions of biomarker molecules mirror the source changes present in the elemental and isotopic compositions. Downslope transport and rapid reburial of shelf-edge sediments within predominantly oxygenated deep-water settings evidently contributed to deposition of the Early Cretaceous black shales. In contrast, the Cenomanian-Turonian black shales record a brief episode of improved preservation of marine organic matter due to mid-water anoxia during the middle Cretaceous. The organic matter in the black shales is immature with respect to petroleum generation, except at Hole 897D where Aptian-Albian black shales appear to contain detrital organic matter.

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### REFERENCES

- Arthur, M.A., 1979. North Atlantic Cretaceous black shales: the record at Site 398 and a brief comparison with other occurrences. *In* Sibuet, J.-C., Ryan, W.B.F., et al., *Init. Repts. DSDP*, 47 (Pt. 2): Washington (U.S. Govt. Printing Office), 719-751.
- Cornford, C., 1979. Organic petrography of Lower Cretaceous shales at DSDP Leg 47B Site 398, Vigo Seamount, eastern North Atlantic. *In* Sibuet J.-C., Ryan, W.B.F., et al., *Init. Repts. DSDP*, 47 (Pt. 2): Washington (U.S. Govt. Printing Office), 523-527.
- Cornford, C., Rullkötter, J., and Welte, D., 1980. A synthesis of organic petrographic and geochemical results from DSDP sites in the eastern central North Atlantic. *In* Douglas, A.G., and Maxwell, J.R. (Eds.), *Advances in Organic Geochemistry 1979*: Oxford (Pergamon Press), 12:445-453.
- Dean, W.E., Arthur, M.A., and Claypool, G.E., 1986. Depletion of  $^{13}\text{C}$  in Cretaceous marine organic matter: source, diagenetic, or environmental signal? *Mar. Geol.*, 70:119-157.
- de Graciansky, P., Brosse, E., Deroo, G., Herbin, J.-P., Montadert, L., Muller, C., Sigal, J., and Schaaf, A., 1987. Organic-rich sediments and palaeoenvironmental reconstructions of the Cretaceous North Atlantic. *In* Brooks, J., and Fleet, A.J. (Eds.), *Marine Petroleum Source Rocks*. Geol. Soc. Spec. Publ. London, 26:317-344.

- Deroo, G., Herbin, J.P., Roucaché, J., and Tissot, B., 1979. Organic geochemistry of Cretaceous shales from DSDP Site 398, Leg 47B, eastern North Atlantic. *In* Sibuet, J.-C., Ryan, W.B.F., et al., *Init. Repts. DSDP*, 47 (Pt. 2): Washington (U.S. Govt. Printing Office), 513-522.
- Dunham, K.W., Meyers, P.A., and Ho, E.S., 1988. Organic geochemistry of Cretaceous black shales and adjacent strata from the Galicia Margin, North Atlantic Ocean. *In* Boillot, G., Winterer, E.L., et al., *Proc. ODP, Sci. Results*, 103: College Station, TX (Ocean Drilling Program), 557-565.
- Engleman, E.E., Jackson, L.L., and Norton, D.R., 1985. Determination of carbonate carbon in geological materials by coulometric titration. *Chem. Geol.*, 53:125-128.
- Erdman, J.G., and Schorno, K.S., 1979. Geochemistry of carbon: Deep Sea Drilling Project, Legs 47A and B. *In* Sibuet, J.-C., Ryan, W.B.F., et al., *Init. Repts. DSDP*, 47 (Pt. 2): Washington (U.S. Govt. Printing Office), 553-559.
- Espitalié, J., Laporte, J.L., Leplat, P., Madec, M., Marquis, F., Paulet, J., and Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pet.*, 32:23-42.
- Farimond, P., Eglinton, G., Brassell, S.C., and Jenkyns, H.C., 1990. The Cenomanian/Turonian anoxic event in Europe: an organic geochemical study. *Mar. Pet. Geol.*, 7:75-89.
- Fontugne, M.R., and Calvert, S.E., 1992. Late Pleistocene variability of the carbon isotopic composition of organic matter in the eastern Mediterranean: monitor of changes in carbon sources and atmospheric CO<sub>2</sub> levels. *Paleoceanography*, 7:1-20.
- Hallam, A., 1984. Continental humid and arid zones during the Jurassic and Cretaceous. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, 47:195-223.
- Herbin, J.-P., Montadert, L., Muller, C., Gomez, R., Thurow, J., and Wiedmann, J., 1986. Organic-rich sedimentation at the Cenomanian-Turonian boundary in oceanic and coastal basins in the North Atlantic and Tethys. *In* Summerhayes, C.P., and Shackleton, N.J. (Eds.), *North Atlantic Palaeoceanography*. Geol. Soc. Spec. Publ. London, 21:389-422.
- Huyck, H.O., 1990. When is a metalliferous black shale not a black shale? *In* Grauch, R.I., and Huyck, H.O. (Eds.), *Metalliferous Black Shales and Related Ore Deposits*. Geol. Surv. Circ. (U.S.), 1058:42-56.
- Jasper, J.P., and Gagosian, R.B., 1990. The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta*, 54:1117-1132.
- McArthur, J.M., Tyson, R.V., Thomson, J., and Matthey, D., 1992. Early diagenesis of marine organic matter: alteration of the carbon isotopic composition. *Mar. Geol.*, 105:51-61.
- McIver, R.D., 1975. Hydrocarbon occurrences from JOIDES Deep Sea Drilling Project. *Proc. Ninth Petrol. Congr.*, 269-280.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.*, 144:289-302.
- Meyers, P.A., Dunham, K.W., and Ho, E.S., 1988. Organic geochemistry of Cretaceous black shales from the Galicia Margin, Ocean Drilling Program Leg 103. *Org. Geochem.*, 13:89-96.
- Newman, J.W., Parker, P.L., and Behrens, E.W., 1973. Organic carbon isotope ratios in Quaternary cores from the Gulf of Mexico. *Geochim. Cosmochim. Acta*, 37:225-238.
- O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. *Bioscience*, 38:328-336.
- Prahl, F.G., Ertel, J.R., Goni, M.A., Sparrow, M.A., and Eversmeyer, B., 1994. Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochim. Cosmochim. Acta*, 58:3035-3048.
- Pratt, L.M., and Threlkeld, C.N., 1984. Stratigraphic significance of <sup>13</sup>C/<sup>12</sup>C ratios in mid-Cretaceous rocks of the Western Interior, U.S.A. *In* Stott, D.F., and Glass, D.J. (Eds.), *The Mesozoic of Middle North America*. Mem.—Can. Soc. Pet. Geol., 9:305-312.
- Premuzic, E.T., Benkovitz, C.M., Gaffney, J.S., and Walsh, J.J., 1982. The nature and distribution of organic matter in the surface sediments of world oceans and seas. *Org. Geochem.*, 4:63-77.
- Shipboard Scientific Party, 1979. Site 398. *In* Sibuet, J.-C., Ryan, W.B.F., et al., *Init. Repts. DSDP*, 47 (Pt. 2): Washington (U.S. Govt. Printing Office), 25-233.
- , 1987. Introduction, objectives, and principal results: Ocean Drilling Program Leg 103, West Galicia Margin. *In* Boillot, G., Winterer, E.L., et al., *Proc. ODP, Init. Repts.*, 103: College Station, TX (Ocean Drilling Program), 3-17.
- , 1994. Site 897. *In* Sawyer, D.S., Whitmarsh, R.B., Klaus, A., et al., *Proc. ODP, Init. Repts.*, 149: College Station, TX (Ocean Drilling Program), 41-113.
- Simoneit, B.R.T., and Mazurek, M.A., 1979. Lipid geochemistry of Cretaceous sediments from Vigo Seamount, DSDP/IPOD Leg 47B. *In* Sibuet, J.-C., Ryan, W.B.F., et al., *Init. Repts. DSDP*, 47 (Pt. 2): Washington (U.S. Govt. Printing Office), 565-570.
- Stein, R., Rullkötter, J., Littke, R., Schaefer, R.G., and Welte, D.H., 1988. Organofacies reconstruction and lipid geochemistry of sediments from the Galicia Margin, Northeast Atlantic (ODP Leg 103). *In* Boillot, G., Winterer, E.L., et al., *Proc. ODP, Sci. Results*, 103: College Station, TX (Ocean Drilling Program), 567-585.
- Stein, R., Rullkötter, J., and Welte, D.H., 1986. Accumulation of organic-carbon-rich sediments in the late Jurassic and Cretaceous Atlantic Ocean—a synthesis. *Chem. Geol.*, 56:1-32.
- , 1989. Changes in palaeoenvironments in the Atlantic Ocean during Cretaceous times: results from black shales studies. *Geol. Rundsch.*, 78:883-901.
- Summerhayes, C.P., 1981. Organic facies of Mid-Cretaceous black shales in the deep north Atlantic. *AAPG Bull.*, 65:3264-2380.
- Thurow, J., Brumsack, H.-J., Rullkötter, J., Littke, R., and Meyers, P.A., 1992. The Cenomanian/Turonian boundary event in the Indian Ocean—a key to understand the global picture. *In* Duncan, R.A., Rea, D.K., Kidd, R.B., von Rad, U., and Weissel, J.K. (Eds.), *Synthesis of Results from Scientific Drilling in the Indian Ocean*. Geophys. Monogr., Am. Geophys. Union, 70:253-273.
- Thurow, J., Moullade, M., Brumsack, H.-J., Masure, E., Taugourdeau-Lantz, J., and Dunham, K., 1988. The Cenomanian/Turonian Boundary Event (CTBE) at Hole 641 A, ODP Leg 103 (compared with the CTBE interval at Site 398). *In* Boillot, G., Winterer, E.L., et al., *Proc. ODP, Sci. Results*, 103: College Station, TX (Ocean Drilling Program), 587-634.
- Vail, P.R., Mitchum, R.M., Shipley, T.H., and Buffler, R.T., 1980. Unconformities of the North Atlantic. *Philos. Trans. R. Soc. London A*, 294:137-155.
- Verardo, D.J., Froelich, P.N., and McIntyre, A., 1990. Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Analyzer. *Deep-Sea Res. Part A*, 37:157-165.
- Waples, D.W., 1983. Reappraisal of anoxia and organic richness, with emphasis on Cretaceous of North Atlantic. *AAPG Bull.*, 67:963-978.

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