1996

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Publication Info

Published in *Proceedings of the Ocean Drilling Program, Scientific Results*, Volume 149, 1996, pages 705-712.

Whitmarsh, R.B., Sawyer, D.S., Klaus, A., and Masson, D.G. (Eds.), 1996
Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 149

46. ORGANIC MATTER ACCUMULATION, SULFATE REDUCTION, AND METHANOGENESIS IN PLIOCENE-PLEISTOCENE TURBIDITES ON THE IBERIA ABYSSAL PLAIN[1]

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ABSTRACT

A Pliocene-Pleistocene turbidite sequence sampled at four drill sites in a 75-km-long transect on the landward edge of the Iberia Abyssal Plain illustrates the effects of non-steady-state sedimentation on postdepositional geochemical processes. Organic carbon concentrations average 0.7% in sediments of this sequence at Sites 897 and 898 and 0.4% at Sites 899 and 900. Headspace concentrations of interstitial methane exceed 100,000 ppm in sediments from Sites 897 and 898 but are essentially zero in those from Sites 899 and 900. Methane concentrations do not rise until interstitial sulfate concentrations are virtually depleted, suggesting the presence of in situ methanogenic bacterial activity to sub-bottom depths of 300 m at Site 897 and 170 m at Site 898 and its absence at Sites 899 and 900. The turbidity flows that created the turbidite sequence on the Iberia Abyssal Plain evidently influenced postdepositional diagenesis at these sites. The principal factor is that the thicker turbidite sequences at Sites 897 and 898 protected organic matter from oxic, early degradation and thereby permitted anoxic, later degradation to proceed. In contrast, organic matter in the thinner turbidite sequences at Sites 899 and 900 was oxidized soon after deposition and was therefore not suitable for later microbial utilization. The difference in organic matter preservation between the sites has impacted microbial sulfate reduction and methane production in the turbidite sequences.

INTRODUCTION

Geochemical processes that occur in marine sediments have significant impacts on the seafloor-seawater exchange of soluble elements and the subsequent composition of sediments. Postdepositional oxidative degradation of sedimentary organic matter is a central element of many of these processes. The oxidation of organic matter follows a general sequence of terminal electron acceptors of, from first to last, interstitial oxygen, nitrate, Mn(IV) oxides, Fe(III) oxides, and sulfate (Froelich et al., 1979; Schulz et al., 1994) in the transition from oxic to suboxic to anoxic sediment conditions. Various mineral dissolution and precipitation processes occur during this sequence (Berner, 1980; von Breymann et al, 1991; Canfield, 1993), and the interplay of oxidizing and reducing conditions influences the mobilities of many metals (Wilson et al., 1986; Pruysers et al., 1993; Thomson et al., 1993). Moreover, evolution of interstitial dissolved CO_2 from oxidation of organic matter increases in situ dissolution of $CaCO_3$ (Emerson and Bender, 1981; Berelson et al., 1990).

Most models of organic matter degradation and related geochemical processes assume that steady-state reaction and diffusion are dominant, yet non-steady-state conditions prevail in many areas of the floor of the deep-sea, particularly in those regions where turbidites accumulate (Buckley and Cranston, 1988). An opportunity to evaluate the consequences of turbiditic sediment accumulation on sedimentary geochemical processes that subsequently occurred over a time span of several million years is provided by the transect of sites drilled by Ocean Drilling Program (ODP) Leg 149 across the landward edge of the Iberia Abyssal Plain. In this synthesis, we use interstitial sulfate and methane concentrations as indicators of oxidation-reduction processes that have happened within and are influenced by a turbidite unit emplaced during Pliocene-Pleistocene times.

SEDIMENTARY SETTING

A transect of four closely spaced sites was drilled on the landward edge of the Iberia Abyssal Plain during Leg 149 (Fig. 1). Seismic surveys performed in preparation for Leg 149 identified a series of seaward-dipping reflectors on the landward edge of the Iberia Abyssal Plain that are overlain by a horizontal succession of sediment layers. The seismic profile spliced together from three east-west surveys suggests that the sediment layers are continuous across most of the drill sites (Fig. 2). Sediments obtained from the drilling transect revealed that the seismic reflectors represent a succession of Miocene-to-Pleistocene turbidite layers that vary somewhat in composition and thickness among the four sites (Table 1). Concentrations of $CaCO_3$ are quite variable in the sediments (Figs. 3-6). This variability reflects the intermix of pelagic and hemipelagic sediment types in these turbidites, which have contents ranging from nannofossil ooze to fine sand (Shipboard Scientific Party, 1994a-d).

Sediments of Pliocene-Pleistocene Unit I at Site 897 and 898 are composed of interbedded distal turbidites that accumulated rapidly. Individual turbidite sequences range in thickness from 5 cm to over 1 m (Shipboard Scientific Party, 1994a, b). The typical sequence consists of a layer of dark sand overlain by silty clays and capped by a thin layer of lightly colored nannofossil ooze. The dark color of the sands is attributed to higher organic carbon contents in these layers. The small contribution of biogenic ooze indicates that pelagic sediments constitute a minor amount of the unit. Averaged sedimentation rates for Unit I range from 90 m/m.y. at Site 898 to 532 m/m.y. at Site 897 (Shipboard Scientific Party, 1994a, b).

Drilling at Site 899 recovered sediments from the basal 50 m of a 132-m-thick Pliocene-Pleistocene layer of terrigenous distal turbidites. These turbidites are comparable in composition and texture to those at Sites 897 and 898, but they accumulated less rapidly. Sedimentation rates are estimated to have averaged 35 m/m.y. (Shipboard Scientific Party, 1994c). The Pliocene-Pleistocene sediments at Site 900 consist of siliciclastic muddy turbidites that accumulated much less rapidly than they did at Sites 897 and 898. Individual sequences range in thickness from 10 cm to more than 1 m and are separated by layers of nannofossil ooze up to 60 cm thick (Shipboard Scientific Party, 1994d). Averaged sedimentation rates range from 22 to 24 m/m.y.

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[1] 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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Underlying Miocene sediments at all four sites were more pelagic, accumulated more slowly, and contained fewer turbidite sequences than the Pliocene-Pleistocene sequences. The averaged sedimentation rates for these sediments ranged from 2 to 13 m/m.y. (Shipboard Scientific Party, 1994a-d).

The differences in the accumulation rates of the four sites may result from differences in sediment transport routes, and bottom topography is a part of this explanation. The sites were positioned above basement highs to more easily recover basement rock. The sedimentary units above the basement highs are typically thinner than in the surrounding basins (Fig. 2) because of sediment focusing into the topographic lows. Sites 897 and 898 were drilled prior to loss of drill string, which subsequently limited drilling to the thinner sedimentary sequences present at Sites 899 and 900. The four Leg 149 sites consequently provide a unique comparison of diagenesis of sedimentary organic matter at closely spaced locations having different accumulation rates.

GEOCHEMICAL PROPERTIES OF SEDIMENTS

Organic Carbon Concentrations

Meyers and Silliman (this volume) compare organic carbon concentrations measured by different shipboard and shorebased procedures. The shipboard procedure, which uses the difference between whole sediment total carbon measurements and carbonate carbon measurements to arrive at total organic carbon (TOC) concentrations, is slightly less reliable in sediments containing little organic carbon than is the shorebased procedure, which directly measures organic carbon concentrations of Carbonate-free samples. Our discussions of TOC concentrations and organic matter C/N ratios will consequently use the shorebased data only.

Averaged TOC concentrations of the shorebased Unit I samples are: Site 897, 0.78%; Site 898, 0.68%; Site 899, 0.44%; Site 900, 0.36%. These values are slightly higher to more than twice the average organic carbon content of 0.3% of deep-sea sediments and rocks from DSDP Legs 1 through 33 compiled by McIver (1975). Many of the samples, however, are poor in organic carbon, and their low concentrations are not related to their lithology as represented by $CaCO_3$ concentrations (Fig. 3-6). Of particular note, the uppermost lithologic units drilled at Sites 897, 898, and 899 seem to be parts of a single, continuous turbidite layer (Fig. 2; Table 1), yet the TOC concentrations at Sites 897 and 898 are significantly higher than those at Site 899, which is located between the other two. In addition, TOC concentrations vary with depth in Unit I as it is expressed at each of the four drill sites. The delivery of organic matter to the landward edge of the Iberia Abyssal Plain evidently has varied both spatially and temporally during the Pliocene and Pleistocene. Part of this variability may result from the turbidites originating from different locations on the Iberia Margin, but the primary cause is probably the greater thicknesses of the turbidites at Sites 897 and 898 relative to Sites 899 and 900, which affects the degree of postdepositional preservation of organic matter (Shaw and Meyers, this volume).

The TOC concentration differences suggest that a greater fraction of the available carbon is consumed at Sites 899 and 900, which have slow accumulation rates, than at Sites 897 and 898. Although concentrations are variable at each site, averaged concentrations are lower at Sites 899 and 900 than they are at Sites 897 and 898. This difference is consistent with more efficient and therefore more complete consumption of organic matter under oxic conditions as opposed to anoxic conditions. Preservation of organic carbon is consequently poorer in the more slowly accumulated sediments at Sites 899 and 900.

Organic Matter C/N Ratios

Atomic 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 the consequent relative richness of proteinaceous material in algae, and it is largely preserved in sedimentary organic matter.

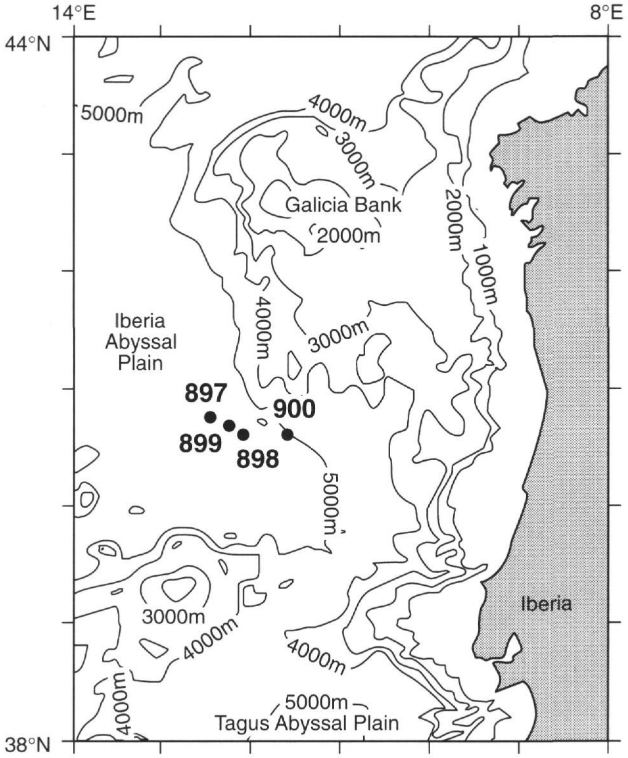

Figure 1. Locations of Leg 149 Sites 897-900 on the Iberia Abyssal Plain and their relationships to topographically elevated parts of the eastern North Atlantic Ocean seafloor and the Iberia Margin.

The averaged shorebased atomic C/N ratios of the Unit I samples are as follows: Site 897, 4.6 ± 1.6; Site 898, 3.8 ± 3.9; Site 899, 3.7 ± 1.8; Site 900, 2.9 ± 2.1 (Meyers and Silliman, this volume). These ratios indicate that marine contributions dominate the organic matter in these turbidite layers and that the organic matter has been at least partially degraded within its host sediment. Fresh algal organic matter typically has C/N ratios between 4 and 10 (Meyers, 1994). Degradation of organic matter in organic-carbon-poor marine sediments tends to lower C/N ratios as nitrogenous compounds break down to produce ammonia, which is retained by clay minerals, and the CO_2 released by oxidation of organic carbon escapes (Müller, 1977). Some of the samples have C/N ratios of 1 or 2, too low to represent undegraded organic matter. A few samples have C/N ratios between 10 and 20; these samples probably contain elevated proportions of land-derived organic matter. Furthermore, the higher average C/N ratio of 4.6 in the Site 897 Unit I samples suggests that the marine organic matter at this location has experienced less degradation than has occurred at the other sites. Variation in the degree of preservation of marine-derived organic matter is suggested by the differences in C/N ratios from site to site and with depth at each site.

Organic 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

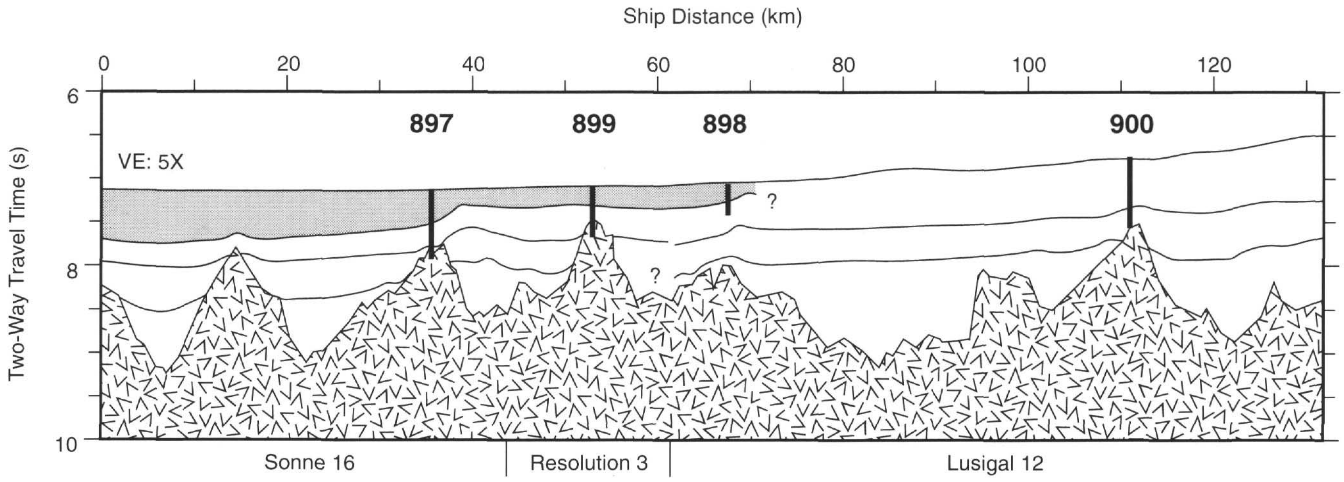

Figure 2. A composite seismic profile of the turbidite and other layers encountered by drilling during Leg 149. The layer of Pliocene-Pleistocene terrigenous sediments that are the focus of this study is shown as shading. The composite profile is spliced from seismic data generated by cruises of the *Sonne, JOIDES Resolution,* and *Lusigal.* Vertical exaggeration (VE) is fivefold.

Table 1. A summary of the turbidite units encountered by drilling at Sites 897, 898, 899, and 900 on the Iberia Abyssal Plain.

	Site 897	Site 899	Site 898	Site 900
Water depth (m):	5320	5291	5279	5037
Lithologic unit (mbsf):				
Pleistocene to Pliocene terrigenous turbidites (silty clay, silt, fine sand)	0–292	81–132	0–162	—
Pleistocene to Pliocene hemipelagic turbidites (nannofossil clays and oozes)	—	—	—	0–67
Pliocene to Miocene hemipelagic sediments (silty clay with nannofossil clay and chalk)	—	132–207	162–172	—
Late Pliocene to late Miocene hemipelagic turbidites (nannofossil claystone and chalk)	292–301	—	—	67–96
Late Miocene to early Miocene hemipelagic turbidites (nannofossil claystone and chalk with fine sandstone)	301–360	—	—	96–181

Note: The variations in the thicknesses and compositions between the units at the four sites, which represent a transect of only 75 km, have influenced postdepositional diagenesis in the sediments at these sites.

using the C_3 Calvin pathway, which biochemically discriminates against ^{13}C to produce a $\delta^{13}C$ shift of about -20‰ from the isotope ratio of the inorganic carbon source. Organic matter produced from atmospheric CO_2 ($\delta^{13}C \approx -7‰$) by land plants using the C_3 pathway consequently has an average $\delta^{13}C$ (PDB) value of about -27‰ (cf. O'Leary, 1988). The source of inorganic carbon for marine algae is dissolved bicarbonate, which has a $\delta^{13}C$ value of about 0‰. Marine organic matter consequently typically has $\delta^{13}C$ values between -20‰ and -22‰. The isotopic difference between organic carbon produced by C_3 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; Prahl 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. Prominent among the factors that can impact $\delta^{13}C$ values are the availability of CO_2 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‰ (Hayes et al., 1989; Fontugne and Calvert, 1992; McArthur et al., 1992; Meyers, 1994). Increased availability of dissolved CO_2 to algae, however, would enhance their isotopic discrimination and produce marine organic matter that is isotopically light (Hayes et al., 1989), as would increased delivery of isotopically light fluvial dissolved inorganic carbon (Fontugne and Calvert, 1992) from areas on the continental shelf where some of the turbidite-carried organic matter may have originated.

Organic $\delta^{13}C$ values of Unit I sediment samples from the four sites average about -23‰, a value that indicates that most of the organic matter originated from marine production (Meyers, 1994). The range of these values, from -19.0‰ to -26.8‰ (Meyers and Silliman, this volume), also suggests that the origins have not been identical and that the proportion of land-derived material may be important in some turbidite layers. The isotopically heavy organic matter may have been produced by marine algae during times of diminished availability of dissolved CO_2, such as those that accompany spring blooms or upwelling. This organic matter may have originated from coastal areas of high productivity 200 km to the east of the abyssal plain and experienced transport to the deep-sea by turbidity flows of continental shelf sediment.

Rock-Eval Analyses

Rock-Eval pyrolysis was originally developed to characterize the organic matter that is present in oil source rocks (Espitalié et al., 1977) and that is typically is more thermally mature and at higher concentrations than is the organic matter commonly found in sediments obtained by 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 (HI, defined as mg hydrocarbons per gram TOC) and higher oxygen indices (OI, defined as mg CO_2 per gram TOC) than found in lipid-rich and cellulose-poor algal organic matter. This dis-

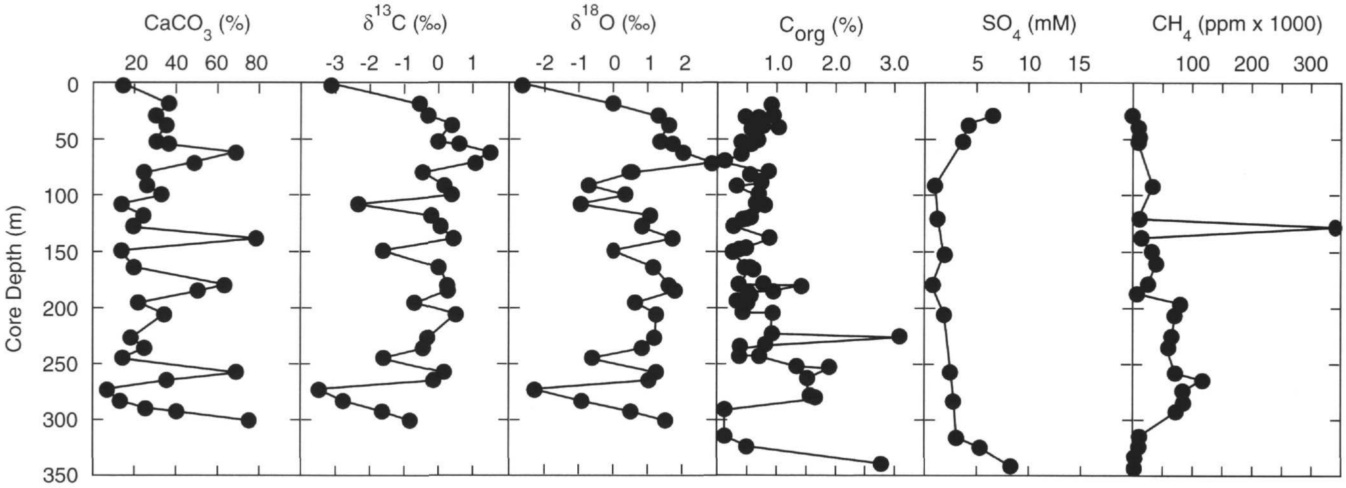

Figure 3. $CaCO_3$, $\delta^{13}C$, and $\delta^{18}0$ values and concentrations of $CaCO_3$, organic carbon, dissolved interstitial sulfate, and headspace-analyzed interstitial methane in Pliocene-Pleistocene sediments from Site 897 on the Iberia Abyssal Plain. The base of turbiditic Unit I is 292 mbsf at this site.

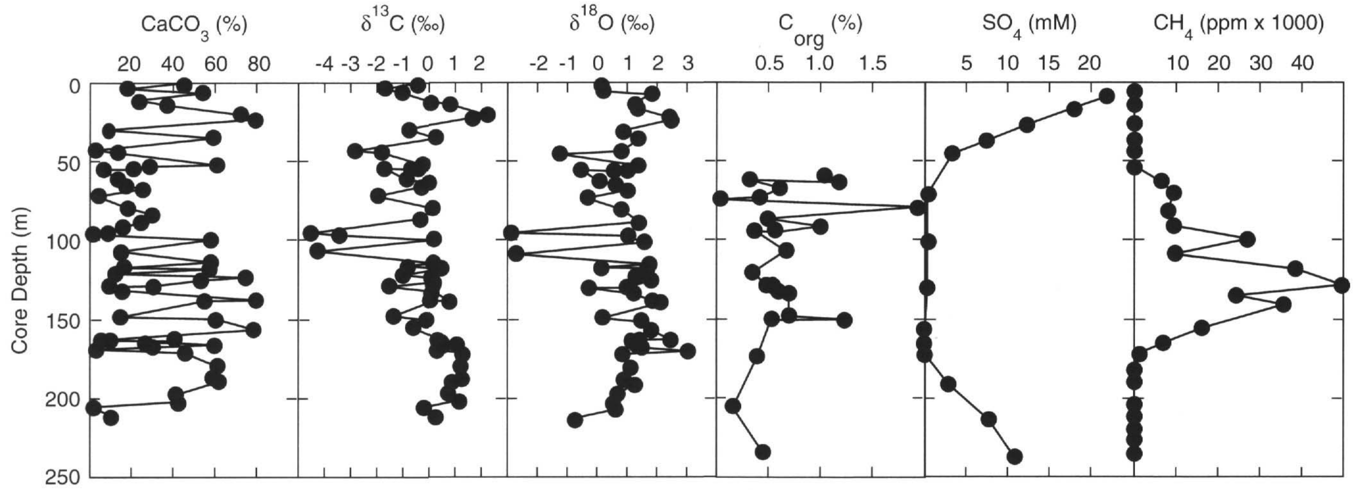

Figure 4. $CaCO_3$, $\delta^{13}C$, and $\delta^{18}O$ values and concentrations of $CaCO_3$, organic carbon, dissolved interstitial sulfate, and headspace-analyzed interstitial methane in Pliocene-Pleistocene sediments from Site 898 on the Iberia Abyssal Plain. The base of turbiditic Unit I is 162 mbsf at this site.

tinction between organic matter from continental and marine sources becomes blurred by diagenesis as marine matter oxidizes and gradually takes on HI and OI values similar to those of land-plant material.

A Van Krevelen-type plot of the HI and OI values suggests that the Leg 149 turbiditic sediments contain Type III (land-derived) organic matter (Fig. 7). This source assignment for the organic matter conflicts, however, with the low C/N ratios and the $\delta^{13}C$ values for these samples, both of which suggest that the organic matter is predominantly marine. The contradiction between the Rock-Eval source characterization and the elemental and isotopic source characterizations indicates that the original Type II (marine) organic matter has been heavily oxidized, probably by microbial reworking. The microbial reworking of the organic matter in the turbiditic units at Sites 899 and 900 evidently happened prior to, or shortly after, redeposition of these sediments on the Iberia Abyssal Plain, inasmuch as little sulfate reduction has occurred at these locations (Figs. 5, 6). In contrast, in situ microbial reprocessing of organic matter deeper below the sediment/water interface is indicated at Sites 897 and 898 by the disappearance of interstitial sulfate and accompanying appearance of pore-water methane with increasing sediment depth at these locations (Figs. 3, 4). The HI values of samples from Sites 897 and 898 are in general higher than those of samples from Sites 899 and 900 (Fig. 7), indicating that the marine organic matter at Sites 897 and 898 remains not as severely microbially reworked as at Sites 899 and 900.

Calcium Carbonate Carbon and Oxygen Stable Isotopic Compositions

Microbial oxidation of marine organic matter ($\delta^{13}C$ values between -20‰ and -22‰) can produce isotopically light dissolved inorganic carbon in the pore waters of deep-sea sediments (von Breymann et al., 1991). The remineralized CO_2 can reprecipitate as carbonate and produce calcium carbonate with $\delta^{13}C$ values as light as -19‰ (Meyers and Snowdon, 1993). Because of the evidence for significant amounts of in situ organic matter degradation in the sediments of Sites 897 and 898, the $CaCO_3$ carbon and oxygen stable isotopic contents were determined by the Stable Isotope Laboratory at The University of Michigan to investigate whether CO_2 derived from organic matter was contributing to $CaCO_3$ precipitation.

Nearly all of the carbonate $\delta^{13}C$ values are within the normal marine values from -1‰ to +1‰ (Figs. 3 and 4). Several excursions to $\delta^{13}C$ values as light as -4.5‰ occur. Although these values might reflect a diagenetic contribution of CO_2 derived from organic matter into $CaCO_3$, two lines of evidence suggest that the isotopic values

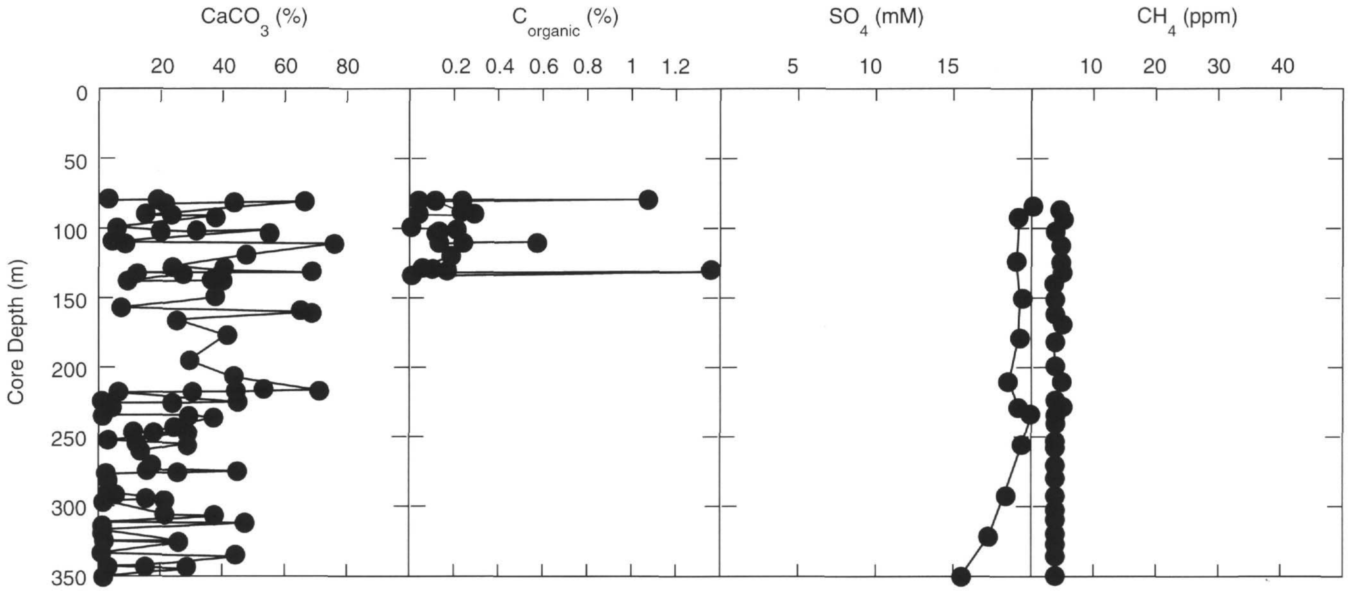

Figure 5. Concentrations of $CaCO_3$, organic carbon, dissolved interstitial sulfate, and headspace-analyzed interstitial methane in Pliocene-Pleistocene sediments from Site 899 on the Iberia Abyssal Plain. The base of turbiditic Unit I is 132 mbsf at this site.

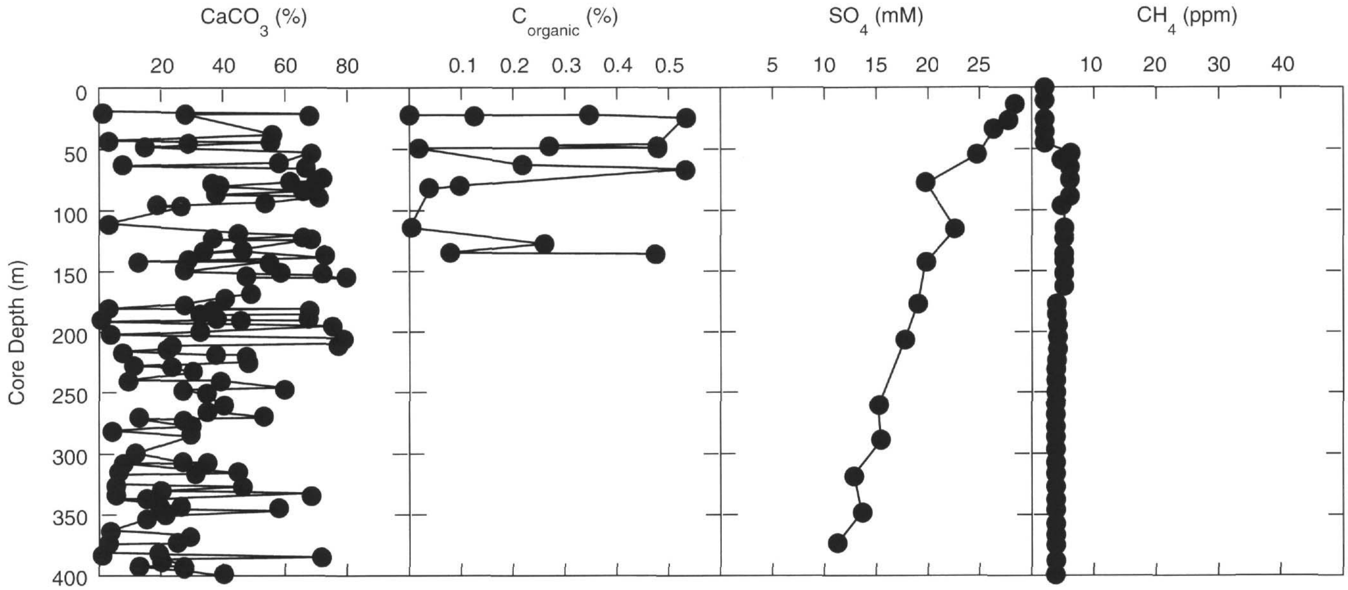

Figure 6. Concentrations of $CaCO_3$, organic carbon, dissolved interstitial sulfate, and headspace-analyzed interstitial methane in Pliocene-Pleistocene sediments from Site 900 on the Iberia Abyssal Plain. The base of turbiditic Unit I is 67 mbsf at this site.

record initial conditions of carbonate formation at the sources of these turbidite components. First, the light $\delta^{13}C$ values consistently occur in sediment samples that contain less than 20% $CaCO_3$ (Figs. 3 and 4), which typically are elastics-dominated turbidite layers (Shipboard Scientific Party, 1994a, b). Diagenetic enrichment of the carbonate contents of these samples is not evident. Second, $\delta^{18}O$ excursions to lighter values coincide with the $\delta^{13}C$ excursions. The general correspondence between $\delta^{18}O$ and $\delta^{13}C$ patterns in the sediments of both Site 897 and Site 898 (Figs. 3, 4) suggests that the isotopic content of seawater at the place of initial $CaCO_3$ formation has controlled the sedimentary isotopic compositions. Moreover, the agreements in excursions to lighter values may record episodes of greater delivery of continental runoff, which is typically isotopically light in both carbon and oxygen, to areas on the continental margin of Iberia where the turbidites originated. Similar excursions to lighter isotopic values have been documented in Mediterranean sapropels by Fontugne and Calvert (1992), who postulated that the excursions record periods of enhanced freshwater delivery to this sea during the Pleistocene.

Interstitial Sulfate Concentrations

Concentrations of pore-water sulfate decrease nearly to zero in the upper 50 m of sediment at Sites 897 and 898 and remain near zero throughout the rest of Unit I at both sites (Figs. 3, 4). The decrease indicates an active zone of sulfate reduction at both sites. Below Unit I (292 mbsf at Site 897; 162 mbsf at Site 898), sulfate concentrations recover to 15 to 18 mM. Sulfate reduction appears not to occur in these deeper sediments. In terms of redox conditions, most of Unit I at Sites 897 and 898 is an anoxic section bounded by an upper and a lower sulfate reservoir.

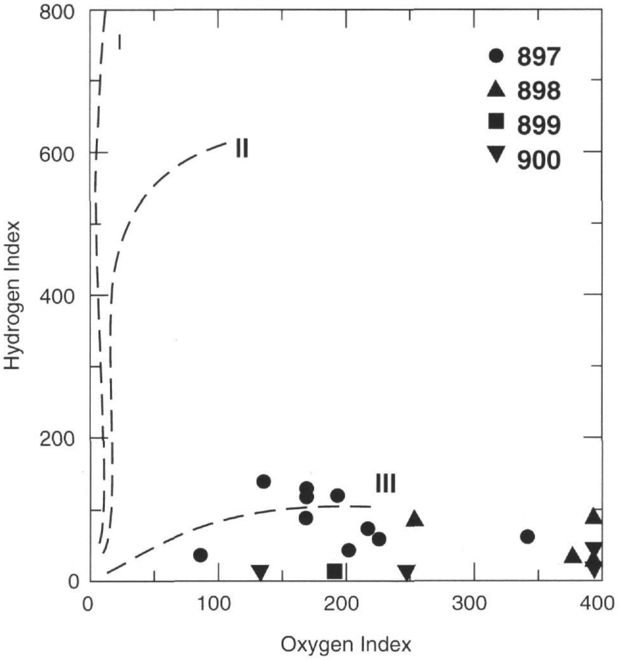

Figure 7. Rock-Eval hydrogen index (mg hydrocarbons/g organic carbon) and oxygen index (mg CO_2/g organic carbon) values for sediments from Sites 897, 898, 899, and 900 on the Iberia Abyssal Plain. Organic matter at all sites has been oxidized from its initial marine (Type II) character.

Concentrations of pore-water sulfate in sediments of Sites 899 and 900 contrast to the pattern present in Sites 897 and 898 by progressively decreasing from near-seawater values (≈29 mM) as sediment depth increases (Figs. 5, 6). At least 15 mM interstitial sulfate is present in all parts of Unit I at these two sites.

The activity of sulfate-reducing bacteria is generally limited by the availability of short-chain organic compounds. As a result, organic matter degradation via sulfate reduction must be preceded by an intermediate fermentation that can break down organic compounds into smaller molecules. Organic matter at Sites 897 and 898 has slightly higher C/N ratios than does the organic matter at Sites 899 and 900 (Meyers and Silliman, this volume), which could be an indicator of better preservation of organic matter in these sediments. The high accumulation rates at Sites 897 and 898 evidently impacted subsequent microbial activity.

Headspace Methane Concentrations

Concentrations of headspace methane are high in Unit I sediments from Sites 897 and 898 and drop to near-background levels in deeper sediments (Figs. 3 and 4). Two sources of the gas are possible. First, gas from some deeper origin may have migrated into the unit, which consists of turbiditic sand, silt, and clay layers. The location of Sites 897 and 898 on basement highs makes this an especially reasonable possibility (Fig. 2). Evidence for migration of methane into porous sediments from deeper sources has been found at Sites 762 and 763 on the Exmouth Plateau where a known thermogenic source exists in underlying Jurassic rocks (Snowdon and Meyers, 1992). A similar deeper source for the methane on the Iberia Abyssal Plain is presently unknown. A second possibility is in situ formation by methanogenic bacteria. High methane/ethane ratios and the absence of higher-molecular-weight hydrocarbon gases indicate that the gas is biogenic, as opposed to thermogenic, in origin (Shipboard Scientific Party, 1994a, b). The source of the methane may be from in situ microbial fermentation of the marine organic matter present in this turbiditic unit. Similar microbial production of methane from marine organic matter has been inferred from high biogenic gas concentrations in Pliocene-Pleistocene sediments from Site 532 on the Walvis Ridge (Meyers and Brassell, 1985) and in middle Miocene sediments from Site 767 in the Celebes Sea (Shipboard Scientific Party, 1990).

Headspace methane concentrations are low in sediments below Unit I at Sites 897 and 898 (Figs. 3, 4). Sub-bottom depths of 200 to 300 m are not likely to be important in limiting microbial methane production inasmuch as viable heterotrophic bacteria have been isolated from upper Miocene sediments more than 500 meters below the seafloor at Site 798 on the Oki Ridge (Cragg et al., 1992). The lower amounts of metabolizable organic matter in deeper sediments is probably the major factor in precluding methanogenesis. The presence of significant concentrations of pore-water sulfate (Figs. 3, 4) indicates that methanogenesis is not energetically favored in sediments deeper than Unit I (Claypool and Kvenvolden, 1983).

In contrast to Sites 897 and 898, the sediments of Sites 899 and 900 contain essentially no methane (Figs. 5, 6). Because methane is present at sub-bottom depths at Sites 897 and 898 that are similar to those at Sites 899 and 900, migration out of the sediments is unlikely. Instead, it is probable that methane was never generated in the sediments at Sites 899 and 900. Organic carbon concentrations are, on average, lower at these two sites than they are at Sites 897 and 898, and the organic matter present in the sediments appears to be detrital and of low metabolizable value (Meyers and Silliman, this volume). The consequent absence of suitable substrate for microbial activity may have prevented methanogenesis. In addition, interstitial sulfate is present at near-seawater concentrations in the sediments of Sites 899 and 900 (Figs. 5, 6), and this may have imposed a further constraint on methanogenic bacterial activity (Claypool and Kvenvolden, 1983). Alternatively, the presence of significant amounts of dissolved sulfate may reflect the absence of much microbial activity at Sites 899 and 900.

SIGNIFICANCE TO DIAGENESIS IN DEEP-SEA SEDIMENTS

Sediments in the Pliocene-Pleistocene turbidite sequence sampled at Sites 897, 898, 899, and 900 illustrate the interplay of sea-bottom morphology, sedimentation rate, and preservation of organic matter in influencing non-steady-state diagenesis in deep-sea sediments. Partially preserved algal organic matter is generally more reactive and therefore more suitable for microbial utilization than is detrital or continental organic matter (Lallier-Verges et al., 1993), and the availability of metabolizable organic matter has evidently impacted microbial processes in these sediments. Sulfate reduction proceeds with depth at Sites 897 and 898 where adequate amounts of reactive organic matter are available to support bacterial activity. In contrast, little sulfate reduction occurs at Sites 899 and 900. Headspace concentrations of interstitial methane are high in sediments from Sites 897 and 898 but are essentially zero in those from Sites 899 and 900. Because methane concentrations do not rise until interstitial sulfate concentrations are virtually depleted, the existence of in situ methanogenic bacterial activity is indicated at sub-bottom depths of several hundred meters at Sites 897 and 898 (Claypool and Kvenvolden, 1983). Similar methanogenic activity is evidently absent at Sites 899 and 900. Heterogeneity in delivery and preservation of organic matter has controlled sulfate reduction and methanogenesis in these deep-sea sediments.

The ratio of carbon degraded under oxic versus anoxic conditions will impact the character of the buried carbon. In the more rapidly accumulated turbidites of Sites 897 and 898, much of the carbon degradation occurred under anoxic conditions (Shaw and Meyers, this volume). At depths greater than 10 cm into any one turbidite sequence, the maximum oxygen flux into the remaining interval can be calculated to be on the order of 0.02 moles/m^2/yr, assuming a bottom water oxygen concentration of 200 µM. For thick turbidite sequences such as those in Sites 897 and 898, sulfate reduction was consequently the predominant mode of carbon degradation. The character of the surviving carbon in deep-sea turbidite sequences in general may therefore be a function of the rate of burial, resulting in diagenetic differences from location to location and from depth to depth.

The turbidite layers in the sequences at Sites 899 and 900 are thinner and were deposited less frequently than at Sites 897 and 898. The generally thicker intervals of interlayered nannofossil ooze suggest longer periods of slow sedimentation. In thin turbidite sequences, oxic degradation of the carbon probably occurred via the "burn down" mechanism described by Wilson et al. (1986), Thomson et al. (1984; 1993), and Pruysers et al. (1993). Oxygen would slowly diffuse into the carbon-enriched turbidite layer during the slow deposition of the pelagic oozes that separate turbidite layers at these two sites. The slow sedimentation and thin turbidite emplacement would result in early diagenetic oxic degradation being the predominant mode of organic carbon degradation, and little oxidizable, or microbially metabolizable, organic matter would survive in deeper sediments. Sulfate reduction and subsequent methane production deeper in the sediments would therefore not be significant.

If the origins of the turbidite layers on the Iberia Abyssal Plain are assumed to be similar settings on the Iberia Margin, then the turbidite sequences encountered at the four drill sites can be considered compositionally uniform deposits that originally differed only in their thickness. In other words, the presence or absence of basement highs controlled the emplacement of thinner or thicker turbidite deposits, respectively. Subsequent oxidation of organic matter, however, would proceed by different geochemical processes depending on the thickness of each layer. The thinner deposits would have a greater proportion of organic carbon oxidized under oxic conditions, whereas anoxic conditions would dominate in the thicker deposits. Interstitial sulfate concentrations support this concept (Shaw and Meyers, this volume). The presence of relatively high sulfate concentrations in sediments from Sites 899 and 900 indicates that little organic carbon survived oxic degradation in these slowly accumulated turbidites to be available to consume sulfate. In contrast, sulfate consumption during organic matter oxidation has removed essentially all of the dissolved sulfate from the sediments of Sites 897 and 898.

SUMMARY

The amounts and types of organic matter and concentrations of dissolved sulfate and headspace methane have been determined in sediments of a Pliocene-Pleistocene distal turbidite sequence that was recovered during Leg 149 in four closely spaced drill sites on the landward edge of the Iberia Abyssal Plain (Sawyer, Whitmarsh, Klaus, et al., 1994). Organic carbon concentrations average 0.7% in this sequence at Sites 897 and 898 and 0.4% at Sites 899 and 900. Atomic C/N ratios are generally between 3 and 10 and indicate an algal origin (Meyers, 1994). Organic $\delta^{13}C$ values vary little from -23‰, which is typical of marine algae (Meyers, 1994). Rock-Eval results reveal that the marine organic matter in the sediments is heavily oxidized. Headspace concentrations of interstitial methane exceed 100,000 ppm in sediments from Sites 897 and 898 but are essentially zero in those from Sites 899 and 900. Partially preserved marine organic matter is present in the sediments of Sites 897 and 898, whereas poorly preserved, detrital marine material is found at the other two sites. Moreover, the degree of preservation of organic matter in Site 897 and 898 sediments fluctuates with depth. A correlation between low organic matter C/N ratios and low concentrations of organic carbon indicates that postdepositional diagenesis of organic matter controls TOC concentrations. The amount of in situ oxidation of organic matter has been controlled by rates of turbidite sedimentation, which are high at Sites 897 and 898 and low at Sites 899 and 900. An additional factor is that the turbidity flows may have obtained their entrained organic matter from different environments and consequently delivered organic matter with different characteristics. Both factors contribute to heterogeneity of the types and amounts of organic matter in these deep-sea sediments, and this variability has influenced subsequent sulfate reduction and methanogenesis. Methane concentrations do not rise until interstitial sulfate concentrations are virtually depleted, suggesting the presence of deep in situ methanogenic bacterial activity at Sites 897 and 898 and its absence at Sites 899 and 900.

ACKNOWLEDGMENTS

Comments from Richard Tyson and Ronald Oremland helped improve this contribution. We thank the Ocean Drilling Program for providing us with the special opportunity to spend two oddly enjoyable months at sea. Post-cruise studies were supported by grants from JOI-USSSP.

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Date of initial receipt: 1 May 1995
Date of acceptance: 13 November 1995
Ms 149SR-258