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14. THE IMPLICATIONS OF TURBIDITE-DRIVEN REDOX CHANGES IN SEDIMENTS OF THE IBERIA ABYSSAL PLAIN[1]

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ABSTRACT

Three Ocean Drilling Program sites in the Iberia Abyssal Plain were compared to study the impact of turbidite emplacement on redox conditions in abyssal sediments. Pore-water sulfate and methane concentrations were used as indicators of redox conditions. Two sites showed massive turbidite emplacements in the Pliocene-Pleistocene sequence, coincident with the onset of climate-driven sea-level change. These sites showed sediment redox conditions more characteristic of shallow margin sediments than abyssal sediments. Calculations suggest that oxygen diffusion into thick turbidite sequences is limited, thus most of the degradation of emplaced organic carbon occurs under anoxic conditions. Sulfate reduction is the primary mode of carbon degradation in recent turbidites. However, profiles indicate that a significant fraction of the older buried carbon is refractory with respect to sulfate reduction, but not to methanogenesis. Thus, in the deeper sections of the cores, methane is the primary carbon source for sulfate reduction.

INTRODUCTION

Recent studies indicate that continental margins (which comprise <10% of the seafloor) are the locus of as much as 50% of carbon cycling in deep oceans. Yet little is known of the fate and impact of this carbon reservoir during low sea-level stands when margins are scoured by intensified erosion. The probable sites of deposition for shelf and slope carbon are distal turbidites which make up ocean abyssal fans. These deposits make up from 5% to 20% of the deep ocean area. Assuming that a significant fraction of the margin carbon reservoir is lost to the deep ocean during low sea-level stands, then deep abyssal plains should contain the record of this process. This deep carbon burial should have produced a major redox shift in abyssal sediments coincident with the onset of turbidite emplacement. Assuming that sea-level change triggers turbidite emplacement, then the onset of the major Northern Hemisphere ice formation of the mid Pliocene mark a major shift in abyssal carbon burial.

Recent turbidites are characterized by high organic carbon and anoxic conditions within the turbidite sequence (Thomson et al., 1984; de Lange, 1986; Wilson et al,1986; Thomson et al., 1993). The implication of these data is that carbon-rich sediments are transported and deposited without significant dilution by low-carbon sediments, or that the initial material has very high carbon levels. Recent turbidites interbedded between oxic sediments result in distinct redox boundaries at the top and bottom of the sequence. Similar conditions should exist at the boundaries marking the onset of climate-related turbidite emplacement.

Dating of turbidite sequences with oxygen isotopes has shown a strong correlation between turbidite emplacement and climate-driven eustatic sea-level change (Weaver and Kuijpers, 1983; Johnson and Rasmussen, 1984). Turbidites originate as debris flows down a depth gradient and can deliver from centimeters to meters of accumulated material in a single event. Turbidites can be triggered by earthquakes, rapid accumulation of sediments, and, most predictably, by intensified erosion of shelf sediments during sea-level regression and transgression. Elevated levels of organic carbon in deep abyssal turbidite sequences are common and used as evidence for their shallow-water origin. The importance of intensified carbon transport caused by shelf erosion has been postulated as a mechanism of climate-related carbon burial (Broecker, 1982). However, there have been few opportunities to quantify this potential sink for carbon in the deep ocean.

In this paper we present data from three proximally similar sites in the Iberian Abyssal Plain that have very different sediment accumulation histories. Two sites show a major shift in organic carbon deposition and burial coincident with the major climate shift in the mid-Pliocene. The third shows a much lower carbon input during this period. The major difference in these sites is the magnitude of turbidite emplacement. We use these sites to examine the relative impact of climate-driven turbidite emplacement on abyssal carbon budget and redox conditions.

METHODS

Core Handling

Cores at Sites 897 and 900 were obtained with a rotary corer, resulting in significant core disturbance in the upper 100-150 m of core. Cores at Site 898 were obtained with the hydraulic piston corer (HPC) down to 130 mbsf, resulting in much better samples in that zone of the core.

Sample Handling and Analysis

A detailed explanation of sampling and analytical methods used in this study is contained in the Initial Reports for Leg 149 (Sawyer, Whitmarsh, Klaus et al., 1994; see "Inorganic Geochemistry" and "Organic Geochemistry" sections in the "Explanatory Notes" chapter). A brief synopsis of those methods is presented here. Interstitial water samples for shipboard analysis and archive samples were collected either with the Brumsack squeezer or a titanium Manheim squeezer. Whole-round core sections were handled under nitrogen to prevent oxidation of analytes. The effluent from squeezers was filtered through in-line pre-cleaned 0.22-µm acrodisc filters prior to

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collection in pre-cleaned syringes. Headspace gas samples were collected immediately after core recovery and sealed in headspace vials. The sulfate concentration was determined in duplicate using a Dionex-DX100 ion chromatograph. All samples were run at 1:200 dilution. Standards were run at the start and end of each run, to test for drift in the response of the conductivity detector. Precision on separate dilutions was better than 2%. Ammonium concentrations were determined by the spectrophotometric techniques described in Gieskes and Peretsman (1986). Headspace methane concentration was determined by gas chromatography with flame ionization detection. The concentration (as PPM) was converted to a volume of methane by dividing by the sample vial dead volume. The final concentration in pore waters was calculated as the quotient of the volume of methane and the molar conversion (22.4 1/mole), divided by the volume of pore water in the sample plug. The current sampling method is not well suited for quantitative measurement of methane. Thus our numbers probably underestimate the true methane values due to degassing during recovery and sample collection.

RESULTS

Pliocene and younger sediments (Unit I) in Sites 897 and 898 were characterized by interbedded turbidites, relatively high organic carbon contents, and rapid accumulation (Sawyer, Whitmarsh, Klaus, et al., 1994). The turbidites at these sites consist of sequences ranging in thickness from 5 cm to over 1 m (Sawyer, Whitmarsh, Klaus, et al., 1994). The typical turbidite consists of a dark-colored sequence of sand overlain by silty clays capped by a narrow pelagic layer of light-colored nannofossil ooze. The dark color is attributed to higher organic carbon contents (confirmed by smear slides, Sawyer, Whitmarsh, Klaus, et al., 1994. Organic carbon ranged from 0.4% to 2.7% in Site 897 sediments and 0.1% to 1.8% in Site 898 sediments with averages closer to 0.6%. The narrow bands of pelagic sediment indicate that local sedimentation contributed only a fraction of the net accumulation. Sedimentation rates (determined by biostratigraphy, Sawyer, Whitmarsh, Klaus, et al., 1994) range from 90 m/m.y. in Unit I at Site 898 to a maximum of 532 m/m.y. in Unit I at Site 897.

Pliocene and younger sediments at Site 900 were characterized by siliciclastic muddy turbidites, lower organic carbon contents (0.3% or less) and lower accumulation rates (22-24 m/m.y.) relative to Sites 897 and 898. The turbidites at these sites consist of sequences ranging in thickness from 10 cm to over 1 m overlain by a layer of pelagic nannofossil ooze of a thickness up to 60 cm.

The Miocene sediments at all three sites were more pelagic, having lower organic carbon contents, slower accumulation rates, and fewer interbedded turbidites. Sedimentation rates ranged from 2 to 13 m/m.y. in this sequence and organic carbon contents ranged from 0.04% to 2.5% with an average closer to 0.1 %. Whereas turbidites are present in these sequences, the slow accumulation rate indicates very little net impact by turbidites.

Pore-water Data

Sites 897 and 898 display a sharp redox discontinuity at the base of the Unit 1 turbidite sequence. Pore-water sulfate concentrations decrease to near zero in the upper 50 mbsf of the cores and remains near zero through Unit I (310 mbsf at Site 897 and 162 mbsf at Site 898). The sulfate gradient at Site 898 is steepest near the sediment water interface and becomes near linear (Fig. 1B) between 10 and 50 mbsf. The gradient indicates an active zone of sulfate reduction in the most recent sediments and a narrow zone of active removal at the base of the gradient. Below Unit I, sulfate concentrations return to 15-18 mM and remain high through much of the remaining sequence. The gradients below Unit I do not show any evidence of sulfate reduction in this sulfate-containing sequence. In terms of redox conditions, the bulk of the Unit I sediments make up an anoxic sequence bounded by two sulfate reservoirs, bottom water and the pore waters below Unit I.

Methane concentrations increase at the zero sulfate boundaries to maxima in excess of 15 mM for Sites 897 and 898, presumably because of methanogenesis (these sediments are not thermally altered) Methane concentration gradients indicate removal coincident with the zones of sulfate reduction in both sites. This suggests that methane is an important carbon source in the narrow sulfate reduction zones. Below, a comparison is made of both the methane and sulfate fluxes to the redox boundaries in order to evaluate the importance of methane as a carbon source. Methane concentrations at Site 897 reach higher levels than at Site 898, but show greater scatter, an artifact probably caused by disturbance by the rotary corer. Core disturbance and methane loss during sample collection probably lead to underestimation of in situ methane concentrations, but HPC cores used at Site 898 result in minimal disturbance. Thus the Site 898 data are used for flux calculations (below).

Pore-water ammonia concentrations for Sites 897 and 898 increase from the interface to a broad maximum in the middle of the methane-rich zone. The ammonia maximum is coincident with the methane maximum, suggesting that the majority of ammonia production is linked to methanogenesis rather than sulfate reduction.

In contrast to Sites 897 and 898, Site 900 sulfate profiles show a near linear decrease from surface values (~29 mM) to near zero by 700 mbsf (Fig. 1C). No sharp discontinuity is observed at the onset of turbidite emplacement. Ammonia values increase gradually from a near interface value of ~300 mM to a broad maximum of ~600 mM at 400 mbsf (Fig. 2C). No measurable methane was present in any sample from Site 900.

DISCUSSION

The pore-water sulfate profiles from Sites 897 and 898 indicate that redox conditions changed dramatically in the early to middle Pliocene. No such dramatic shift in redox conditions is observed al Site 900. The redox discontinuity of Sites 897 and 898 is indicated *by* the sulfate-depleted sediments overlying sulfate-rich sediments. Such discontinuities at previous sites have been attributed to sharp changes in sediment accumulation rates (Gieskes, 1974). The Unit I/Unit I] boundary at both sites is marked by the onset of massive turbidite emplacements, which account for the rapid sediment accumulation. O1 greater interest is the increase in carbon input to these deep abyssal sediments, accompanying turbidite emplacement.

Turbidite formation can be attributed to climate-driven eustatic sea-level change (Weaver and Kuijpers, 1983; Johnson and Rasmussen, 1984). While typically associated only with periods of sea-level regression, correlations of turbidites with periods of transgression have been documented as well (Weaver and Kuijpers, 1983). During periods of regression, fluvial deposits are eroded from the shelves and deposited primarily onto continental slopes. Likewise, much of the ambient biodetritus would also be deposited on slopes. Thus, the source material for turbidite flows would contain a mixture of young (reactive) carbon combined with the shelf reservoir of older (more refractory) carbon. In fact, the sulfate gradients at Sites 897 and 898 indicate sulfate reduction rates more typical of high-productivity margin sediments (Berelson et al., 1987). The sharp contrast in redox conditions of Sites 897 and 898 when compared to Site 900 suggests that turbidite deposition accounts for the bulk of the difference in carbon accumulation. However, variations in accumulation rate preclude determining the carbon burial rates directly from solids data.

Oxic degradation of the carbon in an emplaced sequence probably occurs via the "burn down" mechanism proposed by Wilson et al.. (1986). That is, entrained oxygen would be consumed shortly after the rapid deposition period, leaving an anoxic sequence. Oxygen would slowly burn through the carbon-rich turbidite during the slow deposition phase. We can only speculate on the magnitude of carbon

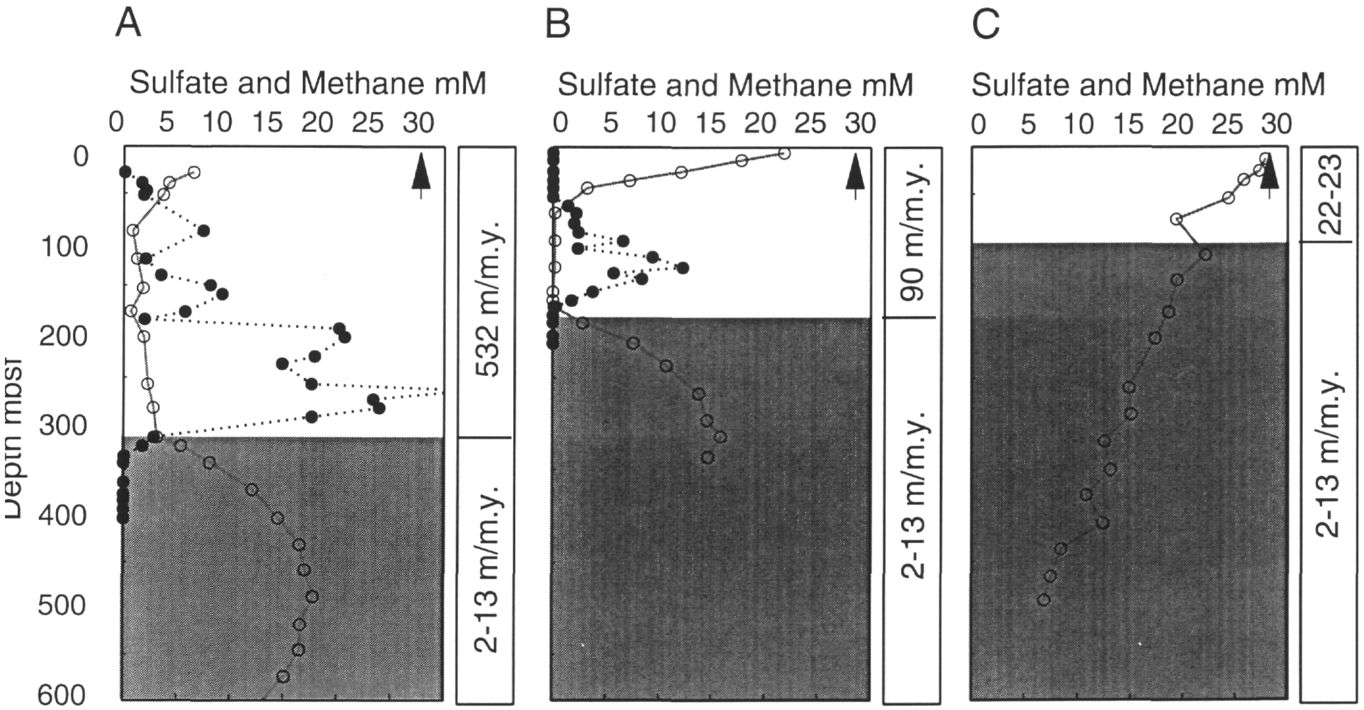

Figure 1. Pore-water sulfate (open circles) and methane concentrations (closed circles) and accumulation rates. Arrows indicate bottom-water sulfate concentraions. The shaded area indicates the approximate Miocene/Pliocene transition.

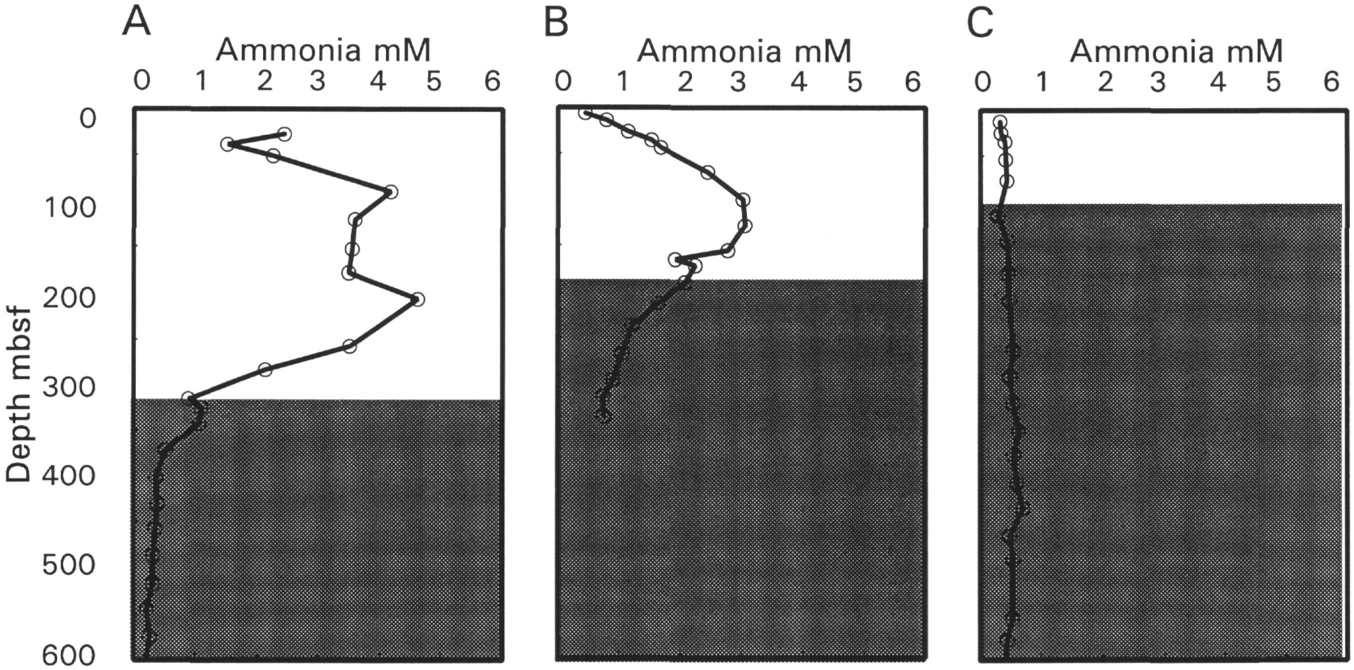

Figure 2. Pore-water ammonia concentration. The shaded area indicates the approximate Miocene/Pliocene transition.

consumed due to oxic degradation by this process. But, at depths greater than 10 cm into any one turbidite sequence, the maximum oxygen flux into the remaining interval can be calculated, and is on the order of 0.02 moles/m^2/yr (assuming a bottom-water oxygen concentration of 200 mM). A cubic meter of sediment containing 0.5% organic carbon (at 60% porosity) contains ~450 moles of carbon (much higher concentrations are found in modern turbidites). Thus, in the thicker turbidites, the majority of the carbon degradation must occur under anaerobic conditions. Thus, carbon preservation and burial may be a function of mechanism of burial (as rate) rather than bottom-water redox.

The near linear sulfate gradient between 5 and 50 mbsf at Site 898 indicates little or no sulfate reduction in the contained sequence. Ammonia gradients confirm that most of the deep carbon degradation occurs within the zero sulfate zone. The sulfate reduction at the base of the gradient coincides with the zone of maximum methane consumption suggesting a coupled reaction. Fluxes of both sulfate and methane were calculated from gradients and physical property data (after Berner, 1981) to determine if methane could be an important carbon source for sulfate reduction. We assumed two moles of methane consumed for each mole sulfate reduced in the comparison of fluxes determined as below:

$$F = Ds(dC/dZ)$$

where F = flux, C = concentration, Z = depth, Ds = bulk sediment diffusion coefficient (from Berner, 1981).

The sulfate flux at 50 mbsf is 2.0-3.0 $mM/m^2/yr$ while the methane is 1.5-2.5 $mM/m^2/yr$. The sulfate flux at 162 mbsf is less than 2.0 $mM/m^2/yr$ while the methane is 3.5-4.0 $mM/m^2/yr$. Methane consumption accounts for between 25% and 65% of the sulfate consumption in the upper sequence and 100% of the sulfate reduction at the base of the anoxic zone. Thus, the relatively refractory organic carbon that is buried below 5 mbsf can be utilized via methanogenesis and converted to a reactive carbon source (with respect to sulfate) as methane. However, this is only a fraction of the total carbon input to this site.

CONCLUSIONS

The comparison of these abyssal sites suggests that carbon burial associated with turbidite emplacement leads to unique mechanisms of degradation. These findings may have important implications with regard to the relationship between eustatic sea-level change and carbon transport to the deep ocean.

Regular turbidite emplacement results in sediment redox conditions more characteristic of margin sediments than abyssal sediments. Rates of sulfate reduction in the rapidly accumulating turbidite sequences indicate that shelf carbon is deposited at abyssal depths with little or no dilution. Consequently, shelf-derived organic carbon controls the redox conditions.

The mechanism of emplacement of thick turbidite sequences minimizes the role of oxygen in the degradation of the emplaced organic carbon. The nearly instantaneous deposition of sequences as thick as a meter limits the flux of oxygen into the sequence. Thus, oxic degradation is only important for the ambient (slow deposition) component of the sediment accumulation. Sulfate reduction and methanogenesis dominate in the turbidite sequences.

A significant fraction of the buried carbon is refractory with respect to sulfate reduction, but not to methanogenesis. The linear sulfate gradient at Site 898 indicates little or no sulfate reduction between the surface few meters and the zone of methanogenesis. The relatively high organic carbon content of this sequence is not available for sulfate reduction, but does support methanogenesis in the absence of sulfate. As a consequence, methane is the primary carbon source for sulfate reduction in the older segments of the sediment column.

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