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Early diagenesis in rapidly accumulating sediments on the Alboran slope, ODP site 976

Abstract The oxidation and reduction that occur during early diagenesis of sediments has been studied in the interstitial waters of a rapidly accumulating sedimentary sequence from the Mediterranean margin of Spain. A series of reactions that are mediated by progressively lower free energy derived from oxidation of organic matter is evident in the sedimentary sequence. Iron and manganese are rapidly reduced. Phosphate and alkalinity maxima at a subbottom depth of 15 m indicate maximal organic matter degradation. Methane first appears at ~20 m subbottom after sulfate is depleted, and its concentrations quickly climb.

Introduction

Geochemical processes that occur in marine sediments impact the sea floor–seawater exchange of soluble elements and the subsequent composition of sediments. Postdepositional oxidation of sedimentary organic matter is central to 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–suboxic–anoxic sediment conditions. Various

mineral dissolution and precipitation processes occur during this sequence (Berner 1980; von Breymann et al. 1990; Canfield 1993) and affect sediment properties. For example, Torii (1997) documents changes in magnetic susceptibility of sediments that accompany dissolution of magnetite and maghemite. The interplay of oxidizing and reducing conditions also 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 1982; Berelson et al. 1990).

We have studied the oxidation and reduction that occur during early diagenesis of a rapidly accumulating sedimentary sequence. This expanded sequence, a turbiditic unit on the southern margin of Iberia, provides good resolution of the biogeochemical changes that occur to sedimentary constituents. Our data provide information about the interactions of redox-sensitive constituents of interstitial water and bulk sedimentary organic matter in the course of diagenetic alterations.
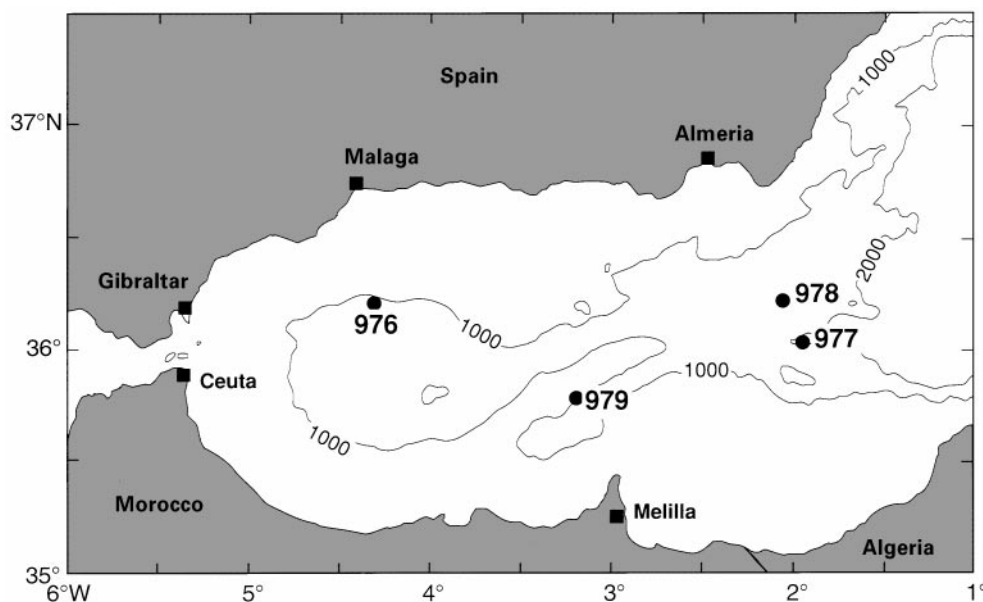
Sampling and analysis

Depositional settings

Sediments for this study were obtained from Ocean Drilling Program (ODP) site 976, which is located on the southern Iberian continental slope at a water depth of 1108 m in the Western Alboran Basin (Fig. 1). Pliocene–Pleistocene sediments at this site consist of hemipelagic nannofossil-rich clay, nannofossil clay, and nannofossil silty clay (Comas et al. 1996). Their sedimentation rate averages 23 cm/ka, which is about 10 times the typical deep-sea sedimentation rate (Kennett 1982, p. 464). The elevated rate reflects delivery of sediments to this site by a combination of repetitive turbidity flows and settling of pelagic sediments.

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Upper Pleistocene sediment samples for porewater analysis and headspace gas analysis were collected at frequencies of one per 1.5-m core section for the upper 40 m below sea floor (mbsf) and one per 9-m core from 40 to 70 mbsf. The total 70-m sedimentary sequence represents approximately 300 ka of burial time, with individual sediment samples ranging between ca. 6.5 ka (1.5 mbsf) to 300 ka (70 mbsf) in age.

Interstitial water analyses

Concentrations of selected cations and anions in the interstitial water of sediment samples were determined by squeezing 5-cm whole-round intervals of cores immediately after their arrival on deck of the *D/V JOIDES Resolution*. A titanium squeezer, modified from the stainless steel squeezer of Manheim and Sayles (1974), was used to minimize chemical interactions between the constituents of the interstitial water and the metal of the squeezer. Water forced out of the sediment was collected in polyethylene syringes, filtered through 0.45 Gelman polysulfone filters, and stored in plastic vials until analysis.

A variety of the interstitial water constituents that are sensitive to early diagenesis were analyzed using standard ODP procedures (Gieskes et al. 1991) that are summarized here. Iron and manganese concentrations were quantified by flame atomic absorption spectrometry using a Varian SpectrAA-20. Sulfate concentrations were determined by ion chromatography using a Dionex DX-100 instrument. Phosphate and ammonium concentrations were measured spectrophotometry with a Milton Roy Spectronic 20 spectrophotometer. Alkalinity was measured by Gran titration with a Metrohm autotitrator.

Concentrations of calcium and magnesium were determined by titration.

Headspace methane concentrations

Samples for headspace gas analyses were taken immediately after each sediment core arrived on deck. A sample of approximately 5 cm^3 of sediment was removed from the end of a freshly cut core section and placed in a glass vial that was then crimp-sealed with a rubber septum. The septum-sealed glass vials were heated at 70°C for 30 min. A 5-cm^3 sample of headspace gas was drawn into a syringe and injected into a Hewlett-Packard 5890 II gas chromatograph equipped with a Haysep (80–100 mesh) packed column and a flame ionization detector. After the headspace gas had been analyzed, the sediment plugs were dried and weighed in preparation for subsequent determinations of carbon concentrations. Methane concentrations are normalized to a nominal 5-g sample of dry sediment to compensate for variations in actual sample masses.

Organic carbon measurements and C/N ratios

The total organic carbon contents (TOC) were determined by the difference between total carbon concentrations as measured by a Carlo Erba NA 1500 NCS analyzer (Verardo et al. 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 differential TOC concentration procedure used in our study has been tested against the direct-determination analysis of carbonate-free sediment samples by Meyers and Silliman (1996). Agreement is good above TOC concentrations of 0.1%. The TOC and total nitrogen values were used to calculate atomic C/N ratios of the samples.

The C/N ratios were used 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; Emerson and Hedges 1988; 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 it is largely preserved in sedimentary organic matter (Jasper and Gagosian 1990; Meyers 1994).

Results and discussion

The classic series of diagenetic reactions that are mediated by progressively lower free energy derived from oxidation of organic matter (Froelich et al. 1979; Schulz et al. 1994) is evident in the sedimentary sequence at site 976. The elevated sedimentation rate expands the effects of the series of biogeochemical alterations over much of the upper 70 m of the sediment column.

Redox profiles

Concentrations of Fe^{2+} and Mn^{2+} in the interstitial water decrease rapidly from 1.5 mbsf (Fig. 2), indicating that the reduction zones for iron and manganese lie above this depth. The elevated concentrations of Fe^{2+} and Mn^{2+} in the uppermost sample indicate that oxidation of organic matter has reduced Fe and Mn in the surficial sediments. These data agree with the findings of Torii (1997), who determined that the minerological iron redox boundary coincides with a tan–green color transition at 1.2 mbsf in site 976 sediments. The decreases in interstitial concentrations in deeper sediments show that ferrous and manganous ions evidently are readily absorbed from the interstitial waters by solid phase components of the sediments. Nitrate concentrations were not determined inasmuch as the NO_3^- reduction zone is located stratigraphically above those of Fe and Mn (Froelich et al. 1979), and the reduced states of these cations indicate that nitrate reduction occurred very quickly in this sediment column.

Oxidation of organic matter after reduction of Fe^{3+} and Mn^{4+} ceases is done by reduction of sulfate (Froelich et al. 1979; Schulz et al. 1994), which consumes dissolved sulfate and releases a number of species that are derived from organic matter. This interchange is described by the general reaction:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow$$

$$106\,HCO_3^- + 53\,HS^- + 16\,NH_3 + H_3PO_4 + 53\,H^-$$
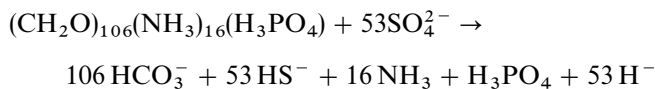
Concentrations of dissolved sulfate decrease progressively from seawater concentrations (~ 29 mM) and reach essentially zero by 20 mbsf (Fig. 2). This sediment depth corresponds to ca. 90 ka. The decrease in sulfate concentrations is accompanied by increases in concentrations of dissolved PO_4^{3-} and NH_4^-, verifying that sulfate reduction is the major process involved in organic matter oxidation over this depth range. Moreover, the broad maximum in phosphate concentrations between 12.5 and 20.5 mbsf records the zone of maximum organic matter degradation.

Fig. 2 Redox-sensitive changes in concentrations of total iron, manganese, sulfate, phosphate, and ammonia in interstitial water samples from site 976. Sediment depths are given in meters below seafloor (mbsf)
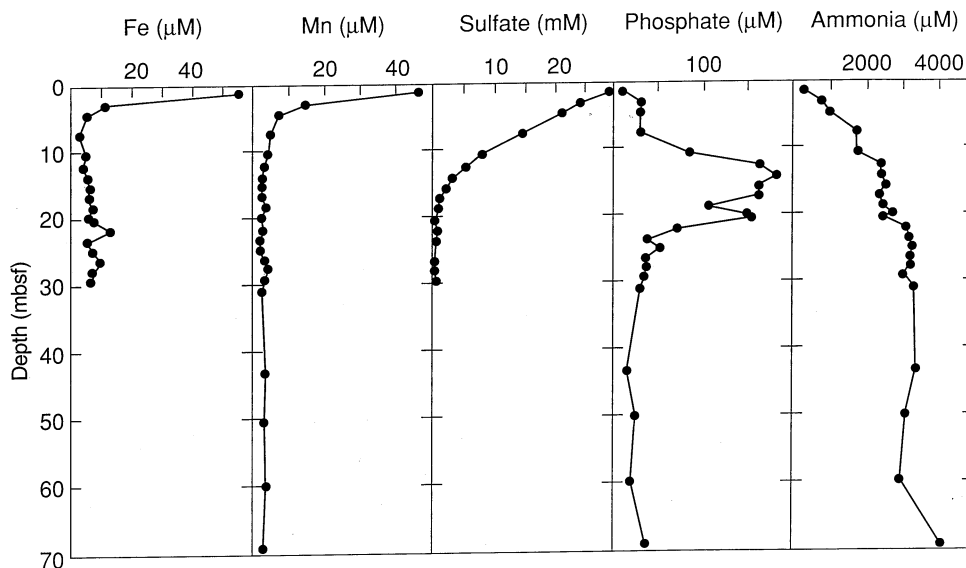
Carbonate diagenesis

The $CaCO_3$ content of sediments from the upper 70 m at site 976 averages $25.5 \pm 3.8\%$ and does not change systematically with depth (Fig. 3). Good preservation of nannofossils indicates that little carbonate dissolution has occurred in these sediments (Comas et al. 1996). Nonetheless, early diagenesis has created changes in interstitial water constituents that participate in carbonate equilibria.

A broad maximum in the alkalinity of the interstitial water between 10.5 and 20.5 mbsf follows the dissolved phosphate profile and reflects the release of CO_2 from oxidation of organic matter during sulfate reduction (Fig. 3). Böttcher et al. (1998) report $\delta^{13}C$ values of dissolved inorganic carbon (DIC) that are more negative than seawater in these sediments. Values decrease from -10.7% at 1.3 mbsf to -17.8% to -19.1% from 10.5 to 29.4 mbsf (Fig. 3). These negative DIC values confirm the oxidation of organic matter, which adds isotopically light organic carbon to the interstitial CO_2 and is accompanied by increases in alkalinity and in phosphate concentrations (Fig. 2).

Concentrations of both Ca^{2+} and Mg^{2+} in the interstitial water decrease with depth. The decreases of these two cations may result from in situ precipitation of high magnesium calcite or possibly dolomite, or they may indicate cation exchange with clay minerals during early diagenesis. Because systematic changes are not evident in the sediment $CaCO_3$ content, interaction with clay minerals seems the more likely possibility. The magnitudes of the changes in concentrations of Ca^{2+} and Mg^{2+}, however, are small, so any increases in the mass of sedimentary $CaCO_3$ would be masked by the large difference in relative sizes of the dissolved and solid phases.

Organic matter oxidation

In contrast to the redox-sensitive constituents of the interstitial waters and like the $CaCO_3$ content of the solid phase, TOC concentrations of the bulk sediment do not systematically change over the 70-m interval. The mean TOC is $0.7 \pm 0.2\%$, and the range of concentrations is from 0.4% to 1.1%. These sediments contain over twice as much organic carbon as the average of 0.3% compiled by McIver (1975) from DSDP legs 1–33, which can be taken as representative of deep-sea sediments. The TOC concentrations evidently are adequate to conceal the oxidation of organic matter implied by the changes in redox-sensitive constituents. This observation implies that only a small fraction of the available sedimentary organic matter need be oxidized to have significant impact on redox processes. It is also noteworthy that the variability in TOC concentrations (Fig. 4), which probably reflects the initial turbiditic emplacement of this sediment sequence, is not mirrored in the distributions of the dissolved constituents (Figs. 2 and 3), which are to a large degree smoothed by postdepositional diffusion.

Like the TOC concentrations, the organic C/N ratios fluctuate with depth and do not consistently increase or decrease (Fig. 4). The mean value of 7.7 ± 1.4 indicates that the organic matter in these sediments originates predominantly from marine sources (Premuzic et al. 1982; Emerson and Hedges 1988; Jasper and Gagosian 1990; Meyers 1994; Prahl et al. 1994). In general, marine organic matter is considered more susceptible to in situ oxidation in marine sediments than is the more refractory organic matter derived from land plants (Lallier-Vergès et al. 1993). Degradation of organic matter in organic-carbon-poor 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

Fig. 3 Concentrations of calcium carbonate, alkalinity, calcium, and magnesium in sediment samples from site 976. Dissolved inorganic carbon $\delta^{13}C$ values reflect oxidation of isotopically light organic matter and microbial reduction of dissolved CO_2. Sediment depths are given in meters below seafloor (mbsf)
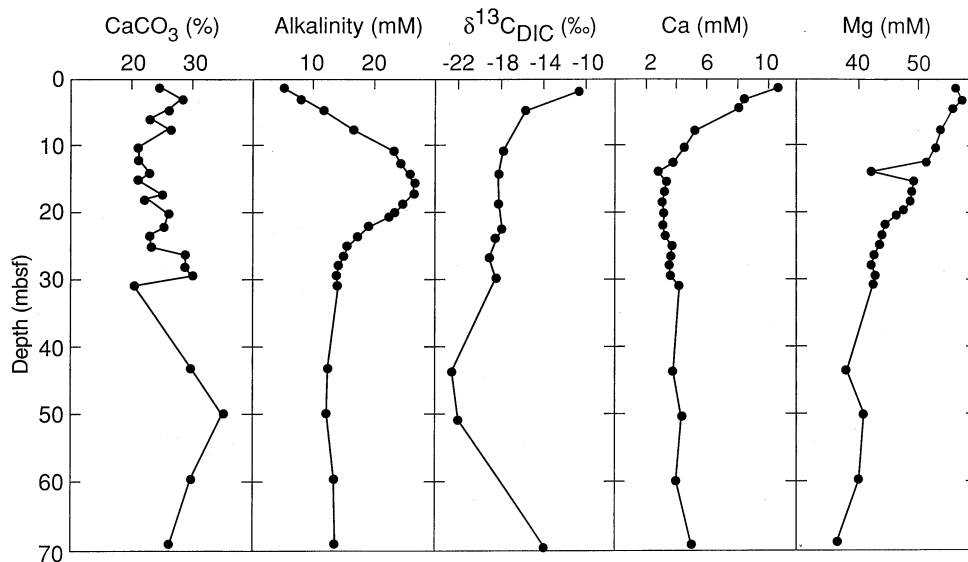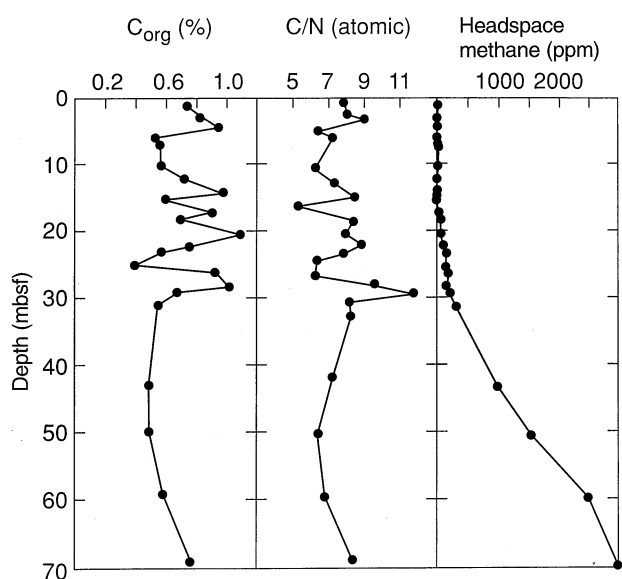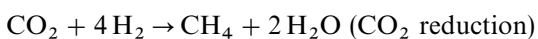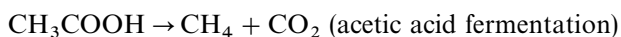
Fig. 4 Concentrations of total organic carbon, atomic organic C/N ratios, and concentrations of headspace methane in sediment samples from site 976. Methane concentrations begin to rise after interstitial sulfate is depleted. Sediment depths are given in meters below seafloor (mbsf)

oxidation of organic carbon escapes (Müller 1977). The amounts of organic matter present in the sediments on the Alboran Margin are evidently sufficient to mask this diagenetic effect, inasmuch as C/N ratios do not respond to the significant variations in ammonia concentrations (Fig. 2).

Methanogenesis

In sediments devoid of interstitial sulfate but containing metabolizable organic matter, methanogenesis becomes important. This process has two stages in which a consortium of microorganisms first convert the various forms of organic matter into short-chain alcohols and acids, CO_2, and H_2. In the second stage, some of these products are converted to CH_4 by a metabolically limited group of obligate anaerobic microbes (Mechalas 1981; Whiticar 1996). The general reactions that represent the production of methane in the second stages are:

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ (acetic acid fermentation)}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ (CO}_2 \text{ reduction)}$$

Concentrations of headspace methane begin to increase in sediments below 20 mbsf (Fig. 4). It is not until this sub-bottom depth that interstitial sulfate, an electron acceptor that enables organic matter oxidation, is depleted (Fig. 2). The appearance of methane in the interstitial waters of deep-sea sediments generally indicates methanogenic fermentation of organic matter, but methane can also

originate from the thermal breakdown of organic matter in deeper sediments and upward migration to shallower levels (Claypool and Kvenvolden 1983). High methane–ethane ratios and the absence of higher-molecular-weight hydrocarbon gases site 976 (Comas et al. 1996) indicate that the gas is microbial, as opposed to thermal in origin. The source of the methane is probably from in situ microbial reduction of the CO_2 produced from oxidation and fermentation of the marine organic matter present in this turbiditic unit. The microbial reduction of CO_2 has a kinetic isotope effect that discriminates against ^{13}C. CH_4 so produced is isotopically light, and the residual CO_2 is isotopically heavier (Whiticar 1996). The increase in $\delta^{13}C$ of interstitial dissolved inorganic carbon observed by Böttcher et al. (1998) from $-22.5‰$ at 43 mbsf to $-14.0‰$ at 59.5 mbsf (Fig. 3) is consistent with microbial CO_2 reduction. Similar microbial production of methane from marine organic matter has previously been inferred from high biogenic gas concentrations in Pilocene–Pleistocene sediments from site 532 on the Walvis Ridge (Meyers and Brassell 1985), in Middle Miocene sediments from site 767 in the Celebes Sea (Rangin et al. 1990), and in Pliocene–Pleistocene turbidites from sites 897 and 898 on the Iberia Abyssal Plain (Meyers et al. 1996).

Summary and conclusions

Early diagenesis in the rapidly accumulating hemipelagic sediments of the Alboran Margin has produced a succession of changes in interstitial water contents that are sensitive to oxidation–reduction reactions:

- Iron and manganese are reduced in the upper 1.5 m of the sediment column.
- Alkalinity and phosphate maxima centered on ~ 15 mbsf indicate the zone of maximum organic matter degradation.
- Sulfate decreases systematically and is depleted in sediments below 20 mbsf.
- Headspace methane first appears at 20 mbsf and increases in deeper sediments.

This succession reflects microbial degradation of the organic matter content of these sediments, using in order, dissolved oxygen, dissolved nitrate, dissolved sulfate, and finally by methanogenesis, and in the process reducing other oxidized species. The elevated sedimentation rate at this site has expanded these redox zones and made the changes more evident than in most sedimentary settings.

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