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Quantitative Assessment of Changes Occurring in Organic Matter during Early Diagenesis [and Discussion]

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Quantitative assessment of changes occurring in organic matter during early diagenesis

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It is perhaps a truism that sedimentary organic geochemical processes can best be quantified if the concentrations of the major organic chemicals are known. While numerous authors have reported the concentrations of one or other compound classes, relatively few studies have accounted for all of the organic carbon in a well-resolved depth sequence of Recent sediments.

In the present study, we report a *mass balance* for organic carbon in 1 cm sections of Recent sediment (0–10 cm) from offshore Peru by measuring the major, operationally defined classes of biochemicals: proteins, carbohydrates and lipids. However, in deeper sediments in the same core (200 cm), the proportion of organic carbon that can be accounted for by present analytical methods is only about 60%, and recalculation of published data shows that this decreases to only a few percent at 100 m depth. We discuss briefly, methods which have proved useful for characterization of the uncharacterized fraction which some workers have termed humin or 'proto-kerogen'.

The smooth and rapid decreases in the proportions of 'protein' and 'carbohydrate' carbon and 'bound' lipids in this core are attributed to diagenetic alteration rather than to variations in input, confirming many previous results. The overall proportions of free lipids, in contrast, did not decrease systematically in the shallowest sediments (0–25 cm). This is not reflected in most previous studies of individual lipids, many of which decrease rapidly with depth in these sediments. We suggest that interactions within the lipids may account for this apparent discrepancy.

1. Introduction

That organic matter deposited at the sea-floor is subject to rapid diagenetic changes is, in many environments, beyond dispute (reviewed by Henrichs 1992). For example, remineralization rates of organic matter in sediments have been calculated from pore water profiles of simple metabolic species such as ammonium, nitrate and carbon dioxide (Berner 1980; Jahnke 1990). In other studies, the decrease in operationally defined fractions of the sedimented organic matter have been measured directly for classes such as acid-hydrolysable amino acids ('proteins'), acid-hydrolysable sugars ('carbohydrates') and solvent extractables (lipids) and the results clearly demonstrate that early diagenetic changes are occurring in some fractions of the organic matter (Henrichs *et al.* 1984; Farrington *et al.* 1988; Seifert *et al.* 1990; ten Haven *et al.* 1992). (The terms 'protein', etc., are written in inverted commas since some other substances react to the colourimetric assays.)

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Several workers have quantified the fraction of organic matter that is isolable from sediments by extraction with alkali (so-called humic substances; Reimers & Suess 1983*a*) but the quantitative variations in this fraction with increasing depth and the relationship to the other biochemical fractions is less clear.

The number of studies in which all of the organic matter has been identified and measured (i.e. a mass balance achieved) is much more limited. Klok *et al.* (1983, 1984) identified and measured all of the organic matter in one sample of marine sediment, but no diagenetic changes were investigated. Reimers & Suess (1983*a*) investigated the down-core concentrations of lipids, hydrolysable humin and humic substances in Peru upwelling sediments from three 2 m cores near 11° S and noted that the main organic fraction consisted of insoluble and non-hydrolysable (6N HCl, 16 h) 'proto-kerogen'.

More recently, Patience *et al.* (1990) attempted to address the perceived paucity of mass balance information and reported an extensive integrated characterization of the total organic matter in sediments of the Peru central upwelling zone (oxygen minimum zone). They reported significant diagenetic alteration in five sediments from ODP Leg 112 spanning depths of *ca.* 1–22 m below sea-floor (mbsf). The data from these studies suggested that, in addition to the changes occurring below 1 mbsf, extensive changes in the organic matter must also be occurring within the top 1 m of these sediments, in agreement with the findings of Reimers & Suess (1983*b*) and as was also demonstrated in these sediments by others for discrete fractions such as hydrolysable amino acids, 'carbohydrates' and some lipids (Henrichs *et al.* 1984; McCaffrey *et al.* 1990; Seifert *et al.* 1990; ten Haven *et al.* 1992).

The major aim of the present research was to examine the concentrations of 'proteins', 'carbohydrates' and free and 'bound' lipids in 1 cm sections of the Peru sediments adjacent to those examined by Patience *et al.* (1990) and, if possible, to obtain a mass balance for the organic carbon. By combining and comparing the results with published data for individual biochemical fractions and humic substances from other sediments in the area, it was hoped that the generality of any trends might be verified.

2. Materials and methods

(*a*) *Samples*

Freeze-dried sediment samples (1 cm sections to 9 cm, box core, 147 m water depth; 14–15 cm, 24–25 cm, 199–200 cm, gravity core, 154 m water depth) were obtained from offshore Peru during the RRS *Charles Darwin* cruise (figure 1) at 10° 58.7′ S 77° 57.5′ W (box core) and 10° 58.5′ S 77° 57.42′ W (gravity core) close to ODP Leg 112, Site 681 in the Salaverry Basin, central upwelling zone (oxygen minimum zone; Suess *et al.* 1987) from which additional samples (*ca.* 1, 5, 9 and 22 m) were obtained as detailed previously (Patience *et al.* 1990).

(*b*) *Experimental methods*

Elemental carbon was determined on a Carlo Erba 1106 analyser after removal of carbonate as described previously (Patience *et al.* 1990). Similarly, details of the colourimetric assays for 'proteins' and 'carbohydrates' have been given (Patience *et al.* 1990 and references therein). Typically, colourimetric quantification was performed in quintuplicate on single samples and for the 6–7, 7–8 and 199–200 cm sections, replicates were taken through the entire multistep procedure. Free and

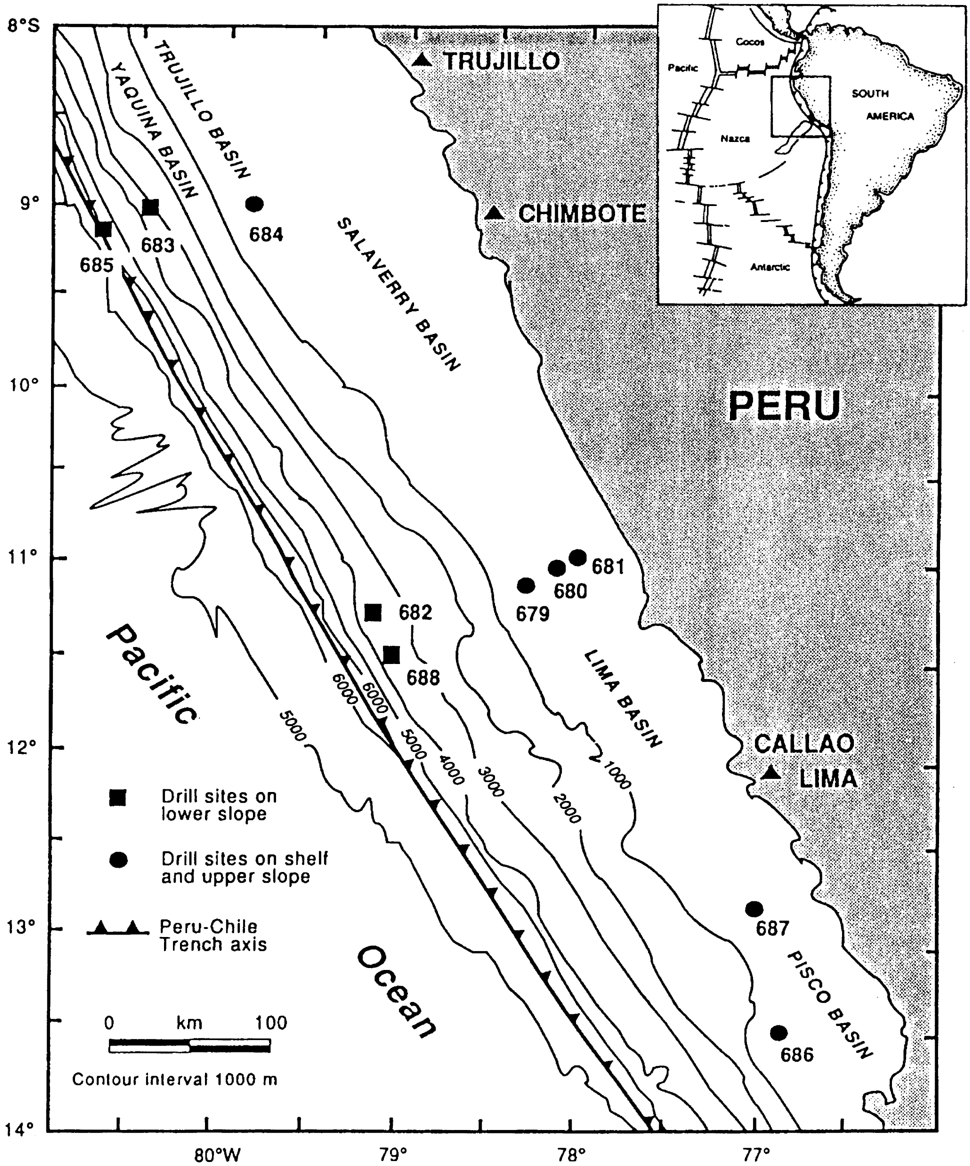

Figure 1. Map of study area. Leg 112 ODP sites annotated 679, 680, etc.

'bound' lipids were obtained by solvent extraction of the sediments in mixtures of methanol and dichloromethane before and after base hydrolysis, respectively, again as reported elsewhere (Patience *et al.* 1990).

3. Results and discussion

(*a*) *Sediment character and age*

The characteristics of the depositional setting and sediments of the central upwelling zone have been clearly and concisely described by Farrington and co-workers in a number of comprehensive studies (e.g. Henrichs & Farrington 1984; Henrichs *et al.* 1984; McCaffrey *et al.* 1990, 1991). Briefly, the Quaternary sediments of the Peru shelf and upper slope represent one of the longest known sequences of recent high-organic-carbon deposits. The sediments, which consist of laminated and bioturbated diatomaceous muds alternating on a scale of metres, have been the subject of extensive research partly because of the high organic content resulting from normal upwelling and also because the sediments may contain a record of the perturbation of upwelling by El Niño events (for recent compilations of research see, for example, Suess *et al.* (1990) and Summerhayes *et al.* (1992)). The establishment of an oxygen minimum zone that impinges on the Peru margin from *ca.* 75–500 m water depth, inhibits bioturbation in the sediments and increases their usefulness for the study of diagenetic changes and input influences.

Published sedimentation rates have been summarized by McCaffrey *et al.* (1990). Rates vary considerably throughout the 11–15° S region (0.05–1.1 cm a^{-1}) partly due to the effects of compaction and sediment hiatuses (McCaffrey *et al.* 1990) but also because supported ^{210}Pb activity may be high, making lead dating erroneous (Henrichs & Farrington 1984). McCaffrey *et al.* (1990) obtained a value of 0.47 cm a^{-1} at 11° 04.21′ S (applicable to 2–12 cm depths) by ^{210}Pb dating whereas Henrichs and Farrington (1984) cited values of about 0.6 and 1.1 cm a^{-1} for sediments close to 15° S, and some authors have found lower rates (0.15 cm a^{-1}) below 10 cm depth where a discontinuity in ^{210}Pb activity was observed (14° 39′ S; Koide & Goldberg 1982). Rates calculated for the present core by ^{210}Pb methods, were *ca.* 1 cm a^{-1} for the 0–260 cm (N.B. Price, personal communication). The majority of the present samples (i.e. *Charles Darwin*, 0–20 cm) are of the order of at most a few tens of years old, while the deeper ODP Leg 112 samples (extending to depths of 126 m in some studies; Seifert *et al.* 1990) are at least a million years old. Thus the age span of our samples plus published data may allow us to draw some more general conclusions about the diagenetic changes in the oxygen minimum zone.

(*b*) *Elemental concentrations*

Organic C, H and N data for the 0–200 cm samples (*Charles Darwin*) are shown in figure 2. There appear to be no readily discernible trends with depth even though our sampling allowed 1 cm resolution in the 0–10 cm region. The data probably reflect the original sediment composition and variable dilution by clastics rather than diagenetic effects. A similar interpretation was made by Seifert *et al.* (1990) for sediments from nearby ODP Site 681. Between 25 and 200 cm there is a fairly distinctive (and reproducible) decrease in C, H and N in our samples (figure 2) but obviously this is far too few samples from which to draw conclusions. None the less, some previous studies have shown a decrease in organic matter in the top 1 m of sediment (McCaffrey *et al.* 1990 examined 50 samples in the top 1 m of sediments from 15° S and observed a 4% decrease in total organic carbon (TOC)) and in some cases this has been attributed to diagenesis (Reimers & Suess 1983*a*, *b*).

(*c*) *Biochemical analyses*

The concentrations of the measured biochemicals in the topmost samples (0–4 cm) accounted for up to 125% (*sic*) of the TOC. The overestimation is probably a result of several factors including, perhaps; the non-specificity of the colourimetric methods used to estimate ‘proteins’ and ‘carbohydrates’; the assumptions made in the conversion of measured units to percent carbon (40% C assumed for carbohydrates, 45% C for amino acids, see Patience *et al.* (1990) for details). While these are drawbacks to the approach we have used, the logistics of conducting mass

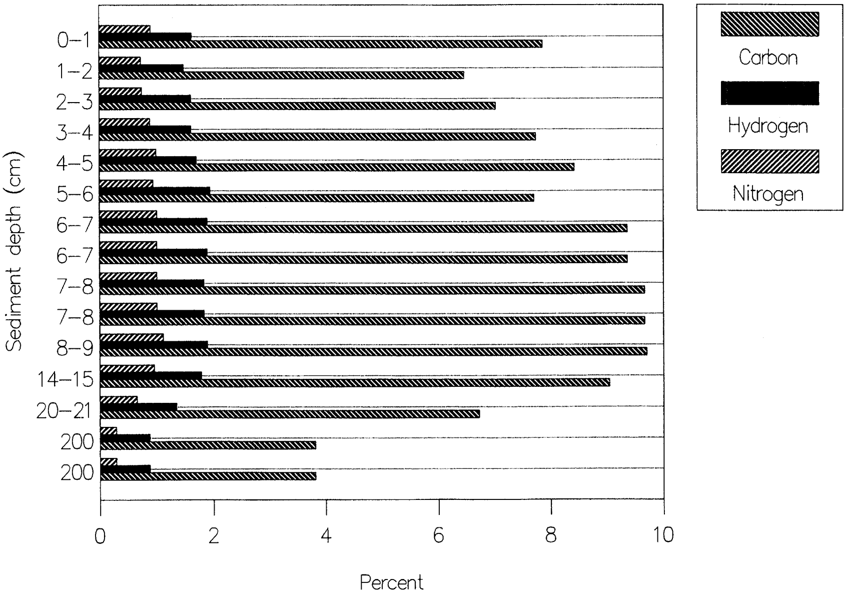

Figure 2. Concentration of total organic carbon, hydrogen and nitrogen (% sediment dry mass) in Peru upwelling zone sediments collected from 11° S (oxygen minimum zone). Note depth scale is not linear.

balance measurements in replicate for all three biochemical classes on 1 cm sections dictated the methods. We feel, none the less, that there are important features to be recognized in the data.

In the topmost samples, the average content of lipids (*ca.* 10% 'free' lipids), 'proteins' (*ca.* 50%) and 'carbohydrates' (*ca.* 10%) can be compared to the average composition of other sediments and probable input organisms as discussed below.

(*d*) *Lipids*

The free lipid concentrations of the sediments are comparable to those found by Reimers & Suess (1983*a*; 13–20%) in the top 0–4 cm of sediments from the present study area, while in an analogous upwelling area off Namibia, diatomaceous ooze contained only 4% free lipid, 11% 'protein' and 4% (min) 'carbohydrate' and 78% of the organic matter was uncharacterized (Klok *et al.* 1984). Bhosle & Dhople (1988) reported 2–4% 'free' lipids, 6–20% proteins and 21–35% carbohydrate in Bengal Bay continental shelf and slope sediments. The lipid content of the topmost Peru sediments can therefore be considered to be quite high, especially if the 'bound' lipid fraction is taken into account. Values for the latter are comparable to those recorded for deeper sediments at this site (Patience *et al.* 1990).

The lipid contents of marine organisms vary widely depending on growth conditions, but Romankevich (1984) calculated 'average' values for phytoplankton and zooplankton to be 9% and 17% of the organic matter, respectively. Reimers & Suess (1984*a*) cite values of 5–25% for marine plankton. Gallardo (1984) noted that up to 80% of the biomass of the surface sediments can comprise the sulphur-oxidizing, filamentous bacteria, *Thioploca* spp., but samples of this organism collected and analysed by McCaffrey *et al.* (1989) from 15° S only contained *ca.* 4% lipids (per gram dry mass), similar to the average for phytoplankton. So, compared with likely source organisms, the sediments can also be considered to be lipid-rich.

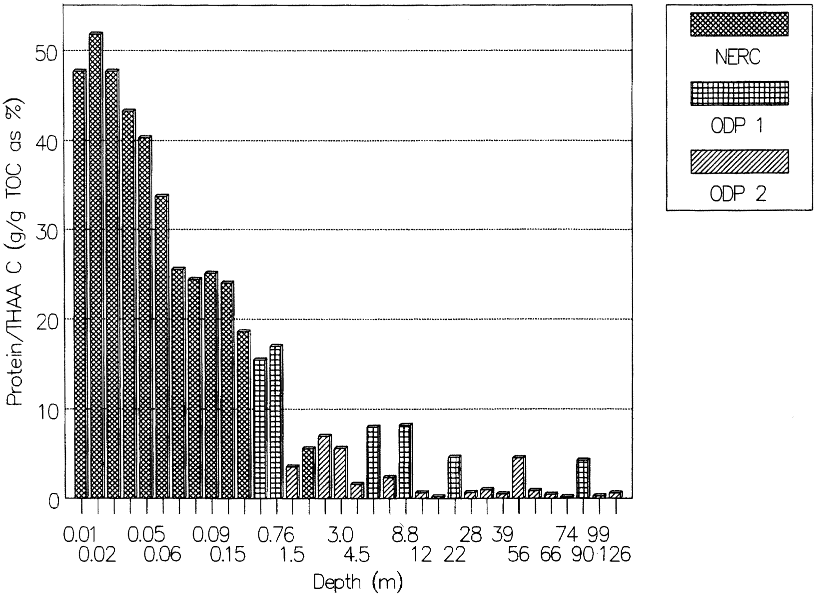

Figure 3. Concentrations of 'proteins' (% total organic carbon) in Peru upwelling zone sediments. Key: NERC, RRS *Charles Darwin* samples; ODP 1, ODP Leg 112, 680B samples (data from Patience *et al.* 1990); ODP 2, ODP Leg 112, 681B and 681C samples (data recalculated from Seifert *et al.* 1990). Note depth scale is not linear.

(*e*) '*Proteins*'

The 'protein' content of the Peru upper sediments is more typical of that expected from the contributing organisms, where values between 15 and 50% are typical for phytoplankton and some bacteria, and where even higher concentrations have been found in zooplankton (Romankevich 1984). Our values also agree reasonably well with previous research on sediments from 15° S (Henrichs *et al.* 1984).

(*f*) '*Carbohydrates*'

The low carbohydrate content of the topmost Peru sediments is probably a result of the deposition of phytoplankton detritus from which carbohydrate has been selectively removed by zooplankton and anchoveta grazing since Peru shelf sediments in this area contain abundant zooplankton and anchoveta faecal pellets. Although undigested diatoms sometimes account for much of the bulk particulate organic carbon associated with the pellets, the preservation of morphologically distinct tests does not necessarily mean that the organic 'soft parts' have remained unaltered. This alteration of primary organic matter is supported by observed alterations of other biochemicals in the surface sediments, compared to water column products (e.g. carotenoids and chlorophylls; Repeta & Gagosian 1987).

(*g*) *Diagenetic changes*

Relative to TOC, the amount of 'protein' carbon decreases dramatically within about the first 15 cm of sediment (figure 3) from about 50% of the total carbon to about 25%, which represents *ca.* 15 years of diagenetic and input changes. This confirms some previous studies, most notably that of Henrichs *et al.* (1984), which for sediments at 15° S, demonstrated that total hydrolysable amino acids decreased with depth to 70 cm in 2 and 3 cm sections of three of five cores examined. A decrease of

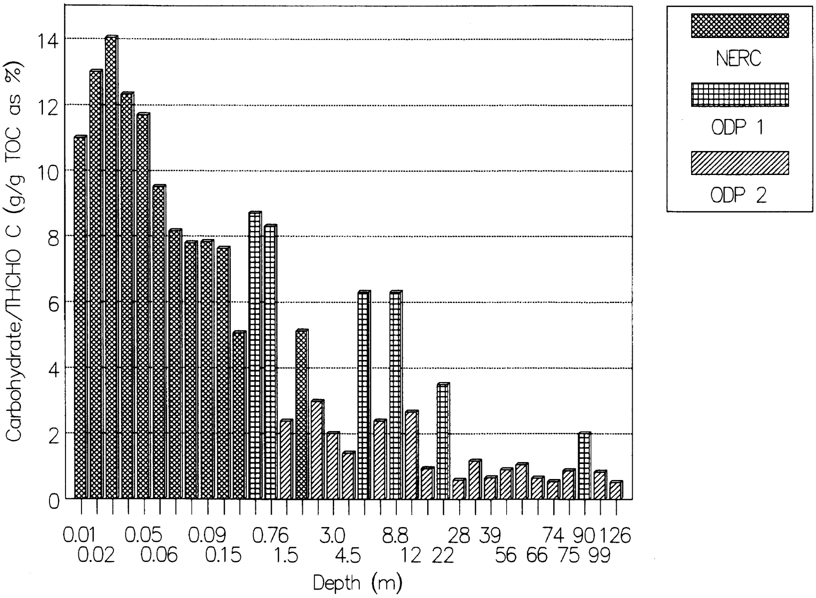

Figure 4. Concentrations of 'carbohydrates' (% total organic carbon) in Peru upwelling zone sediments. Key as figure 3.

about 50% in the total hydrolysable amino acid (THAA)/TOC ratio was measured by these authors. In the remaining cores lower productivity in the past was advanced as a better explanation for the decrease – in the absence of measurable remineralization (Henrichs *et al.* 1984).

Reimers & Suess (1983*a*) also recorded an overall decrease, from about 20% to about 10% of TOC, in hydrolysable (6 N HCl, 16 h) 'humin' (i.e. 'proteins') in two cores from 11° S to 2 m depth.

Recalculating the units and combining and comparing our data for 'proteins' in our shallow Peru samples with those for shallow and deeper samples from the same area (Patience *et al.* 1990; Seifert *et al.* 1990), the proposed diagenetic trend can be seen to extend to depths of 126 m (figure 3). A general trend is evident between the data-sets, over 100 m of sediments, across three laboratories, five locations in the oxygen minimum zone and with two different analytical methods.

While not as dramatic as the decrease in 'protein' carbon, the 'carbohydrate' carbon also decreases with depth (figure 4) from *ca.* 13% within the first 3 cm to *ca.* 5% at 200 cm depth. Unlike the 'protein' concentrations there appear to have been few previous analyses of carbohydrate concentrations in shallow, well-resolved non-bioturbated recent sediments. Seifert *et al.* (1990) examined nearby Site 681 sediments from 1 to > 100 mbsf and noted an exponential decrease with depth and Patience *et al.* (1990) noted a similar trend for Site 680 samples from 1 m to 22 mbsf. Indeed, recalculation of the data from these latter studies appears to extend the downward diagenetic trend of our shallow samples (figure 4) in a similar manner to that observed for the 'proteins'.

The lipids in our analyses were subdivided by our extraction techniques into free lipids and those extractable after base hydrolysis of the extracted sediments (cf. Patience *et al.* 1990 and others). The 'bound' lipids appear to show a systematic decrease with depth (figure 5). In deeper sediments (1–100 m) from the present

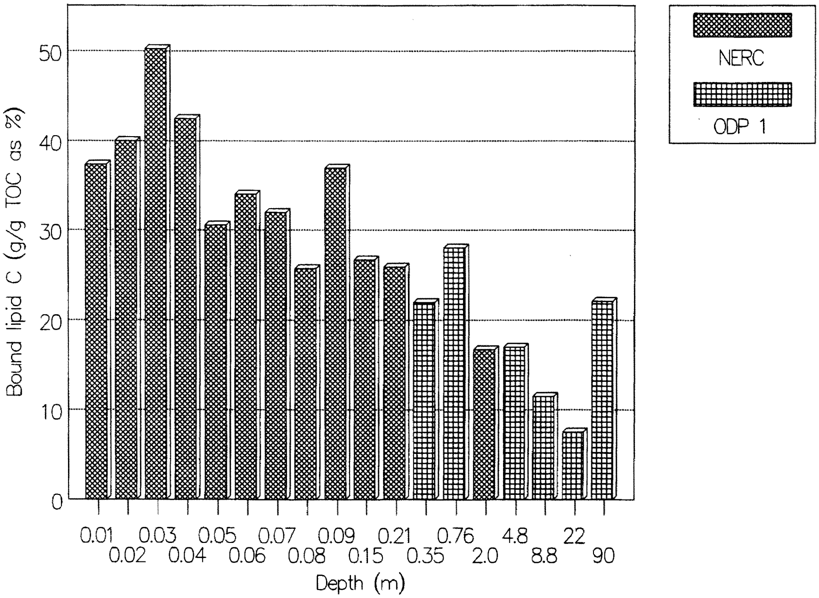

Figure 5. Concentrations of 'bound' lipids (% total organic carbon) in Peru upwelling zone sediments. Key as figure 3.

study area, both free and 'bound' lipids decreased with depth (Patience *et al.* 1990). It is tempting to invoke diagenetic alteration, perhaps including remineralization, of this fraction of the organic matter. If these lipids are not completely remineralized, enzymatic hydrolysis might conceivably release them into the free lipid fraction, or a number of unknown and possible complex, geopolymerizations might occur leading to an increasingly uncharacterized 'proto-kerogen' or humin – a feature which is certainly observed in the sediments (cf. Reimers & Suess 1983*a*).

The free lipids in our samples show no clear trend with depth to 25 cm, although a slight decrease thereafter to 200 cm is evident (figure 6). Reimers & Suess (1983*a*) observed a decrease in free lipids in the top 2 m of nearby sediments which is also reflected in the behaviour of many individual lipids examined in these sediments (Repeta & Gagosian 1987; McCaffrey *et al.* 1990; ten Haven *et al.* 1992). However, it is likely that many of the decreases in individual lipids reflect their conversion into other lipids. For example, the decreases in highly branched alkenes and phytol with depth (Farrington *et al.* 1988) can now almost certainly be explained by their conversion into thiophenes by reaction with sulphur (ten Haven *et al.* 1992; Rowland *et al.* 1993). Indeed, such reactions might be a general mechanism for conversion of unsaturated lipids into organosulphur species (see Sinninghe Damsté & de Leeuw (1990) for an overview). Such conversions would not necessarily remove the compounds from the lipid fraction but an apparent decrease in individual lipids would be observed if both reactant and product were not monitored.

(*h*) *Uncharacterized organic matter*

Our data and those of others (e.g. Reimers & Suess 1983*a*; Patience *et al.* 1990, 1992) reveal a substantial proportion of organic matter which is uncharacterized by the biochemical assays even in shallow sediments (*ca.* 20% at > 6 cmbsf in our samples). This has been variously termed 'proto-kerogen' or non-hydrolysable humin and has been interpreted either as residues of biopolyers which are resistant

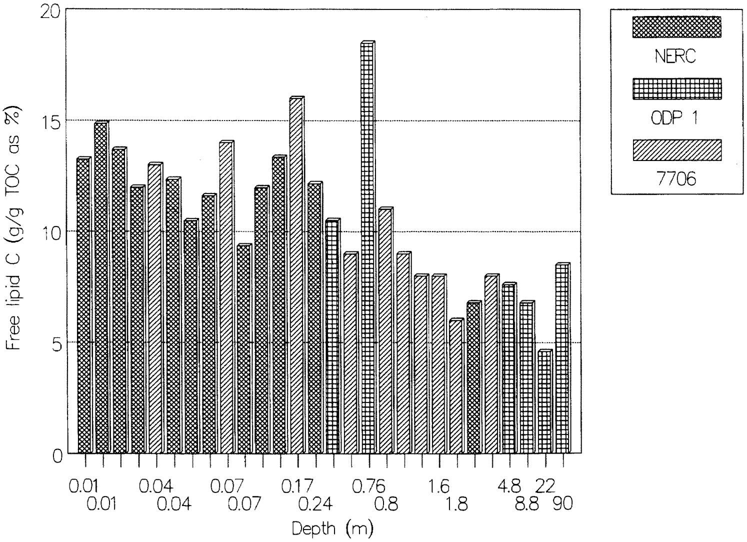

Figure 6. Concentrations of free lipids (% total organic carbon) in Peru upwelling zone sediments. Key: NERC, RRS *Charles Darwin* samples; ODP 1, ODP Leg 112, 680B samples (data from Patience *et al.* 1990); 7706, Core 7706-39, 40 (data from Reimers & Suess 1983*a*).

to remineralization, as neo-formed organic matter, or both (see Rullkötter & Michaelis 1990 for a review). In the sediments from 15° S studied by Reimers & Suess (1983*a*) most (*ca.* 49%) of the organic matter was reported to be non-hydrolysable, non-lipid 'proto-kerogen' even in the top 4 cm of sediment. Since they did not use an oxidizing acid (e.g. sulphuric acid) for the hydrolyses, this 'proto-kerogen' value will include 'carbohydrates' (*ca.* 13% according to our analyses), leaving an uncharacterized 'proto-kerogen' fraction of some 36%. This proportion of uncharacterized organic matter is revealed between 30 cm and 2 mbsf in our core, perhaps suggesting that the rates of formation or accretion are different at the two latitudes. At depths of *ca.* 22 mbsf in the 11° S sediments, over 80% of the organic matter is present in this form.

Most attempts to characterise this fraction have been qualitative studies. Pyrolysis techniques (Patience *et al.* 1990, 1992), NMR (Mann *et al.* 1991) and X-ray photoelectron spectroscopy (Patience *et al.* 1992) have all been applied to the Peru samples and have indicated the decreasing importance of labile functional groups and increasing importance of aromatic and sulphur-containing components. Quantitative characterization of this fraction remains one of the major future challenges for organic geochemists (Rullkötter & Michaelis 1990).

4. Conclusions

The concentrations of major biochemicals in Recent sediments from the oxygen minimum zone of the Peru upwelling region appear to show evidence for the rapid diagenetic alteration of the organic matter. Significant reductions in 'protein', carbohydrate and 'bound' lipids occur within about 50 years. Changes in the free lipids may be more complex.

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Discussion

D. Walton. The diagenesis of proteins in sediments is similar to that found in the intracrystalline sites of fossil proteins. In fossil brachiopods, proteins degrade very rapidly with 80–100% of the available peptide bond being hydrolysed within the first 120000 years. Proteins within shells are trapped from the moment of biomineralization and therefore degradation can only be due to processes acting within the shell rather than external factors. Study of these sites will provide details of how proteins degrade through non-microbial processes which may then be applied to the diagenesis of organic-rich sediments.

S. J. Rowland. It is true that changes are rapid. It is different at the surface where there is re-working by fauna in and above the sediment–water interface.

A. C. Aplin. Do the data hold any implications for the mechanisms by which kerogen or protokerogen forms? The two models presented (selective preservation & polymerization): are they applicable when organic matter forms quickly?

S. J. Rowland. This could be seen in the removal of more mobile/labile chemicals: both mechanisms work but we have no evidence to prefer one over the other.

M. L. Coleman. Are the highest organic matter contents recorded in the samples from just below the surface of the unbioturbated sediments or are they just an artefact of sampling?

S. J. Rowland. They could well be.