

CHAPTER 4

OMAN MARGIN (Abyssal Site)

4.1. INTRODUCTION

In this Chapter, two sediment cores from an abyssal site, close to the base of the Oman Margin continental slope (see Figs. 3.8 i&ii) were chosen as examples of organic rich sediments underlying oxygenated waters. The Oman Margin sediments also provide a good opportunity to study the past variations in the Indian Ocean monsoon because the sediments there accumulate rapidly ($>10 \text{ cm ky}^{-1}$) and can be well dated and contain multiple proxy records of past monsoon variation (Overpeck *et al.* 1996). In the context of the present study, the sediments were expected to be ‘diagenetically-active’ and therefore, to provide an ideal opportunity to study sub-oxic diagenesis. The chapter is divided into separate Results and Discussion sections in order to facilitate access to the data (see Appendix B in Table B.1.1 to B.1.7.1).

4.2. RESULTS

Based on their sedimentology, two abyssal sediment cores (12687#8 and #10, see Chapter 3, referred to as cores #8 and #10 hereafter) can be distinguished into three units, namely “top” (~0-100 mm) for both cores; “middle” ~120-180 and ~120-220 mm for cores #8 and #10 respectively; “bottom” ~220-280 and ~240-320 mm for cores #8 and #10, respectively.

4.3. Bulk parameters

4.3.1. Water content and Particle size

The water content (% wet weight) of the both sediment cores generally decreased with depth from ~ 60-80%, in the top layer to ~60% in the bottom layer. The middle layer was characterised by distinctly lower water content <40% (Fig. 4.1). Particle-size data also emphasised the three distinct units (Fig. 4.2). Hence in core #8 these were:

Top Unit (0-100mm) the average particle-size spectrum having a composition of silt ~70%; sand ~17% and clay ~13%;

Middle Unit (120-180mm) which has a high sand content ~82%, with significantly lower silt ~15% and clay ~2% contents;

Bottom Unit (200-280mm) having a consistent composition of sand ~10%, silt ~75% and clay ~15%.

Core #10 was similar to #8 with average composition for the three units of

Top Unit (0-100mm) having the composition of silt ~70%; sand ~10% and clay ~17%;

Middle Unit (120-220 mm) having a composition of sand ~ 51%, with silt ~ 40% and clay ~ 8%;

Bottom Unit (240-320 mm) having a consistent composition of sand ~12%, silt ~68% and clay ~ 20%.

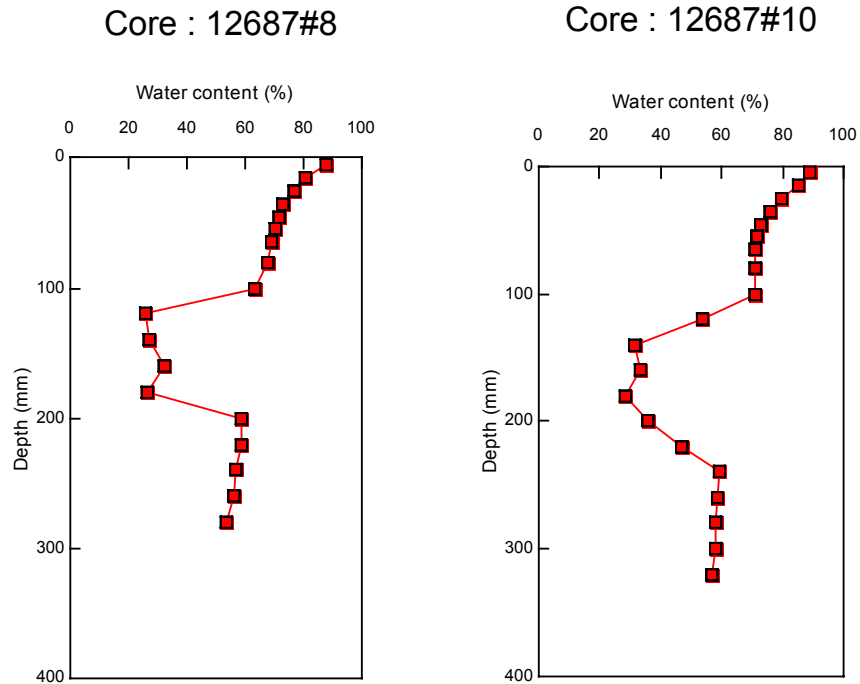


Fig. 4.1. Down-core variation of Water content vs. depth in core 12687#8 and 10.

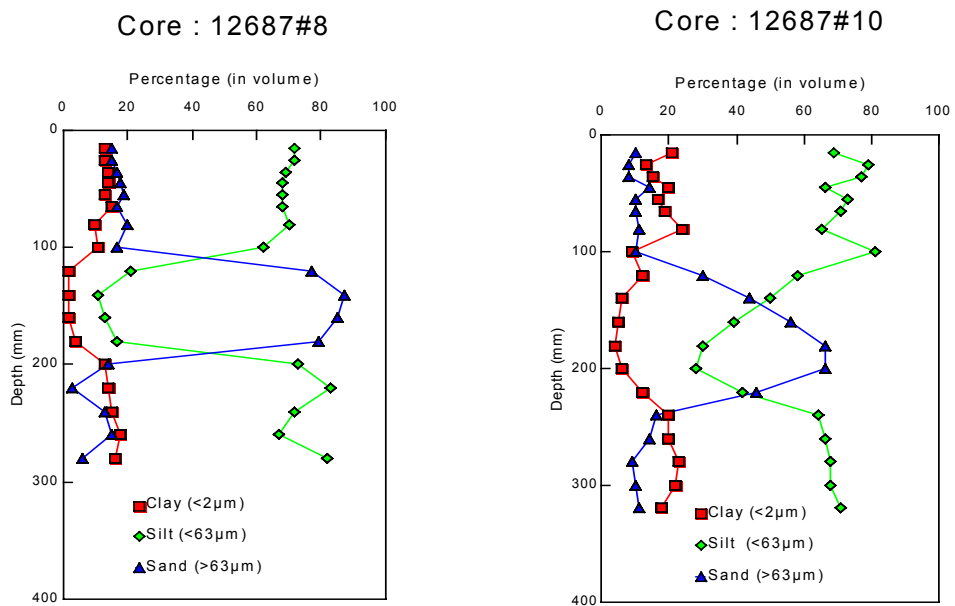


Fig. 4.2. Down-core variation of Particle-size vs. depth in core 12687#8 and 10.

4.3.2. Major elements and calcium carbonate

The major elements Si, Al, Ti, Ca, Mg and K were determined as their oxides (see Chapter 3) and generally covaried with the clay contents of the sediments (see Figs. 4.3 -4.8).

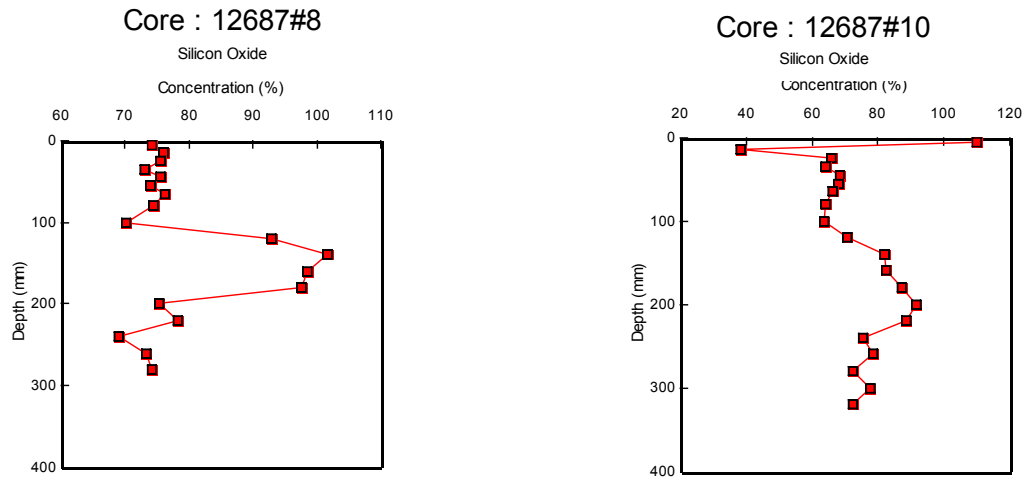


Fig. 4.3. Down-core variation of SiO₂ vs. depth in core 12687#8 and 10.

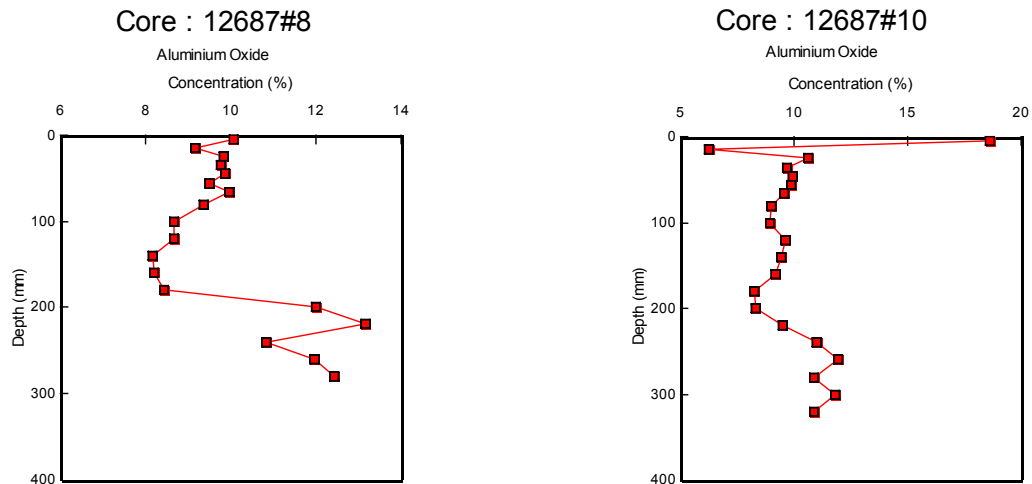


Fig. 4.4. Down-core variation of Al₂O₃ vs. depth in core 12687#8 and 10.

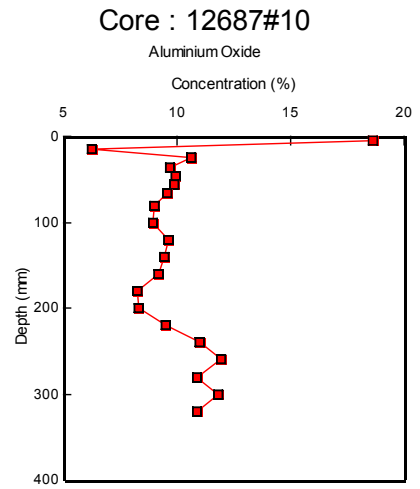
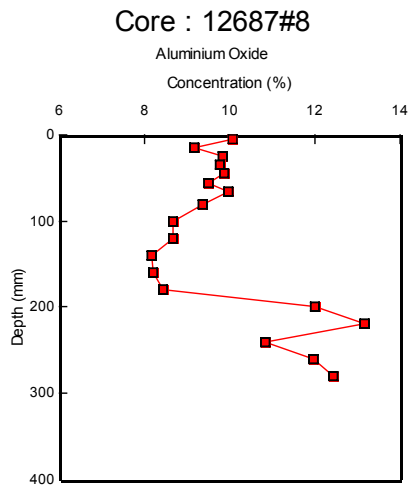


Fig. 4.5. Down-core variation of TiO_2 vs. depth in core 12687#8 and 10.

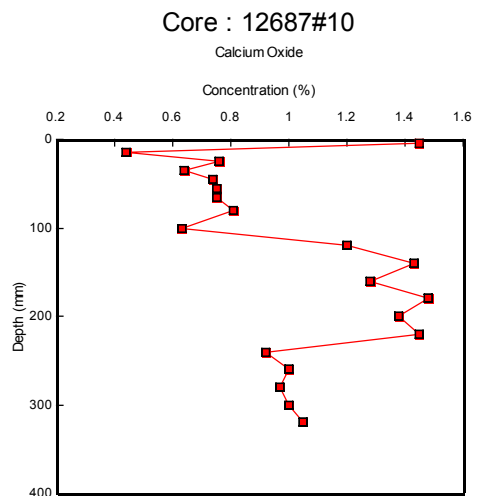
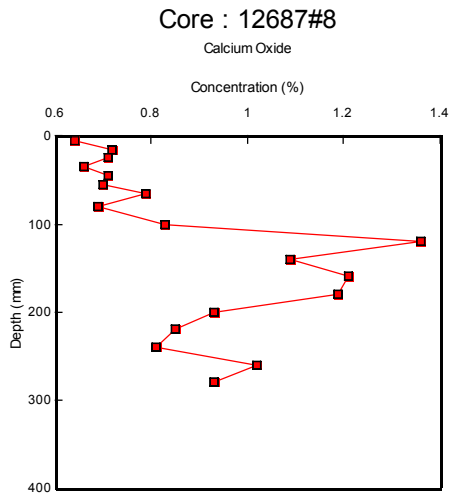


Fig. 4.6. Down-core variation of CaO vs. depth in core 12687#8 and 10.

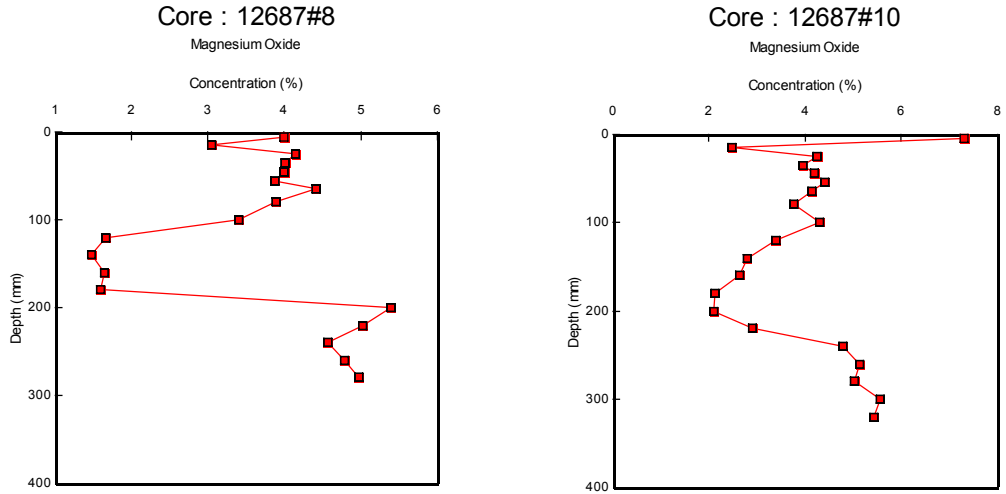


Fig. 4.7. Down-core variation of MgO vs. depth in core 12687#8 and 10.

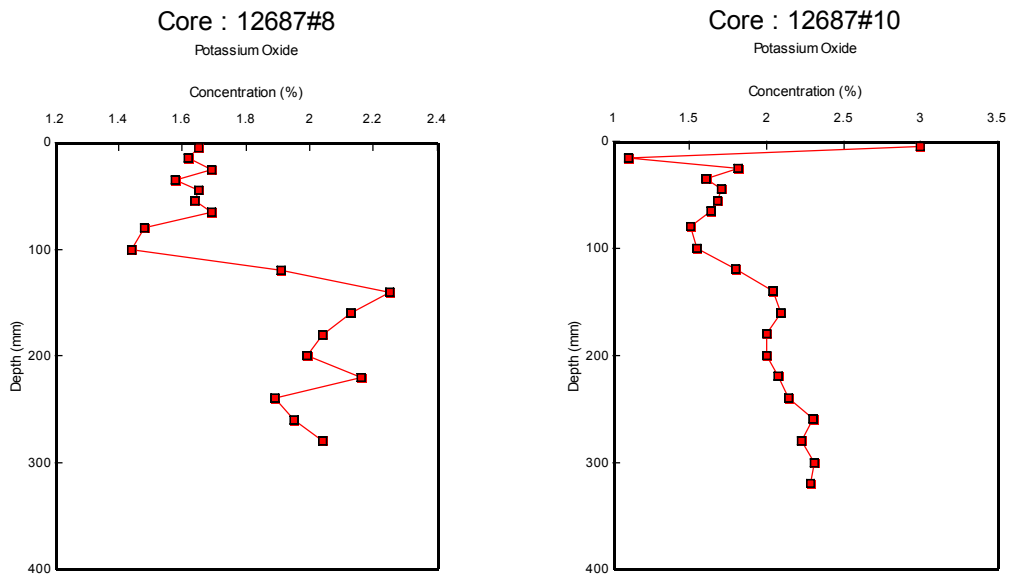


Fig. 4.8. Down-core variation of K₂O vs. depth in core 12687#8 and 10.

The CaCO_3 content of the both cores varied between $\sim 45\text{-}58\%$ (Fig. 4.9). Generally, the profiles are somewhat variable, and do not reveal any strong trends, for example when compared to particle size data.

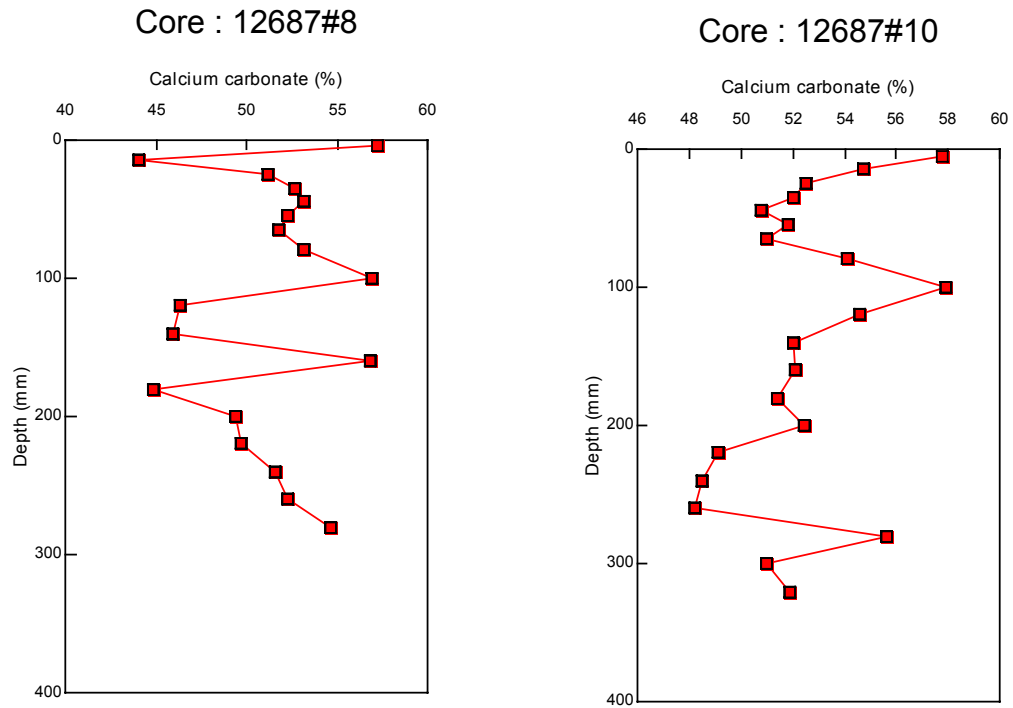


Fig. 4.9. Down-core variation of CaCO_3 vs. depth in core 12687#8 and 10.

4.4. TRACE METALS

4.4.1. Manganese

In the top unit, the average concentrations of manganese in all stages were significantly higher than in either the middle or bottom units in both cores (Figs. 4.10 to 4.15). Furthermore, in the top unit the solid state speciation was dominated by Stage 3 Mn. Hence, the average speciation in top unit was Stage 1 (Mn_1) $\sim 34 \mu\text{g g}^{-1}$; Stage 2 (Mn_2) $\sim 175 \mu\text{g g}^{-1}$; Stage 3 (Mn_3) $\sim 2900 \mu\text{g g}^{-1}$; Stage 4 (Mn_4) $\sim 68 \mu\text{g g}^{-1}$; Stage 5 (Mn_5) $\sim 20 \mu\text{g g}^{-1}$ whereas that in the middle and bottom units was $Mn_1 \sim 21 \mu\text{g g}^{-1}$; $Mn_2 \sim 90 \mu\text{g g}^{-1}$; $Mn_3 \sim 15 \mu\text{g g}^{-1}$; $Mn_4 \sim 34 \mu\text{g g}^{-1}$; $Mn_5 \sim 14 \mu\text{g g}^{-1}$.

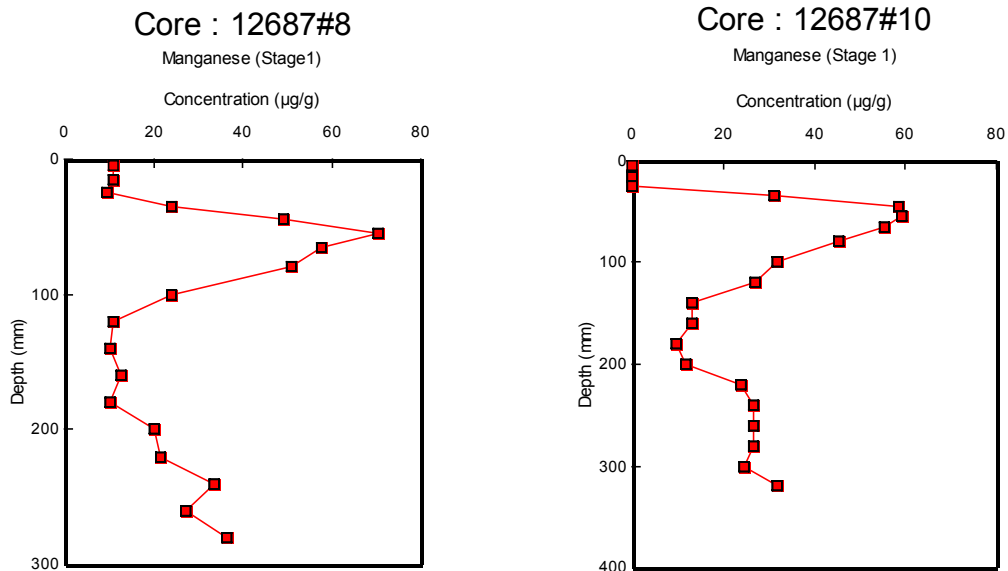


Fig. 4.10. Down-core variation of Mn_1 vs. depth in core 12687#8 and 10.

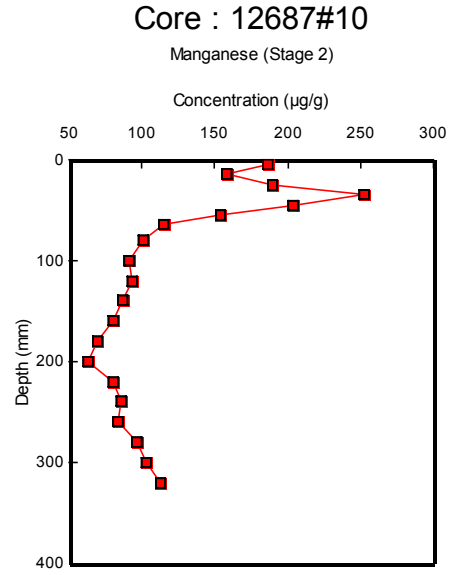
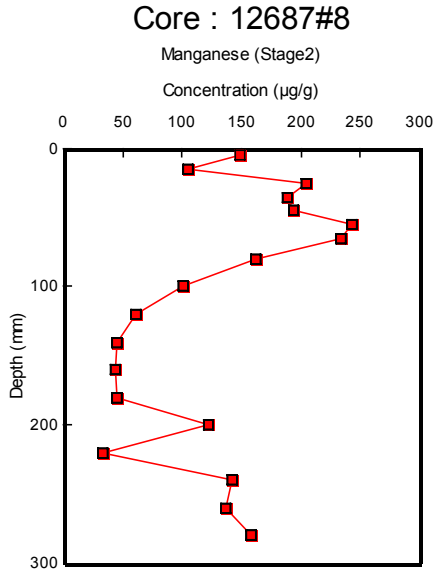


Fig. 4.11. Down-core variation of Mn_2 vs. depth in core 12687#8 and 10.

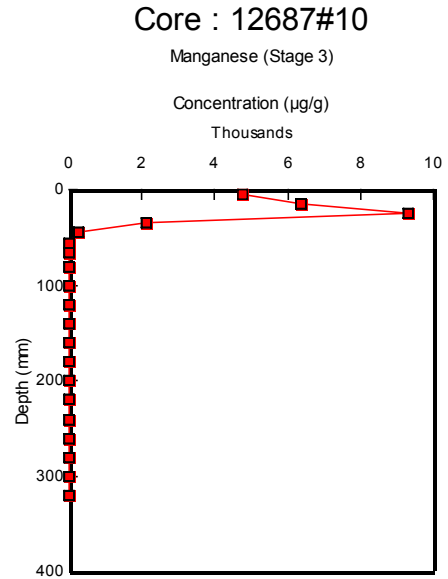
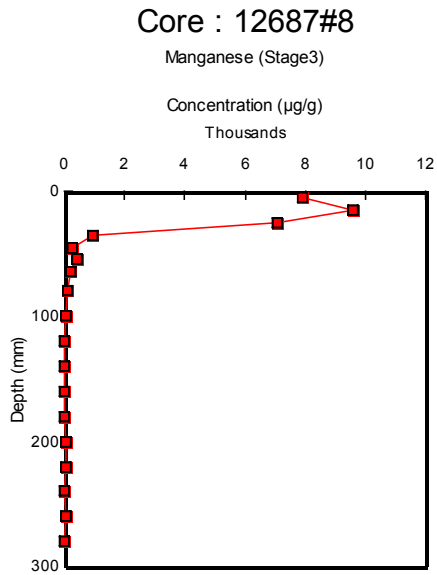


Fig. 4.12. Down-core variation of Mn_3 vs. depth in core 12687#8 and 10.

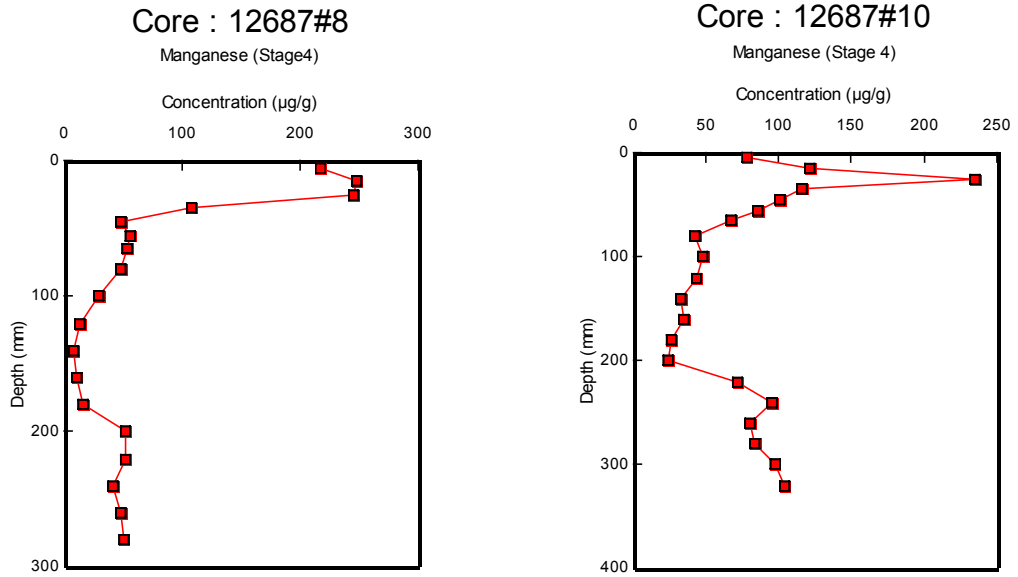


Fig. 4.13. Down-core variation of Mn_4 vs. depth in core 12687#8 and 10.

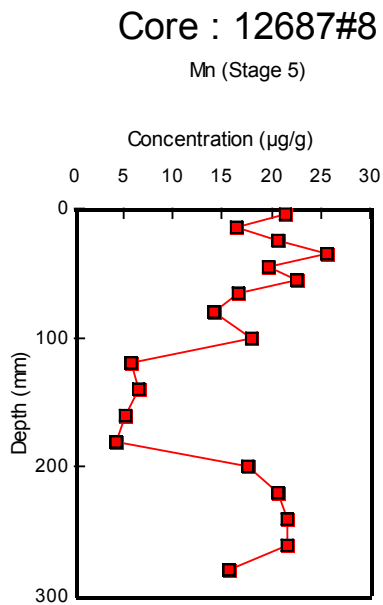


Fig. 4.14. Down-core variation of Mn_5 vs. depth in core 12687#8 and 10.

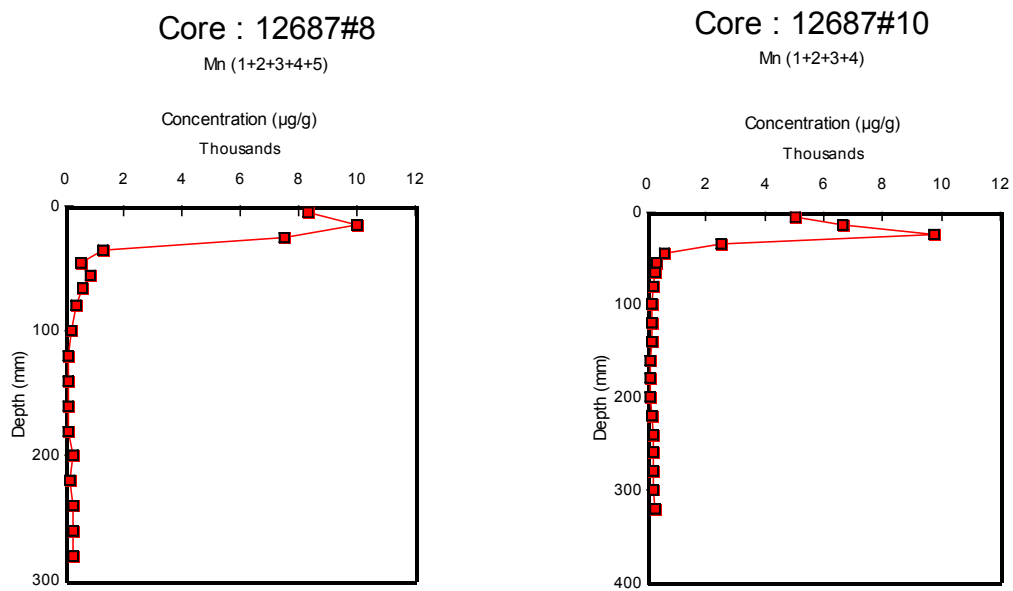


Fig. 4.15. Down-core variation of total Mn₁ - Mn₅ vs. depth in core 12687#8 and 10.

4.4.2. Iron

There was no detectable non-detrital Fe concentration in Stages 1 (Fe_1) and Stage 2 (Fe_2) in either core. The average concentrations for core 12687#8 in the top unit were $Fe_3 \sim 193 \mu\text{g g}^{-1}$; $Fe_4 \sim 786 \mu\text{g g}^{-1}$; $Fe_5 \sim 792 \mu\text{g g}^{-1}$. The average concentration in the middle and bottom unit was $Fe_3 \sim 10 \mu\text{g g}^{-1}$; $Fe_4 \sim 550 \mu\text{g g}^{-1}$; $Fe_5 \sim 900 \mu\text{g g}^{-1}$ (Figs. 4.16-4.19).

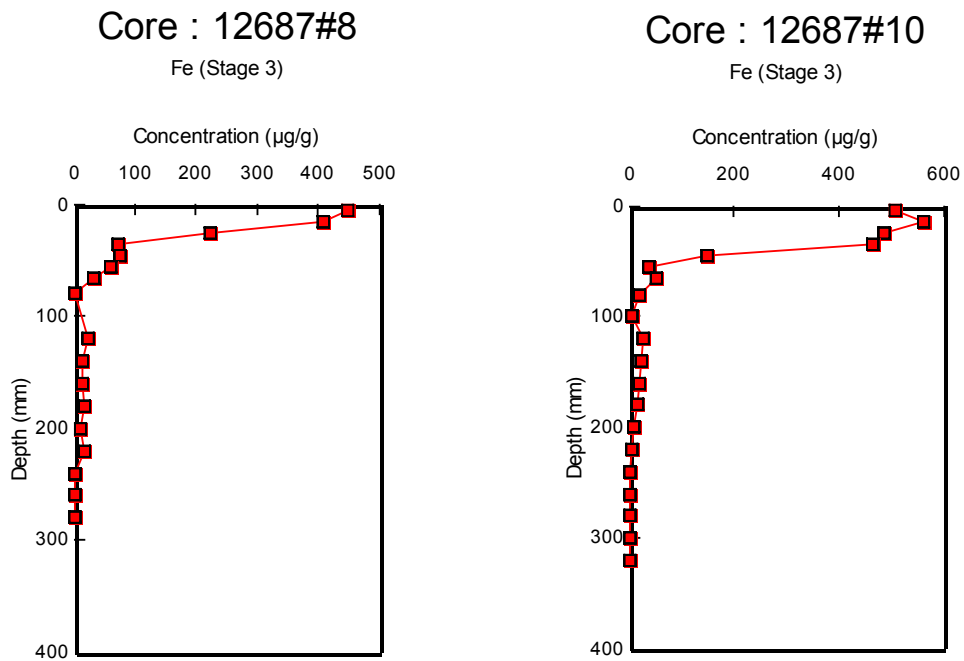


Fig. 4.16. Down-core variation of Fe_3 vs. depth in core 12687#8 and 10.

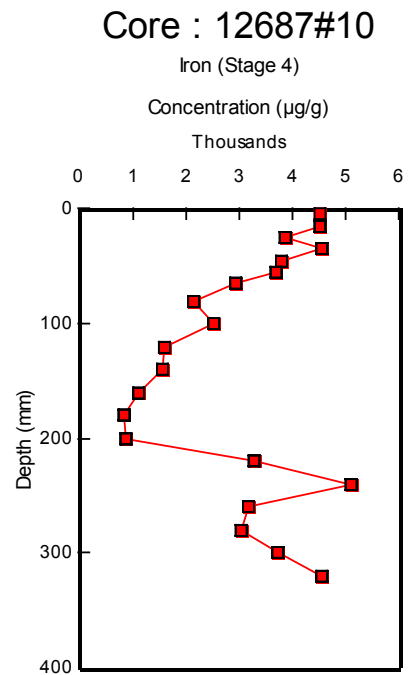
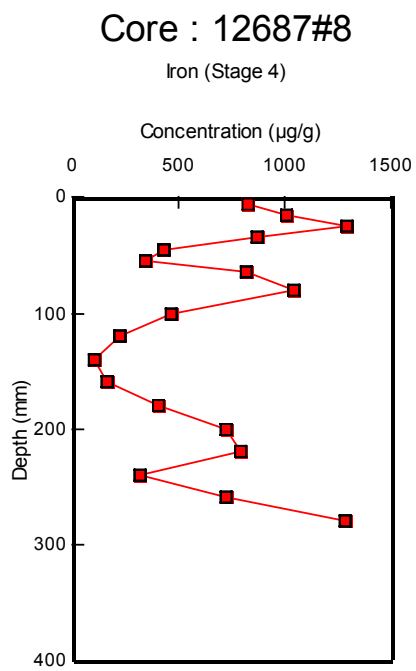


Fig. 4.17. Down-core variation of Fe_4 vs. depth in core 12687#8 and 10.

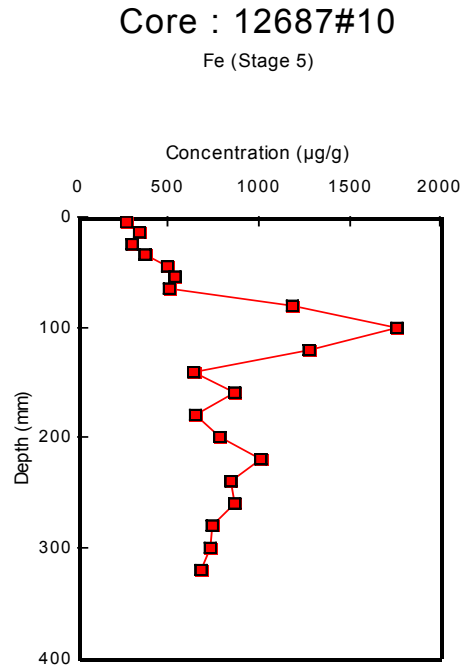
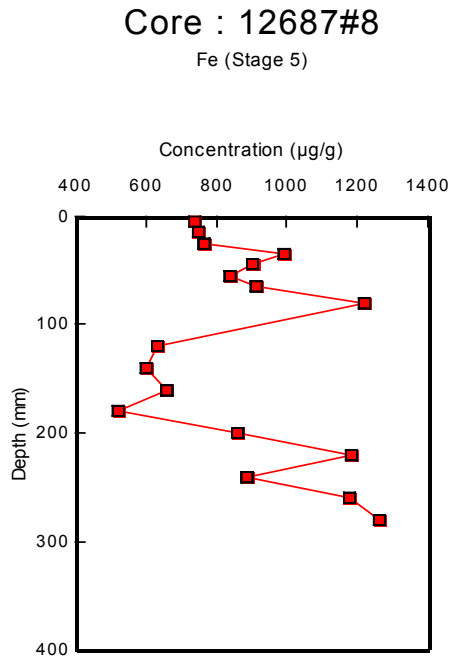


Fig. 4.18. Down-core variation of Fe₅ vs. depth in core 12687#8 and 10.

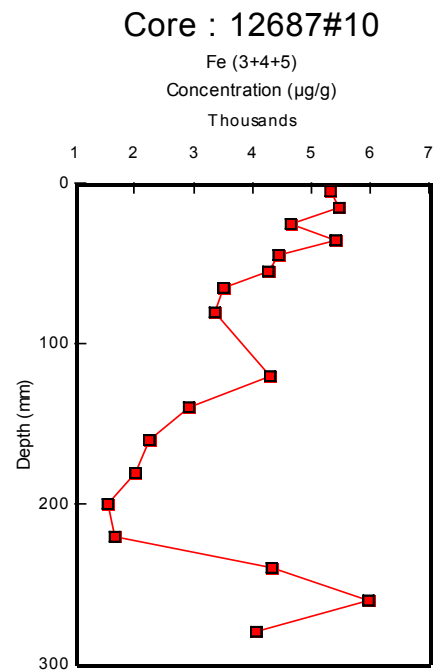
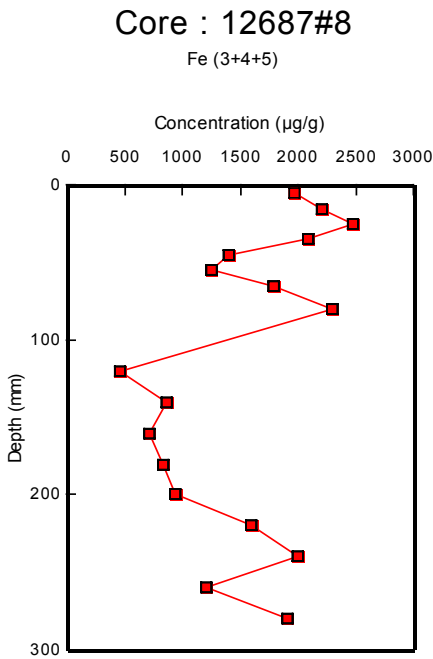


Fig. 4.19. Down-core variation of total Fe₃-Fe₅ vs. depth in core 12687#8 and 10.

4.4.3. Copper

The copper concentrations were low and co-varied with the lithology of both sediment cores (Fig. 4.20). Partitioning data indicate that the non-detrital Cu was held in “organic fractions” (Stage 5 - Cu₅).

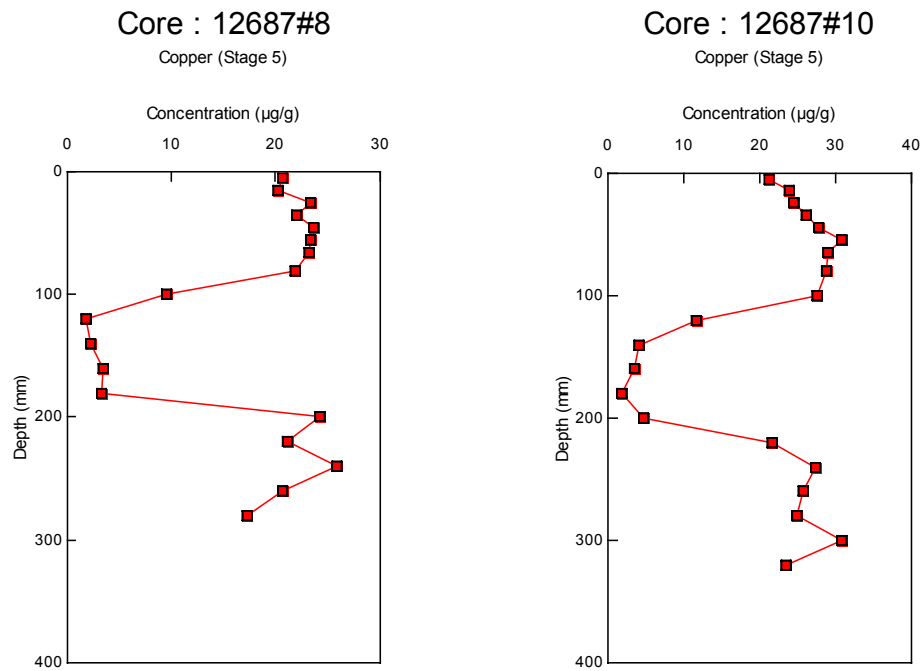


Fig. 4.20. Down-core variation of Cu₅ vs. depth in core 12687#8 and 10.

4.5. Organic Carbon - Bulk parameters

4.5.1. Total Organic Carbon

The total organic carbon (TOC) contents of both cores varied from <1 to 4% and showed considerable variability with depth (Fig.4.21). This variation largely coincided with the three identified sedimentological units.

The mean TOC contents in the three units of core #8 were: top unit ~2.5%; middle unit ~0.3% and bottom unit ~1.7%; In core #10 these were: top unit ~3%; middle unit ~0.7% and bottom unit ~1.6%. The levels of TOC in the bottom units of both the cores were ~85% of the surficial values. The TOC values in the top unit of both cores tended to increase with depth (Fig.4.21).

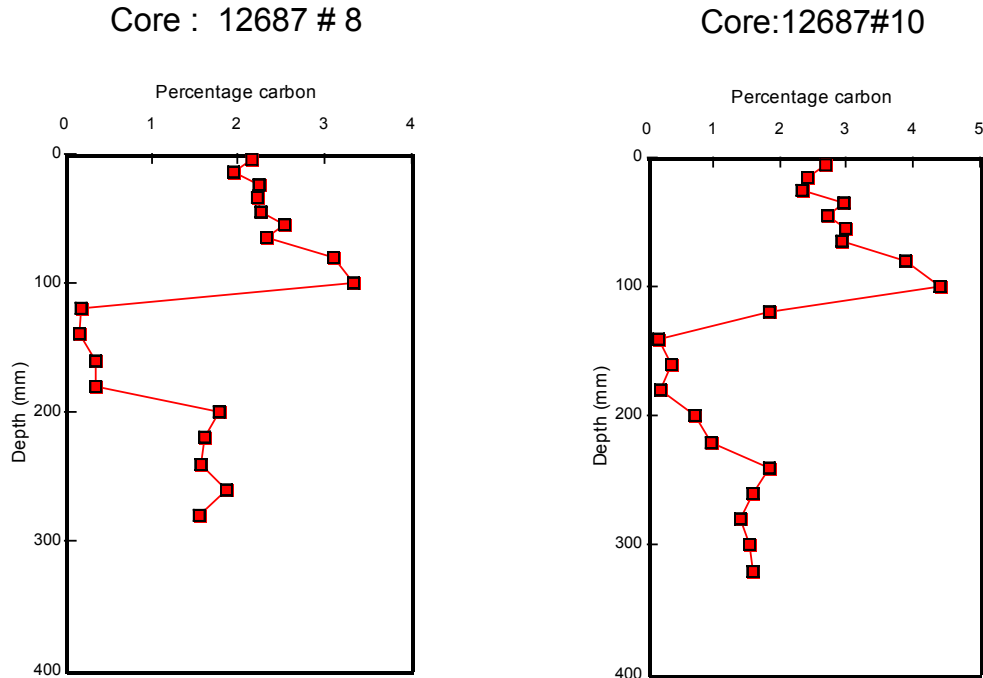


Fig. 4.21. Down-core variation of TOC vs. depth in core 12687#8 and 10.

4.5.2. C:N ratio

C/N ratios of both cores showed a significant increase (mean ~8-10) with depth in the top unit (Fig.4.22). Highest C/N values were in the middle unit (mean ~10-12), whereas those in the bottom unit were similar to the top unit in both of the cores (Fig. 4.22).

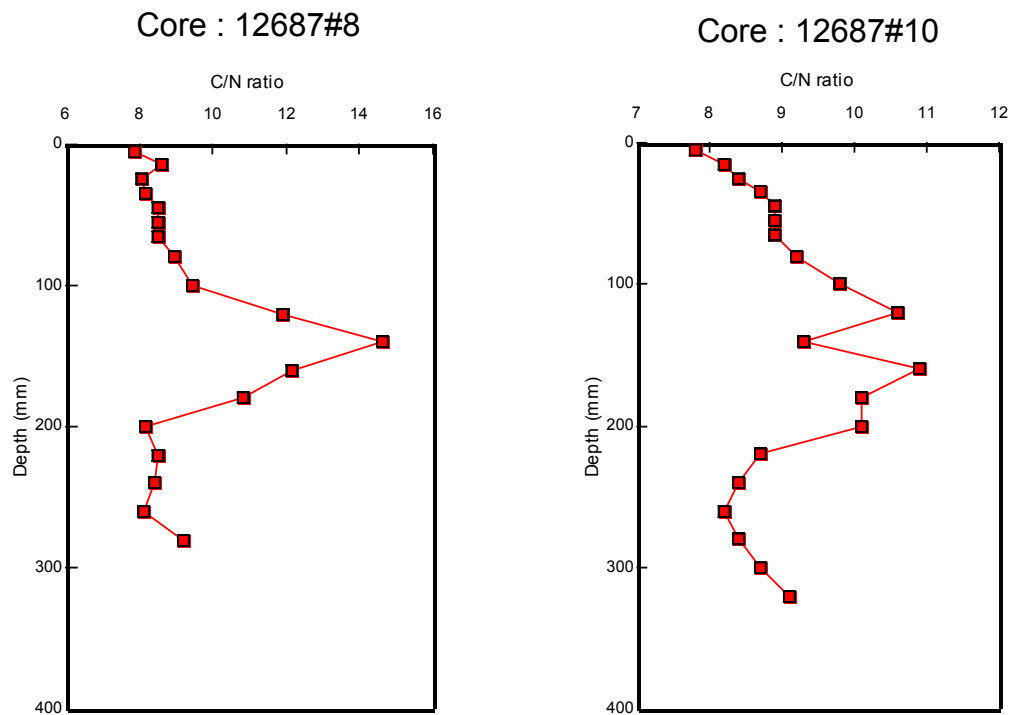


Fig. 4.22. Down-core variation of TOC vs. depth in core 12687#8 and 10.

4.6. Organic carbon-Molecular parameters

4.6.1. *Hydrolysable Amino Acids*

Concentrations of THAA in the abyssal sediments showed a similar trend to those of TOC (Fig.4.23). Hence, the highest concentrations of THAAs were found in the top unit (61.1-39.5 $\mu\text{mol g}^{-1}$; average 43.8 $\mu\text{mol g}^{-1}$); lowest in the middle unit (2.4-3.9 $\mu\text{mol g}^{-1}$; average 3.1 $\mu\text{mol g}^{-1}$) and slightly higher in the bottom unit (6.1-15.0 $\mu\text{mol g}^{-1}$; average 10.6 $\mu\text{mol g}^{-1}$). The THAA profiles of core #10 were very similar, although there was considerably variability in their concentrations in the top unit (Fig.4.23) and the amount of THAA concentrations in the middle and bottom units were three times and twice as high as in core #8, respectively. Normalisation of THAA to TOC (as % Taa-C; Cowie and Hedges, 1992) indicated that there was down core variability with a number of evident sub-surface maxima in both cores. However % Taa-C values generally decreased with depth (Fig.4.24), and further reflected higher values in core #10 than #8, below the top unit.

4.6.2. *Hydrolysable Carbohydrates*

The THCH concentration profiles for both cores (Fig. 4.23) were similar to those of the THAAs, again with the highest concentrations in the top unit compared to middle and bottom units (e.g. core #8, mean values 25.7, 3 and 13.6 $\mu\text{mol g}^{-1}$; core #10, mean values 27.4, 6.6 and 11.2 $\mu\text{mol g}^{-1}$ respectively).

THCH concentration normalised with respect to TOC (as %Tsugars) again showed more variability in core #10 compared to core #8 (Fig.4.25) in a similar way to the % Taa-C profiles (Fig. 4.24).

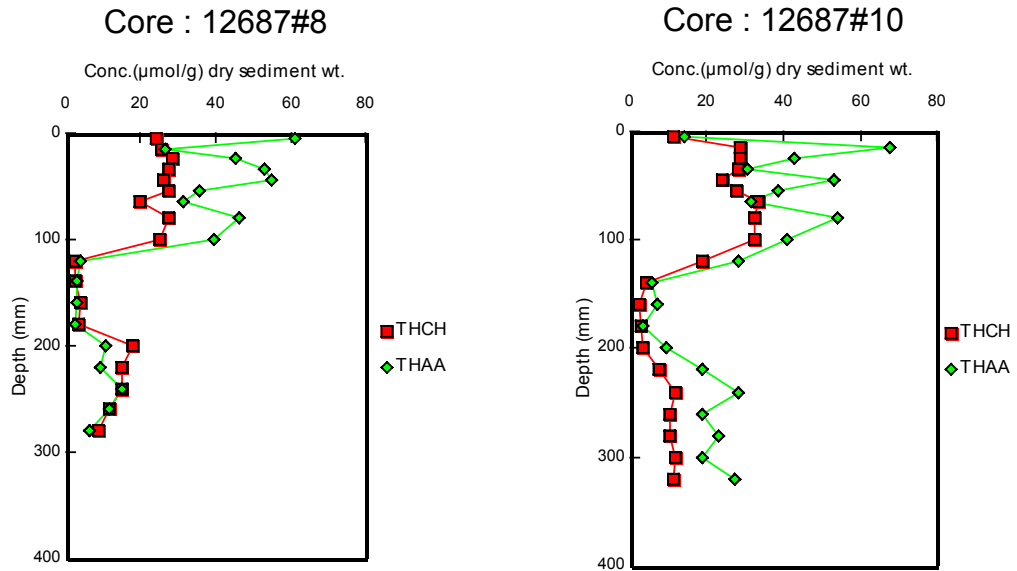


Fig. 4.23. Down-core variation of THCH and THAA vs. depth in core 12687#8 and 10.

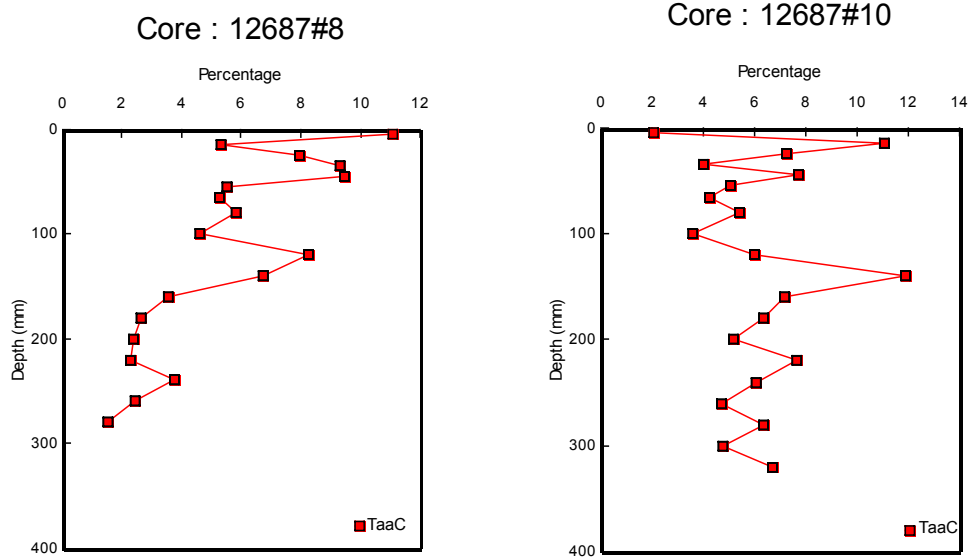


Fig. 4.24. Down-core variation of mole % TaaC vs. depth in core 12687#8 and 10.

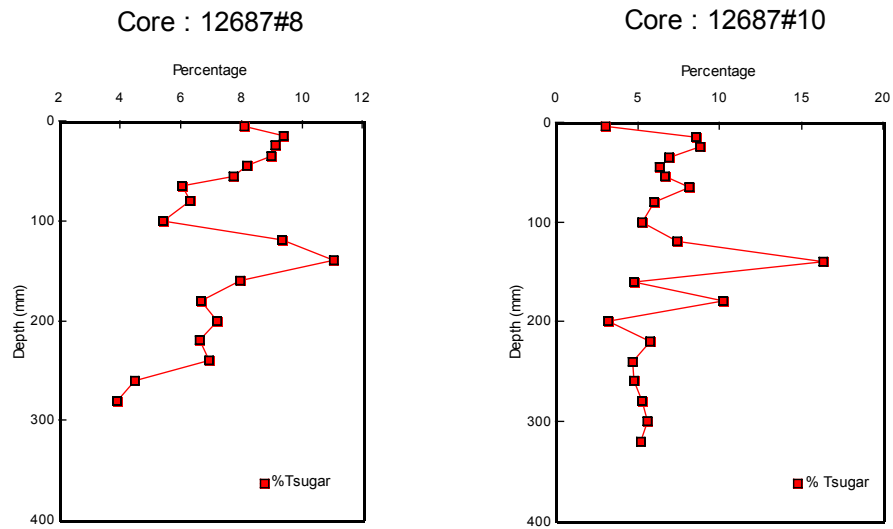


Fig. 4.25. Down-core variation of mole % Tsugar vs. depth in core 12687#8 and 10.

4.7. DISCUSSION

The water contents, particle-size distributions, organic matter composition, and clay mineralogy determined in the cores #8 and #10 suggest that at this abyssal site, sedimentation is influenced by turbidites.

This can be clearly seen in the water contents of the two sediment cores, which show a pronounced feature, decreasing abruptly below ~100 mm, and increasing again below ~210 mm (Fig. 4.1). This is entirely consistent with the particle-size spectrum (Fig. 4.2) and reflects the fact that the porosity of the sands of the middle unit is much lower than are of the silt-rich sediments of top and bottom units (Fig.4.2).

The formation of this sediment 'sandwich' exerts a primary constraint on the down-column distribution profiles of a number of elements because, in general, the silt components are enriched relative to the sand components in most elements (Si being an exception to this; Horowitz, 1991; Ravichandran *et al.* 1995). This makes it possible to distinguish between two kinds of elemental distribution profiles in the sediments.

- i) Those which *have not* suffered from post-depositional reactivity, and are constrained by the composition of the original sedimentary material deposited. The down-column profiles of these elements should, therefore, reflect the sedimentary conditions, and should retain differences between the silt and sand components; *i.e.* these elemental profiles may be regarded as being '*relict*', in so far as they have not suffered from changes affecting the sediment subsequent to its deposition.
- ii) Those which *have* suffered post-depositional reactivity, and which should be independent of constraints imposed by the composition of the original sedimentary

material deposited. These elemental profiles may be regarded as being '*reactive*', in so far as they have resulted from diagenetic processes subsequent to the deposition of the sediment.

The two sediment cores thus offer an ideal opportunity to assess trace-metal solid state speciation changes during early diagenesis.

4.8. Major elements : Si and Al

Silicon can be present in marine sediments in biogenous and lithogenous associations (Bostrom et al. 1972; Bischoff et al. 1979). From the manner in which the SiO₂ in the present cores varies with particle size, it would appear that most of the SiO₂ is lithogenous in the form of sand grains. Pure sand is almost 100% SiO₂ (Mason, 1958), and the effect of the silt-sand-silt sediment 'sandwich' is reflected most strongly in the down-column distribution of SiO₂ (Fig. 4.3) and in the Si : Al ratio (Fig. 4.26). The down-column distributions of both SiO₂ and Si : Al ratio represent 'relict' features, and may be used as a 'template' against which to compare the down-column distributions of the redox-sensitive trace metals, namely manganese, iron and copper.

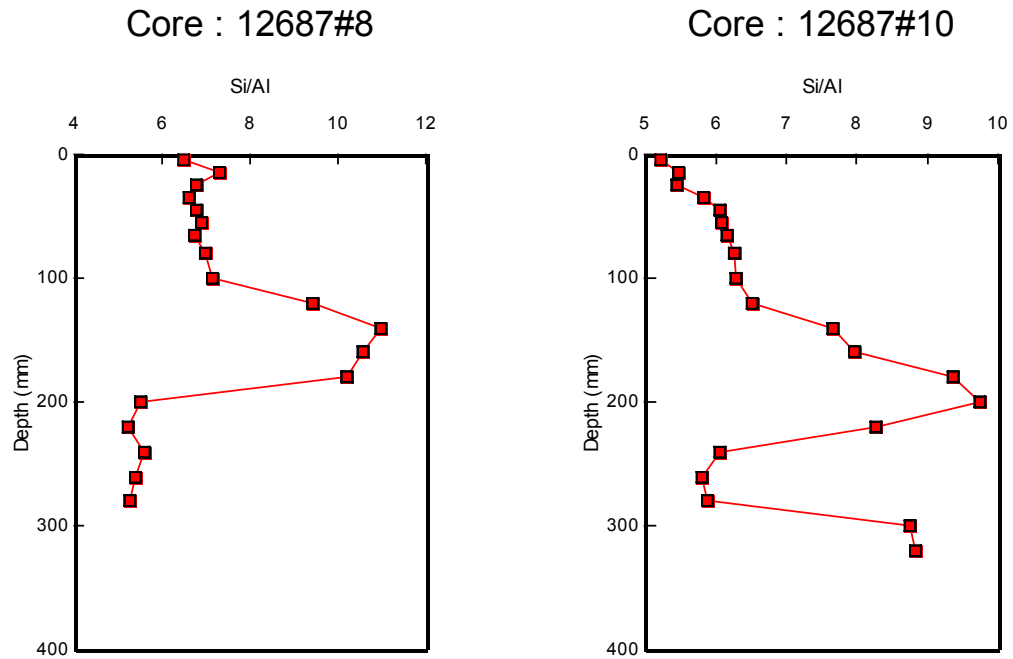


Fig. 4.26. Down-core variation of Si : Al vs. depth in core 12687#8 and 10.

4.9. Manganese

4.9.1. Total non-detrital Mn

i) The down-column profile of the total non-detrital Mn ($\Sigma\text{Mn}_{\text{n-d}}$) i.e. (ΣMn_1 to Mn_5 in the present study; see Chapter 3) is dominated by a Mn ‘spike’ with a maximum concentration at ~10-20 mm in core #8; and 20-30 mm in core #10 (Fig. 4.15). This down-column Mn ($\Sigma\text{Mn}_{\text{n-d}}$) profile does not follow the sediment lithology as shown, for example, by the Si : Al ratio profile described above.

Dymond (1984) reported that Mn scavenged from the water column is held in the exchangeable (Mn_1)/carbonate (Mn_2) association and that this does not change as particulates settle down through the water column. Indeed, Mn_2 dominates the solid state speciation in the middle (58%) and bottom units (50%) in both cores.

However, in the top unit of the sediment the Mn ($\Sigma\text{Mn}_{\text{n-d}}$) is dominated by the ‘new’ oxides of Mn_3 (see Chester *et al.* 1988) which make up an average of ~90% of the Mn ($\Sigma\text{Mn}_{\text{n-d}}$) over the interval (0-30 mm). This type of thin layer of sediment (<2 cm) marked by a distinct brown colour has also been observed in sediments from the upwelling on the continental margin of Latin America (Lyle, 1983). These “easily-reducible” Mn oxides (Chester *et al.* 1988) have probably been produced at the sea-water/sediment interface and are consistent with oxidising conditions in the surficial section of the top unit of the sediments. For example, “easily-reducible” Mn concentrations closely follow the trend for total Mn in other oxic sediments accounting for $68\pm 5\%$ of total in the nearshore areas (Trefry and Presley, 1982); in the oxic layer of a Nares Abyssal Plain Core more than 85% ΣMn was associated with Mn_3 oxides (Jacinto, 1988). It is thought that the Mn_3 oxides form from sedimentary Mn held within a ‘mobile pool’, or from Mn^{2+} in the overlying sea water

(Jacinto, 1988). It is probable that Mn_2 undergoes transformation at the sediment surface to Mn_3 oxides.

As mentioned in Chapter 1, Mn is a redox sensitive element. Under conditions of low Eh and pH, the reduced forms of Mn (generally Mn (II)) are thermodynamically favoured over the oxidised forms (generally Mn (IV)), which are generally found as solid oxides and oxyhydroxides may be reduced to dissolved Mn (II). There was very little change in the percentage of ΣMn held in Mn_3 oxides with depth in core #8, and Mn_3 was not detectable in core #10 below 60 mm. Hence the Mn_3 oxides have been preserved only, in the top unit of the cores (Fig. 4.12).

Overall, therefore, the Mn (ΣMn_{n-d}) down-core profile (Fig.4.15), which is dominated by the Mn 'spike', is constrained by the distribution of the 'new' Mn oxides (*i.e.* Mn_3). The distribution of the Mn_3 'new' Mn oxides is similar to those shown by Froelich *et al.* (1979), in that there is a single solid Mn spike located below the sediment surface. This is consistent with the following series of events. 'New' Mn oxides are formed at the sediment surface under oxic conditions and some of these are buried as the sediment accumulates. At depth, these 'new' Mn oxides are utilized as secondary oxidants under sub-oxic conditions leaving the lower sediments impoverished in the 'new' oxides, dissolved Mn is released into the interstitial waters, migrates upwards, and is precipitated above the base of the oxic layer (Lynn and Bonatti, 1965; Froelich *et al.* 1979; Pedersen and Price, 1982; Buckley and Cranston, 1988; Burdige, 1993). It may be concluded, therefore, that the down-column profiles of both Mn (ΣMn_{n-d}) and the 'new' Mn oxides indicate post-depositional migration, and so represent 'reactive' features.

In contrast to the Mn associated with the 'new' oxides of Mn_3 , that associated with the 'aged' Mn oxides of Mn_4 exhibits a 'relict/reactive' down-column profile

(Fig.4.13). The concentrations of Mn associated with ‘aged’ oxides decrease in the sand layer, relative to the silt layer above and below, indicating a relict distribution profile. However, the Stage 4 Mn concentration in the upper silt layer (av.~68 and ~99 $\mu\text{g g}^{-1}$ in core #8 and 10 respectively) is considerably higher than that in the lower silt layer (av.~ 48 $\mu\text{g g}^{-1}$ and ~92 $\mu\text{g g}^{-1}$ in core #8 and 10 respectively), and apparently there is also a Mn₄, Mn ‘spike’ with a maximum concentration of ~100 and ~200 $\mu\text{g g}^{-1}$ respectively in core #8 and 10 (compared to a maximum of ~9500 $\mu\text{g g}^{-1}$ in the Mn₃ spike).

These results must be treated with some caution, because the concentrations of Mn₃ were relatively so high and there may have been some “over-spill” into the operationally-defined fraction Mn₄. In order to assess this, the residue from Stage 3 was leached for second time with the Stage 3 reagent (1M NaOAc+0.25M NH₂OH.HCl; see Chapter 3). When this was done, it was found that there was virtually no further Mn₃ released in the samples below 40 mm section in both the core. However, in the Mn₃ spike as much as ~100 and 200 $\mu\text{g g}^{-1}$ for core #8 and 10, respectively, was released from the residue. Although, this only amounted to ~1.5% and 3.0% in core #8 and 10, respectively, of the Mn₃ found in the spike, it accounted for ~60% in core #8 and 50% in core #10 of the Mn₄ measured directly from the residue in the first instance. This suggests that the latter values were, in fact, an artifact caused by the extremely high concentrations of Mn₃ oxides in these surficial sediments. At these high Mn₃ concentrations it seems that the Stage 3 leaching agent is not 100% efficient and that the spike found in the Mn₄ is a ‘phantom’ feature. Although this is a trivial fraction of the Mn₃ it can make a very significant contribution to the Mn₄.

Taking this into account, there was still an increase in Mn₄ towards the top of the core. However, the maximum Mn₄ concentrations were now only ~120 and 200 µg g⁻¹ for core #8 and 10 respectively, which is only around three times that in the samples below 30 mm section of the core, and the ratio of the maximum Mn₃ to Mn₄ in the spike is 90 (core #8) and 40 (core #10). The Mn₄ down-core profile is therefore, a 'relict' feature (cf. Stage 3) and the 'aged' Mn oxides have probably not suffered sub-oxic diagenetic changes.

Mn₅ shows a down-column profile (Fig.4.14) in which the Mn has about the same concentrations in the two silt layers, but decreases in the middle sand layer. This indicates that the "organically-associated" Mn has a 'relict' profile in core #8 and has not been affected by diagenetic changes. Mn₅ was absent in core #10. That is, during the diagenetic sequence the "organically-associated" Mn has not been utilized as secondary oxidant; this form of Mn can therefore be stored in the sediments for longer periods than the 'new' oxide.

4.9.2. Integrity of sequential leaching

The down-column profiles of Mn can be used to verify the integrity of the fractions separated by the sequential leaching technique for determination of solid state speciation. The leached stages are 'operationally-defined', and one of the problems with these techniques has been the extent to which the fractions are a) different from each other, and b) geochemically viable (Tessier *et al.* 1979; Ure and Davidson, 1995).

a) It is clear from the down-column Mn solid state speciation data that the fractions associated with Mn₃, Mn₄ and Mn₅ behave differently. The Mn₃ ‘new’ oxides Mn profile clearly indicates a ‘reactive’ profile, the “organically-associated” Mn₅ profile clearly indicates a ‘relict’ profile, with that of the ‘aged’ oxide Mn₄ profile being intermediate between the two.

b) The only way of verifying the viability of the fractions is if ‘geochemical consistency’ can be injected into the data. Quite clearly, this the case for the ‘new’ Mn₃ oxides since their behaviour can be related to oxic/sub-oxic changes occurring in early diagenesis; thus, the distribution of the ‘new’ oxides fits the model and experimental profiles found for total Mn in marine sediments (Froelich et al. 1979; Burdige, 1993; Dhaker and Burdige, 1996).

4.9.3. Summary

The solid state speciation of the non-detrital Mn in the three abyssal sediment units is biased by the Mn₃ ‘new’ oxides spike in the top unit; i.e. a ‘reactive’ feature (Fig.4.12). It is interesting to note, however, that although the concentrations of Mn in the bottom unit are higher than those in middle unit, the speciation of Mn between the non-detrital phases is very similar in the two units. It would appear, therefore, that after the effects of the Mn₃ ‘new’ oxide Mn cycle have been removed, the other Mn fractions follow the particle-size characteristics of the core; i.e. the same Mn template is deposited and the differences in concentration between middle and bottom unit reflect dilution by the trace metal-poor sand of the middle unit. It may be concluded therefore that sub-oxic diagenesis has proceeded to a stage at which Mn oxides are utilized as secondary oxidants. The results from the present study have

shown that it is the 'new' Mn₃ oxides which take part in the Mn diagenesis and are stripped from the sediment at depth. Mn which enters the interstitial waters is reprecipitated as 'secondary generation' Mn₃ oxides at the top of the core in the form of a spike under oxic conditions at the base of the oxic layer, as predicted by Froelich *et al.* (1979). The fact that the Mn spike lies close to the sediment surface indicates that the oxic layer is relatively very thin. If the layer was absent, the dissolved Mn would escape into the overlying sea water, and therefore there would be no deposition of 'new' Mn oxides in the sediment.

4.10. Iron

4.10.1. Total non-detrital Iron

The down-column profile of the total non-detrital Fe (ΣFe_{n-d}) in core #8 shows a considerable scatter (Fig. 4.19), the overall shape of the profile exhibits the general three-unit shape of the particle-size distribution in both cores; *i.e.* the concentrations in core #8 are similar in the silt-dominated top (1771 $\mu\text{g g}^{-1}$) and bottom units (1910 $\mu\text{g g}^{-1}$) and decrease significantly in the sand-dominated middle unit (992 $\mu\text{g g}^{-1}$). Similarly, core #10 showed a high concentration in the top ($\sim 4500 \mu\text{g g}^{-1}$) and bottom units ($\sim 4700 \mu\text{g g}^{-1}$) and decreased significantly in the sand-dominated middle unit ($\sim 2500 \mu\text{g g}^{-1}$). Unlike Mn, only a relatively small amount of the total non-detrital Fe was accounted for by 'new' Fe₃ oxides. In the top unit, Fe₃ accounted for an average of $\sim 11\%$ (core #8) and $\sim 6\%$ (core #10) of the total non-detrital Fe, compared to $\sim 90\%$ of the total non-detrital Mn. However, there is a strong similarity between the stage 3 distributions of Fe and Mn; thus, Fe₃ (Fig. 4.16) has a distribution which is very different from those of Fe₄ (Fig. 4.17) and Fe₅ (Fig.

4.18) and is independent of the three-unit sedimentation, and is concentrated into a spike in the upper region of the top unit. At first sight, therefore, this would suggest that the 'new' oxides in the Fe profile are a 'reactive' feature formed as the result of post-depositional diagenetic activity; *i.e.* Fe₃ 'new' Fe oxides have been used as secondary oxidants and the Fe released has been recycled as in the case of Mn (see above).

Furthermore, the spike appears in same place for both Fe and Mn. However, this raises a paradox, because according to Froelich *et al.* (1979) there is a diagenetic sequence in the utilization of secondary oxidants which manifests itself in a downward zonation, with Mn oxides being destroyed to completion (Fig. 17 in Froelich *et al.* 1979) before Fe oxides are utilised. This, in effect, would lead to a fractionation of Mn from Fe, with the two metals being reprecipitated at different depths in a core:

- i) Mn at the top of the Mn utilization zone (the base of the oxic layer),
- ii) Fe below Mn following its release during the destruction of Fe oxides, resulting in the production of dissolved Fe²⁺ which then diffuses upwards to be precipitated by oxidation, probably by nitrate (Thomson *et al.* 1995). Unfortunately, no pore water data are available that might confirm the involvement of nitrate reduction. However, it seems the most likely oxidant in view of the Froelich scheme (Froelich *et al.* 1979).

In the Arabian margin sediments, however, the 'new'- oxide Fe₃ spike co-occurs with the Mn₃ 'new' oxide spike. It is of interest, therefore to compare the Mn and Fe characteristics in the upper portion of top unit.

- a) The 'new' oxides both occur in the form of a 'spike', with maximum concentrations below the sediment surface. However, the maximum 'new' oxide

concentrations of Mn ($\sim 9.5 \times 10^3 \mu\text{g g}^{-1}$ Mn) were three orders of magnitude higher than those of Fe ($\sim 500 \mu\text{g g}^{-1}$ Fe), the Mn : Fe ratio observed from the both cores at the spike maximum being 19.

b) The ratio between the maximum concentration of Mn₃ in the spike and that at depth of 80 mm (the lowest sample in the top unit which contains both Mn and Fe in Stage 3) is 129, compared to 14 for that of for Fe in core #8, but this ratio in core #10 was at depth of 50 mm is 38, compared to 23 for that of for Fe (Mn₃ concentrations below 50 mm sections were not detectable).

c) At the spike maximum, Mn₃ makes up $\sim 40\%$ of the total non-detrital Mn, compared to the Fe₃, which at the spike maximum makes up only $\sim 25\%$ of the total non-detrital Fe in both cores.

Clearly, therefore, the spike contains considerably more of the total non-detrital Mn than the total non-detrital Fe, and in fact dominates the distribution of total Mn in top unit. An alternative explanation for the Fe₃ 'new' oxides Fe spike is proposed here. It is unlikely that the 'new' Mn oxides formed at the sediment surface are pure oxides of the metal, but rather they contain some amount of Fe and form a 'ferromanganese oxide'. When the 'new' Mn₃ oxides are destroyed as secondary oxidants, either as '**first generation**' oxides or as 'second, third etc., generation' as the Mn cycle proceeds, the Fe₃ associated with them will also be released and will migrate upwards to form a 'minor' Fe spike at the same position as the 'major' Mn spike.

Although there are no other data available on the solid state speciation of Mn and Fe in the Mn spikes of deep-sea sediments, two other lines of information can be used to justify this explanation.

i) **Evidence from interstitial waters:** Froelich et al. (1979) gave data on the distribution of Mn and Fe in the interstitial waters, and solid phase Mn, of Core 4GC1 taken in a water depth of 3612 m off the west Africa continental margin. This sediment exhibited a solid phase Mn spike at the top of the sediment in a similar manner to that in the Arabian Sea abyssal sediments (see Fig. 4.12). The interstitial water data revealed that dissolved Mn had a mirror image of the solid phase Mn decreasing to approach zero concentrations at the sediment surface. There was no data on the solid phase Fe, but the interstitial water profile of dissolved Fe showed that there was a decrease in concentration towards the top of the core (see Fig. 8, cited in Froelich et al. 1979). No actual data were given in the paper, hence concentration data had to be extracted from the diagrams. However, using concentrations derived in this way, it is possible to make a number of tentative predictions from the data provided by Froelich et al. (1979).

1. Assuming that the dissolved Mn reaches zero concentration at the top of the core, and that the dissolved Mn concentration reaches a generally steady level below the region of the solid Mn spike at a concentration of $\sim 75 \mu\text{M}$ then the maximum loss of dissolved Mn is therefore $\sim 75 \mu\text{M}$ and all this is assumed to be taken up in the Mn spike.

2. The dissolved Fe concentration is more varied than that of dissolved Mn, but the value below the Mn spike is $\sim 15 \mu\text{M}$, compared to $\sim 10 \mu\text{M}$ towards the top of the Mn spike. Using the same assumptions as for Mn, therefore, the maximum loss of dissolved Fe is $\sim 5 \mu\text{M}$, and if all of this had precipitated in the spike with Mn, then the Mn : Fe ratio in the upper part of the spike would be ~ 15 , which is reasonably close to the average of 19 in three top samples of the Mn spike in core 12687 # 8 and 10.

Although, the calculation carried out above must be treated with extreme caution, not the least because the data have been acquired directly from Figures in Froelich et al. 1979, it does show that i) dissolved Fe decreases across the solid phase Mn spike, and ii) that if it is consumed by the Mn₃ oxides then the Mn : Fe ratios determined in the spike of both Oman Margin cores are of the same order.

ii) Evidence from ferro-manganese nodules : Ferro-manganese nodules have been sub-divided into a number of types in relation to the principal mechanism which is involved in the supply of Mn and Fe (see e.g. Chester, 1990). The four main types are: a) hydrogenous nodules, i.e. direct precipitation or accumulation of colloidal metal oxides in sea water, b) oxic diagenetic nodules, which refers to a variety of ferromanganese accretion processes occurring in oxic sediments, c) supply from below in the sediment following sub-oxic diagenesis i.e. results from reduction of Mn⁺⁴ by oxidation of organic matter in the sediments, and d) supply from hydrothermal sources i.e. elements that are solubilized during hydrothermal activity and formation of metal-rich precipitates (e.g. Red Sea System). The sub-oxic nodules of type (c) often display a top/bottom compositional difference, with a sea water supply to the top and interstitial water supply to the bottom. Dymond et al.(1984) gave data on the top/bottom differences for Mn and Fe in a series of ferro-manganese nodules from a hemi-pelagic site in the Pacific Ocean.

Table 4.1. Mn : Fe ratios in the top (sea water source) and bottom (interstitial water source) portions of ferro-manganese nodules from a hemi-pelagic site in the Pacific Ocean (MANOP Site H); data from Dymond et al. (1984).

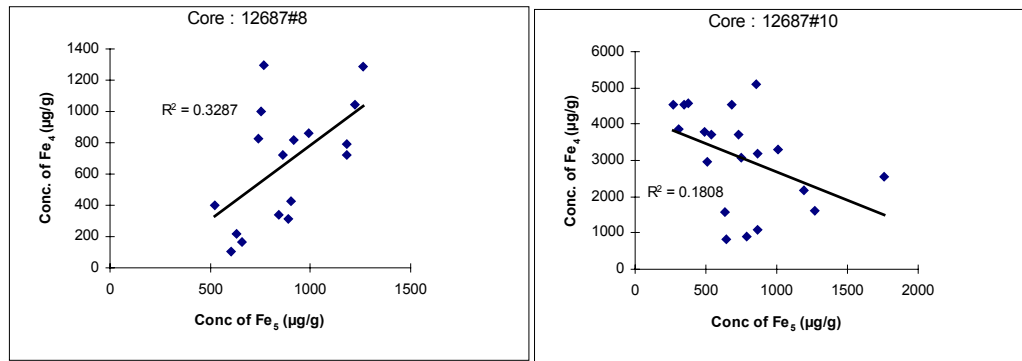
	Geometric average	Mn : Fe range
Nodule tops (n=27)	10	5.3-32 (4 samples >20)
Nodule bottoms (n=27)	43	16-69

From the data in Table 4.1, it can be seen that there is difference between the Mn : Fe ratios for the top and bottom portions of the nodules, the ratio being higher in the bottoms supplied from interstitial water. The Mn : Fe ratio in the abyssal sediment spike falls into the range (16-69) of the nodule bottoms which are supplied from interstitial water following sub-oxic diagenesis.

It may be concluded from Dymonds work (Dymond et.al. 1984) that Fe can be precipitated with Mn from interstitial waters at the upper portions of deep-sea sediments, either into the sediments themselves or into ferro-manganese nodules. It is proposed, therefore, that the Stage 3 spike in the top unit is associated with the utilization of Mn oxides in sub-oxic diagenesis and the co-precipitation of associated Fe following upward migration, and does not indicate that the stage has been reached at which Fe oxides are utilized a secondary oxidants. Adsorption on Fe-Mn oxides and incorporation in authigenic minerals, such as anatase, are also possible sources of trace elements in the Arabian Sea sediments (Satyanarayana and Ramana, 1994).

The dominant component of non-detrital iron in the Arabian Sea abyssal sediments was made up of Fe₄ “aged” oxides with average of ~40% (core #8) and 80% (core #10) of the total non-detrital Fe. The Fe₄ concentration profiles follow the 3-unit distribution; i.e. the concentrations in the top unit (core #8: 786 µg g⁻¹; core #10: 3636 µg g⁻¹) and bottom unit (core #8: 765 µg g⁻¹; core #10: 3931 µg g⁻¹) are similar and are higher than in the middle unit (core #8: 221 µg g⁻¹; core #10: 1551 µg

g⁻¹). However, there are considerable variations in both the concentrations and percentage speciation in all three units, although the shape of overall profile would suggest that the Fe₄ oxides have not suffered significant diagenetic changes. Further, the “organically-associated” Fe₅ (more dominant in core #8 than core #10) varied (see also Mn₅) in the same way as the Fe₄ oxides (more dominant in core #10 than core #8), and unless the two binding fractions undergo similar diagenetic changes their profiles are probably dominated by sedimentary features (Fig. 4.27). However, further work is required on Fe in diagenesis before the Fe₄ trends can be confirmed (see also Chapter 5).



significant at $p < 0.02$

no significant

Fig. 4.27. Relationship between Fe₅ vs. Fe₄ in core 12687#8 and 10.

4.10.2. Summary

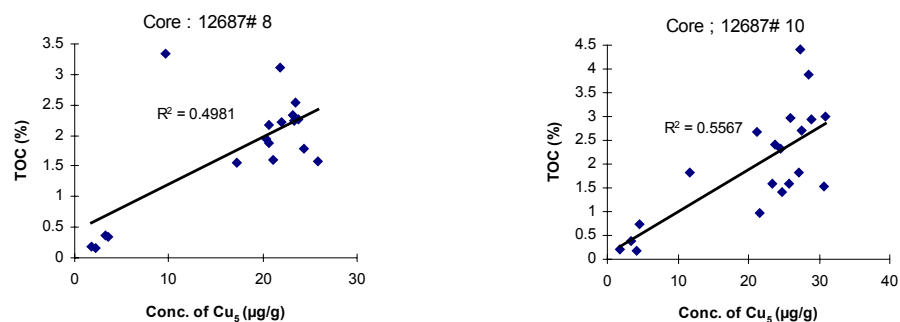
The speciation of non-detrital Fe differed from that of Mn, in that no Fe₁ or Fe₂ was detectable in the samples; on the other hand, there was a Fe₃ spike at an identical depth to that of Mn₃. It is proposed that this reflects Fe associated with Mn oxides in sub-oxic diagenesis, rather than the reduction of Fe₃ oxides through Fe respiration, and subsequent precipitation from Fe-rich pore-waters. Fe_{4,5} do not appear to have undergone any significant diagenetic alteration.

4.11. Copper

Chester *et al.* (1988) reported that ΣCu probably reaches the sediment surface in a variety of forms *i.e.* detrital (Cu₆) oxides (Cu_{3,4}) and in association with organic (Cu₅) phases, with the latter often being important. For example, in particulate material from the North Atlantic Ocean, more than 50% of ΣCu was held in the

“organic” phase (Chester *et al.* 1988). The non-detrital partitioning data for copper concentrations revealed that Stages (1 to 4) were not detectable in the abyssal sediments of Arabian sea, the copper (Cu_5) being held exclusively in “organic-associations” (Fig. 4.20). The Cu in the “organic” phase is mainly associated with biogenic carriers which have settled through the water column (Callender and Bowser, 1980; Chester *et al.* 1988; Dymond, 1984). Once the particulate material is deposited at the sediment surface, the organically-associated copper (Cu_5) generally undergoes phase transformations as the organic carriers are destroyed. However, some of the “organic-associated” copper may remain preserved in sediments, its amount depending on the diagenetic environment of deposition. In rapidly accumulating sediments, the amount of Cu_5 retained can be significant. For example, the concentrations of Cu_5 in diagenetically active hemipelagic sediments of the Atlantic Ocean deposited in the marginal regions were relatively high (>10%; Thomas, 1987) whereas its concentrations decrease (<<10%) towards the open ocean such as in less diagenetically active sediments such as from the Mid-Atlantic Ridge.

In the abyssal sediments analysed in the present study, the Cu_5 distribution is of particular interest and seems to be controlled by changing sedimentology of the three units (Fig. 4.20; see also above). Chester *et al.* (1988) concluded that the preservation of Cu_5 in bottom sediments is directly related to the amount of primary productivity in the overlying waters. This is confirmed by the strong relationship between Cu_5 and TOC ($r^2 = 0.5$) in the Oman Margin sediments (Fig.4.28). This indicates that the “organically-associated” Cu has a relict profile that has not been affected by diagenetic reactions.



significant at $p < 0.01$

Fig. 4.28. Relationship between Cu₅ vs. TOC in core 12687#8 and 10.

4.12. Total organic carbon content of the sediments

The total organic carbon contents of both cores followed the three units that were identified on the basis of particle-size, although there were variations in each unit (Fig. 4.2). Hence the TOC concentrations in the middle unit were significantly lower than in either the top or bottom units, clearly being diluted by organic-poor coarse grained material in the former. The association of OM with smaller grain size fractions in sediments is a well known phenomenon (Liebezeit, 1986) and suggests that these have a high sorptive capacity through their high surface area (Hunt, 1963; Suess, 1973; Hedges and Keil, 1995). Interestingly, in the top unit, which has uniform particle size (Fig.4.2), the TOC concentration increased with sediment depth (from ca 2% in surficial sediments to 3.4% at ~100 mm; Fig.4.21). Unfortunately, no ¹⁴C dates are available for these sediments, however, it is possible, that the decreasing TOC towards the surficial sediments really reflects decreasing magnitude and/or changing reactivity of OM fluxes to the abyssal sea (e.g. through changes in primary

production), since, both cores show the same behaviour. In the absence of core dating, it is difficult to assess the significance of this observation, although examination of molecular parameters suggests that the OM of the lower part of the top unit is more degraded and therefore significantly older (see below).

The C/N ratio also showed an increasing trend in the top unit (mean 8.5 and ~8.8 for core 12687# 8 and 10 respectively), whilst the values in the middle unit of both the cores were higher (mean ~12.4 and ~10 for cores #8 and 10 respectively). In the bottom layer of both cores the average value was similar to the top unit of ~8.5. The C/N ratios reflect both the origin of the carbon and the degree of degradation of OM (Macdonald *et al.* 1991). Nitrogen containing compounds are less stable during diagenesis, hence the C/N ratios normally increase or at least remain constant with increasing sediment age (*e.g.* see Degens and Mopper, 1976; Bender *et al.* 1989). C/N ratios of 6-8 have been observed in freshly deposited and unaltered marine organic matter (Müller *et al.* 1986; Bordovskiy, 1965; Ertel and Hedges, 1983; Jasper and Gagosian, 1990), although humic acids derived from terrestrial plant material may in some cases, approach the C/N ratios reported for marine source material (Nissenbaum and Kaplan, 1972; Ertel and Hedges, 1985). Magnusson *et al.* (1988) reported that C/N ratios of sedimenting particulate material of marine origin at the inner Oslofjord, Norway had C/N ratios of 8.3-8.9 (Bordovskiy, 1965; Müller, 1977). This is in agreement with the low C/N ratios measured on sedimenting particulate material, which varied from 9.3 to 9.6 at these sites (Haake *et al.* 1992) and suggested that the bulk organic matter had been little altered, or that carbon and nitrogen are decomposed at the same rate. C/N ratios of the OM in the abyssal sediments in the top and bottom units 8-10 reflect equally and weakly degraded OM, probably of a dominantly phytoplankton origin. In contrast, the high C/N ratios in the

middle layer, may reflect an increase a contribution of terrestrial organic matter relative to marine organic matter in that unit (Macdonald *et al.* 1991). Sediment particle size data follows this same trend (Fig.4.2) and this seems to play significant role in controlling the distribution of all organic compounds. For example, the sandy sediments in the middle unit of the both cores revealed minimum concentration of all organic compounds as compared with finer-grained sediments of the top and bottom unit. It is possible that this shift in grain size indicates larger proportion of terrigenous sediments and OM in that layer. Alternatively, the high C/N ratios of the middle unit may reflect the degradation of OM *in situ* following turbidite flow to the abyssal site. However, since this OM overlies apparently fresher material in the bottom layer, the degradation must have occurred **prior** to deposition of the middle layer.

The increase of C/N with depth in the top unit is interesting to note, and implies some diagenetic loss of N. This appears more marked in core #10 than in # 8, and corresponds with the increasing concentration of TOC with sediment depth in the top unit. However, the same trend is not apparent in either the THAAs or THCHs, (see below), and does not appear to be related to any physical parameters, such as grain size (see Fig. 4.2). However, in core #10 only, there is a inverse linear relationship between C/N values ($r^2 = 0.65$; $n = 9$ also for TOC and TN) and Fe₄ (Fig. 4.29), in the top unit, but there is no clear diagenetic relationship observed in the whole core.

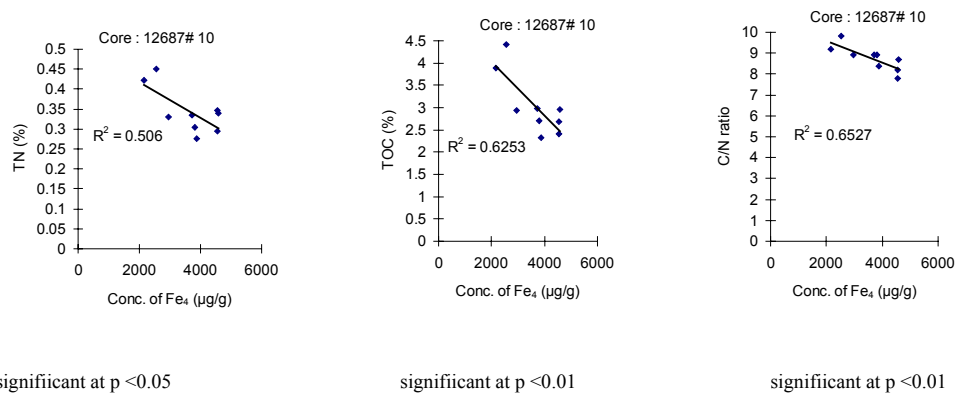


Fig. 4.29. Relationship between Fe₅ vs. TN, TOC and C : N in core 12687# 10.

The higher values of C/N in the middle unit are suggestive of more degraded OM. However, since this OM overlies apparently fresher material in the bottom layer, the “degradation” must have occurred *prior* to deposition of the middle layer.

4.13. Total hydrolysable amino acid and carbohydrates

The down-core concentration profiles of THAAs and THCHs in cores #8 and 10 are similar (Fig. 4.23) and follow those of TOC and TN in the top, middle and bottom unit (Figs. 4.21 and 4.30 respectively).

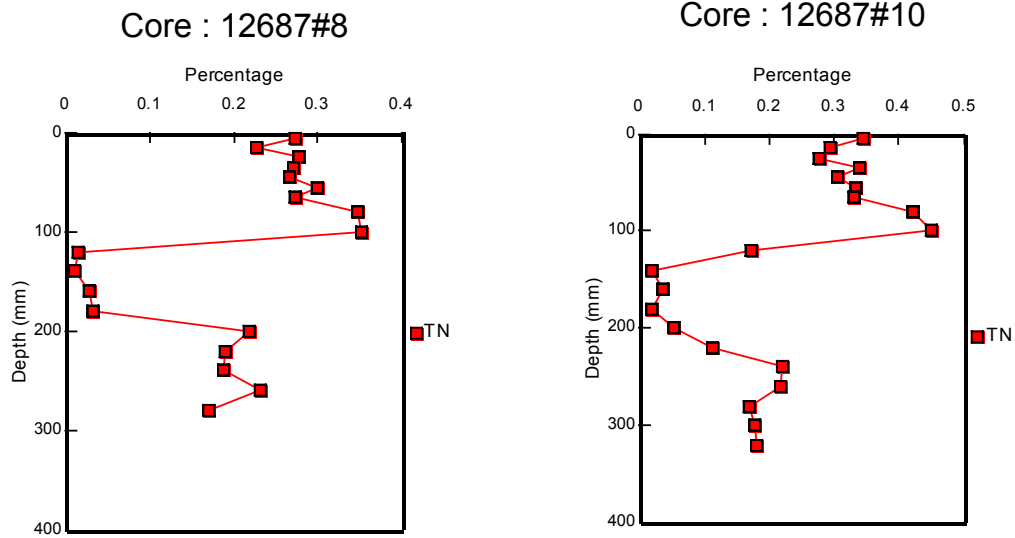
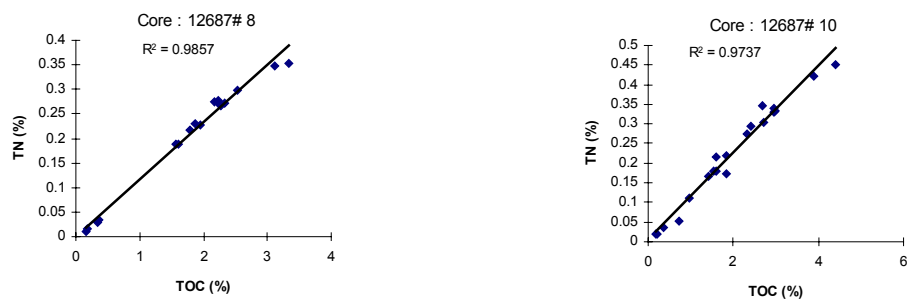


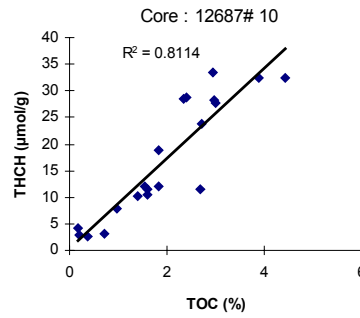
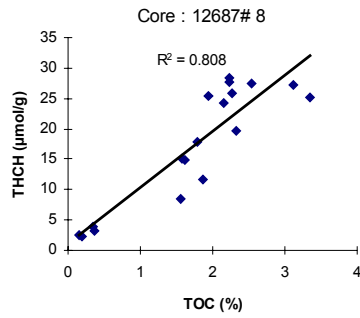
Fig. 4.30. Down-core variation of TN vs. depth in core 12687#8 and 10.

Hence, absolute concentrations of THAA and THCH are highest in the top unit and lowest in the middle unit, whilst levels in the bottom unit are intermediate. Plots of TOC vs. TN (Fig. 4.31), THCH and THAA vs. TOC and TN (Figs. 4.32 - 4.35) all exhibit a strong linear correlation, and pass approximately through the origin.



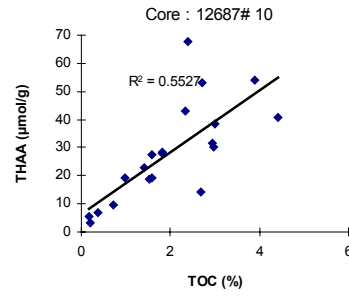
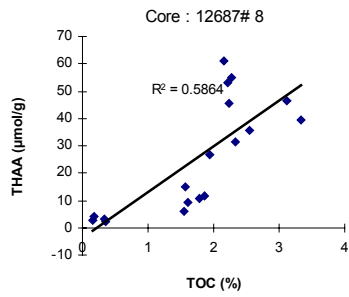
significant at $p < 0.01$

Fig. 4.31. Relationship between TOC vs. TN in core 12687# 8 and 10.



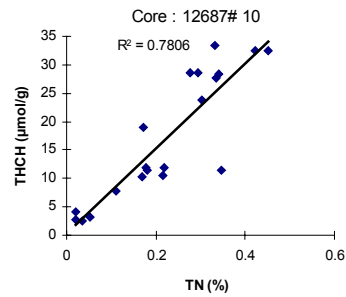
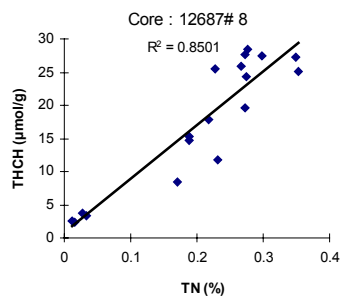
significant at $p < 0.01$

Fig. 4.32. Relationship between TOC vs. THCH in core 12687# 8 and 10.



significant at $p < 0.01$

Fig. 4.33. Relationship between TOC vs. THAA in core 12687# 8 and 10.



significant at $p < 0.01$

Fig. 4.34. Relationship between TN vs. THCH in core 12687# 8 and 10.



significant at $p < 0.01$

Fig. 4.35. Relationship between TN vs. THAA in core 12687# 8 and 10.

This high degree of internal correlation for major components of the OM implies the physical influence of a single source term in dominating the distribution of organic compounds, and a generic relationship with the starting OM (Bhosle and Dhople, 1988; Romankevich, 1984). Hence, this confirms that phytoplankton derived OM dominates the sediments (see previous section) and has been degraded to a lesser, or greater extent during deposition of the sediments and subsequent reworking/diagenesis.

Although the down-core distributions of THAA and THCH are similar to those of TN and TOC, there was some variability in absolute concentrations of THAA in the ‘top unit’, in particular (Fig. 4.23); several sub-surface “spikes” were apparent (e.g. 30-50 mm in core #8; Fig. 4.23). Similar maxima in THAA contents have been reported in oxic and anoxic sediments and have been ascribed to varying supply of THAA through time (Henrichs et al. 1984; Balzer et al. 1987). Alternatively, it has been suggested that “fresh” OM can be transferred to deeper sediments from the surface via bioturbation, and that this can give rise to the sub-surface maxima in THAA concentrations (Horsfall and Wolff, 1987). Cowie and Hedges (1994) described a convenient means of determining the “freshness” of OM by normalisation of THAA and THCH

concentrations to TOC (as mole%; %Taa-C; Fig.4.24; and %Tsugars; Fig.4.25 respectively), and THAA concentrations to TN (as mole%; %Taa-N; Fig.4.36). The %(Taa+Tsugars)OC for the Oman Margin abyssal cores (Fig.4.37) shows values of up to ~20% in surficial sediments, and of ~18% in the “sub-surface” spike (30-50 mm) of core #8. These mole% values are rather high, considering the depth of the water column at this site, and are, in fact more consistent with values reported by Cowie and Hedges (1994) for coastal sediments under oxygenated waters. The %Taa-N values (Fig.4.36) confirm this observation; with relatively high values (~45%) in the sub-surface spike, which are again close to those observed previously in coastal surficial sediments (Cowie and Hedges, 1994). Thus, the “fresh” OM in sub-surface spike could reflect bioturbation (see Horsfall and Wolff, 1997). Unfortunately, ²¹⁰Pb data are not available for this Oman Margin site, however, there is some indirect support for the importance of bioturbation here, in that the macrofaunal abundance are relatively high for abyssal depths (400-500 individuals m⁻²; Levin, personal communication).

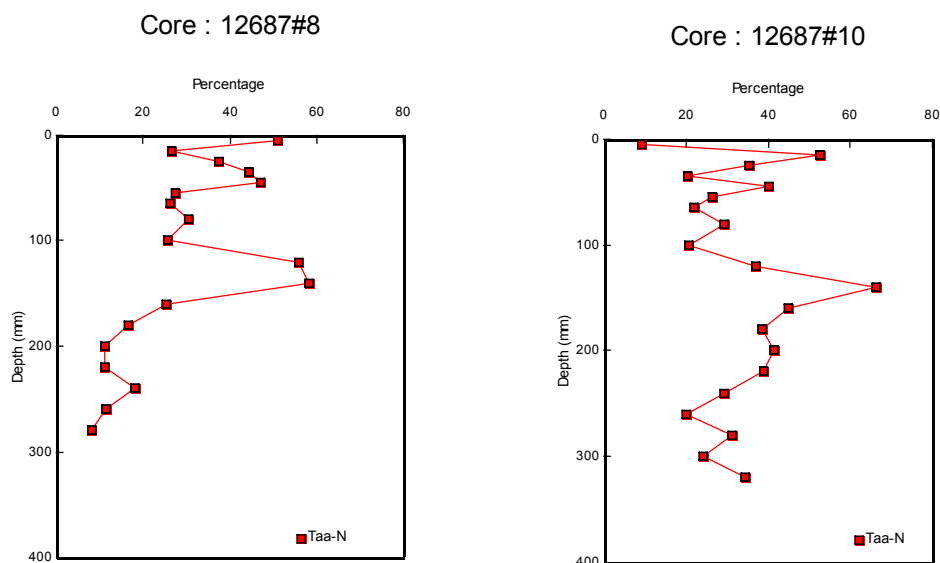


Fig. 4.36. Down-core variation of mole% Taa-N vs. depth in core 12687#8 and 10.

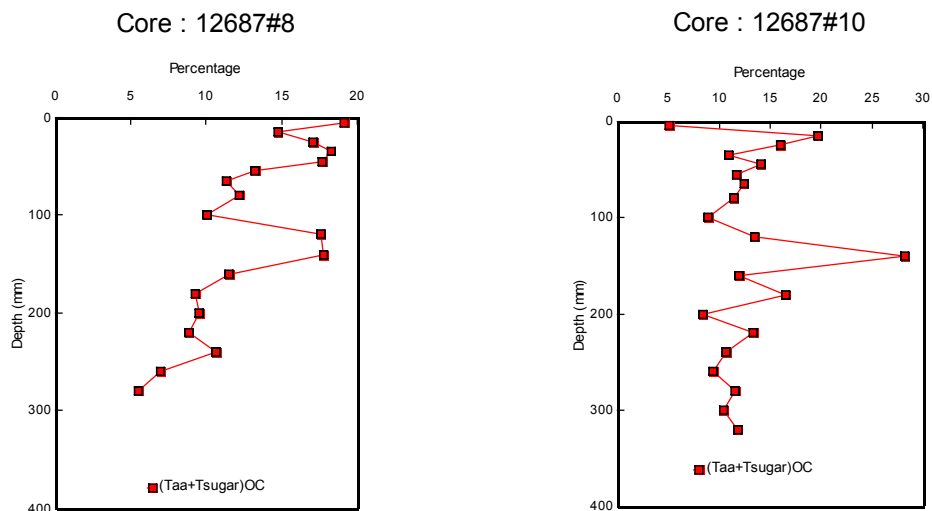


Fig. 4. 37. Down-core variation of mole% (Taa+Tsugar) vs. depth in core 12687#8 and 10.

In the bottom unit of core #8, the $\%(Taa+Tsug)OC$ and $\%Taa-N$ values are much lower than in the top unit, confirming the diagenetic removal of these labile compounds in the preserved older unit. However, this was not as obvious in core #10, although values were still lower than in the top unit. In the absence of radiometric dating (^{14}C) it is difficult to determine the reasons underlying this discrepancy. However, it is suggested that the difference between cores arises through spatial variability, in that during deposition of the sandy turbidite, the underlying unit was probably scoured to a greater or lower extent, thus exposing surfaces for deposition that were older or younger, respectively (and therefore have different $\%(Taa+Tsug)OC$ values). The values of $\%(Taa+Tsug)OC$ and $\%Taa-N$ in the middle sandy unit were surprising high, indeed amongst the highest in the cores. Again, this observation is difficult to explain,

since the C/N data (Fig. 4.22) suggest that this unit contains the most degraded OM. It should be noted, however, that :

i) Both THAA and THCH concentrations in the middle unit were very low (Fig. 4.23), in some sections being almost an order of magnitude lower than in surficial sediments

ii) TN concentrations were also very low.

Hence the experimental errors associated with measurement of THAA and THCH as well that associated with TN determination may well have led to spurious values of % (Taa+Tsug)OC and %Taa-N, and the data should, therefore, be treated with some caution.

Manganese solid-state speciation data clearly shows that manganese respiration of OM occurs in the Oman Margin abyssal sediments (see above). Thus, despite the nature of the sediment 'sandwich', it would be expected that some diagenetic alteration of OM in the deeper sediments of the top unit and bottom unit should be observed. This is indeed the case for core #8. Hence (ignoring the middle unit, where data may not be sound), there is an overall decrease in the %Taa-N and (Taa+Tsug)OC with increasing sediment depth (Figs. 4.36 and 4.37). Thus, the distribution of labile OM in this core presumably reflects its post-depositional degradation, as has commonly been observed both in steady-state depositional settings (e.g. Peru upwelling, Patience *et al.* 1990) and turbidic environments (Cowie and Hedges, 1994; Wolff *et al.* 1995). Seemingly, diagenesis of the Oman Margin sediments proceeds under largely sub-oxic conditions, for example, there is no evidence of oxygen burn down, as at the Madeira Abyssal Plain (Cowie and Hedges, 1994). Furthermore, the presence of the Mn spike close to the surface of both Oman Margin cores, shows that below this depth, diagenesis must

proceed via sub-oxic respiration of Fe oxides, sulphate or carbonate (see Froelich et al.1979).

In young turbidites overlying pelagic sediments sampled from the Madeira Abyssal Plain (MAP), Sutton (1996) observed a linear relationship between the concentration of Mn₃ new oxides and the concentrations of labile organic compounds, namely THAA and THCH. Hence, it was proposed that labile OM was respired through Mn (IV) reduction from the pelagic-turbidite boundary upward. This mechanism was presumably initiated through the stimulation of reduction of Mn oxides by bacteria in the underlying pelagic sediments. The reduction of Mn (IV) oxides at the base of the turbidite (coupled with degradation of labile OM), upward migration of Mn (II) via pore waters and its subsequent oxidation and immobilisation in surficial sediments led to their relative enrichment in the metal. Thus, in the turbidite layer, there was a strong relationship between easily reducible Mn₃ oxides and OM parameters.

This strong relationship was *not* observed in the Arabian Margin sediments. Thus, there was no correlation between OM parameters and Mn₃ (or Fe₃). This can be explained as follows:

The Oman Margin site is more highly productive than the North-West African Margin and carbon flux to the sediments is much higher (Nair et al. 1989; Haake et al. 1992; Schäfer and Ittekkot, 1995). Thus it might be expected that the flux of labile OM to the sediments at the Oman Margin would also be high, and would lead to the rapid onset of sub-oxic conditions in the sediment. Hence, Mn respiration in deeper sediments has proceeded to completion (no Mn₃ - below ~60 mm), and is at present occurring only within the Mn spike. This contrasts with the organic poor MAP turbidite (ca. 0.5 - 0.7% TOC vs 2 - 4% TOC of Oman Margin top unit; Sutton, 1996), where Mn₃ new oxides had not been exhausted, even in deeper sediments (Sutton, 1996). The lack of

correlation between Fe₃ ‘new’ oxides (or ‘aged’ Fe₄ oxides) and OM parameters is also notable in the Oman Margin sediments, but is not necessarily surprising since it is likely that the distribution of the Fe₃ oxides is largely controlled by Mn precipitation at the spike (see section 4.10). Presumably Fe₄ oxides are too recalcitrant to be utilised in Fe respiration.

4.14. CONCLUSIONS

1. The abyssal sediments chosen for this study were influenced by a sandy turbidite, and were subdivided into 3 units on the basis of their sedimentology and geochemistry.
2. The solid state speciation of the non-detrital fractions revealed differences between Mn, Fe and Cu.
3. There is a clear relationship between the precipitation and consumption of Mn₃ oxides, which are concentrated in the top unit as a Mn spike. This spike is a classic feature in the diagenesis of Mn, and the present study has shown that it is composed of ‘new’ Mn₃ oxides.
4. The “organic-associations” of Mn₅, Fe₅ and Cu₅ do not appear to have suffered diagenetic modification; i.e. the binding strength of the Stage 5 “organic-association” appears to be sufficiently strong to preserve the trace metals even though the destruction of OM has been initiated to at least the stage where the ‘new’ Mn₃ oxides are utilized in sub-oxic diagenesis.
5. There are no other clearly defined relationships in the solid state speciations of ‘aged’ oxides of Mn₄, Fe₄ and Cu₄ that can be defined as being diagenetically-mediated.

6. Differences in OM parameters were linked to the distinct sedimentology of the cores. Concentrations of TOC and TN, as well as THAA and THCH were lowest in the sandy middle unit. The sources of the OM throughout the cores were similar.
7. There was some apparent diagenetic modification of OM; labile components (THAA and THCH) were removed with increasing sediment depth (i.e. top vs bottom unit). This trend was clear in 12687#8, but less so in #10.
8. Unlike the Maderia Abyssal Plain (Sutton, 1996) there was **no** relationship between OM parameters and Mn (or Fe) solid state speciation, presumably reflecting the complete removal of ‘new’ oxides from the deeper sediments.
9. Some ‘fresh’ OM is incorporated into the abyssal sediments, however the extent of its burial is difficult to determine due to the influence of turbidite deposition at this site. The absence of “oxygen burn-down” suggests that OM is buried in the abyssal sediments.

CHAPTER 5

OMAN MARGIN (OMZ Site)

5.1. INTRODUCTION

In the previous Chapter, the geochemistry of sediments from an abyssal site at the base of the continental slope at the Oman Margin was studied in order to assess the relationship, if any, between OM diagenesis and trace metal solid state speciation as determined by sequential leaching. The site was of particular interest, as it underlay an area of high productivity, but where overlying waters were oxygenated. In this Chapter, the geochemistry of sediments from further up the continental slope at 400 m b.s.f. is considered in the same way. The site was chosen to correspond to the most intense part of the OMZ, where O₂ concentrations in overlying waters were ~0.1 mL L⁻¹ (Gage, 1995).

Three replicate cores have been analysed in this study (12690#1, 12692#1, 12695#2). Trace metal speciation was determined for Mn and Fe in all of the cores, as were TOC, TN and THAA. THCHs were also determined in one of the cores (12690#1). For ease of discussion, the cores have been divided into two units i.e. top (0-55 mm) and bottom (65-140 mm) and all data are shown in Appendix-C (Table C.1.1-C.1.8).

5.2. RESULTS

5.3. TRACE METALS

5.3.1. Manganese

There was no detectable non-detrital manganese as determined by sequential leaching of the Oman Margin sediments.

5.3.2. Iron

The non-detrital iron in these sediments from the most intense part of the OMZ was partitioned only between ‘aged’ Fe₄ oxides and the “organic association” of Fe₅ oxides in all the cores. There was no detectable non-detrital Fe₁, Fe₂ and or ‘new’ Fe₃ oxides in the sediments.

Concentrations of Fe₄ oxides in core 12690#1 were relatively constant in the top unit, but below this their concentrations increased with depth. The average concentration was ~400 µg/g in the top unit and ~500 µg/g in the bottom unit (Fig. 5.1). Fe₅ in the core 12690#1 showed similar behaviour, increasing with depth down-core (Fig.5.2).

Core : 12690#1

Iron (Stage 4)

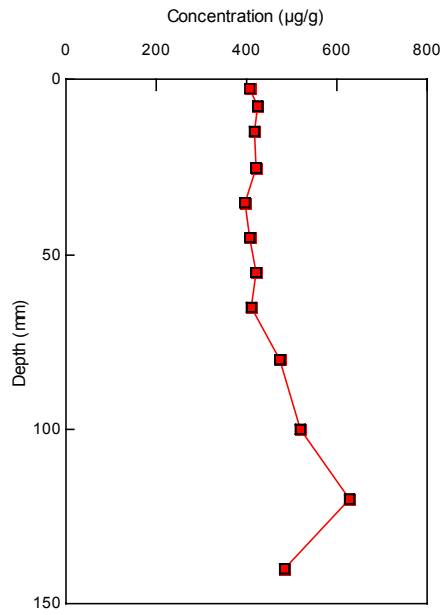


Fig.5.1

Core : 12690#1

Iron (Stage 5)

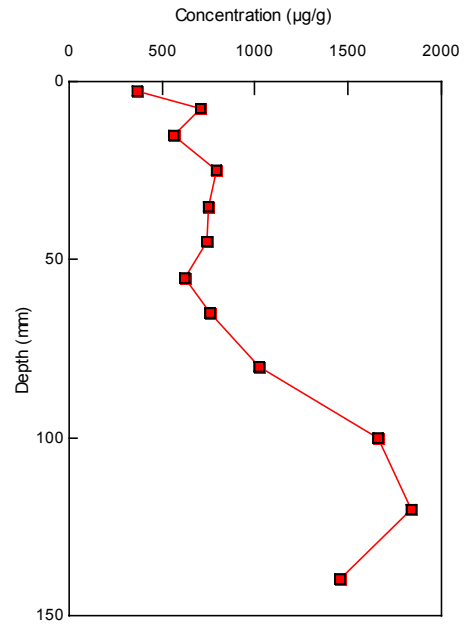


Fig.5.2

Fig. 5.1-5.2. Down-core variation of Fe₄ and Fe₅ vs. depth in core 12690#1.

Fe₄ oxides in core 12692#1 decreased gradually with depth from ~1600 to 500 µg/g, an average concentration in the top unit of ~1300 µg/g, but only ~600 µg/g in the bottom unit (Fig.5.3). Fe₅ in core 12692#1 showed the opposite behaviour to that in 12690#1, increasing with depth from ~400 to ~1100 µg/g. The average concentration in the top unit was ~700 µg/g. The profiles of Fe₅ in this core were a mirror image of Fe₄ profiles (Fig.5.4).

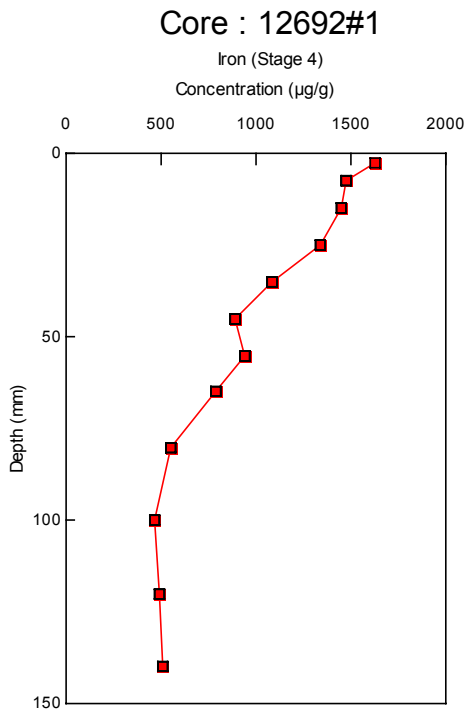


Fig. 5.3

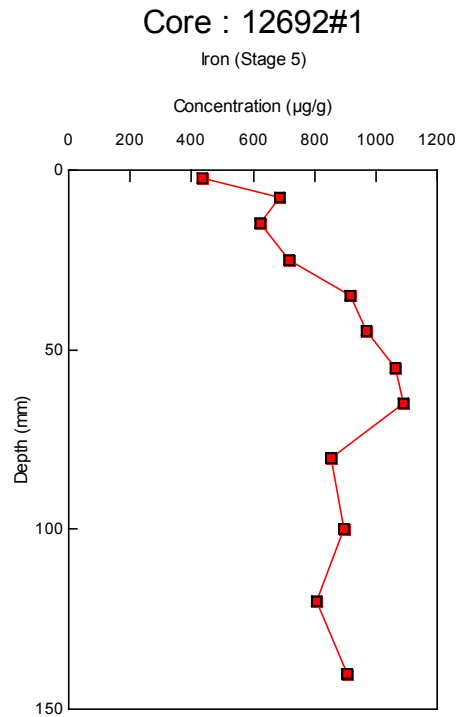


Fig. 5.4

Fig. 5.3-5.4. Down-core variation of Fe₄ and Fe₅ vs. depth in core 12692#1.

Concentrations of Fe₄ oxides in core 12695#2 decreased with depth down-core. However, there was some variability and a significant sub-surface maximum between 10 and 30 mm. In the top unit, the average concentrations in the top and bottom units were ~550 µg/g and ~500 µg/g, respectively (Fig.5.5). Fe₅ in core 12695#2 increased gradually with depth down-core, from ~400-2000 µg/g. The average concentration in the top unit was ~600 µg/g and ~2000 µg/g in the bottom unit (Fig.5.6).

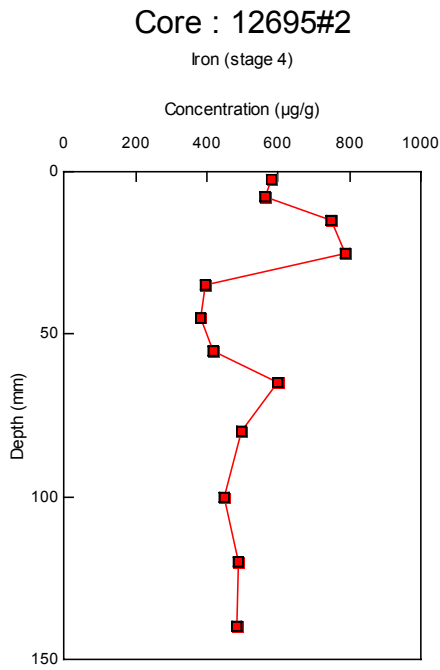


Fig. 5.5

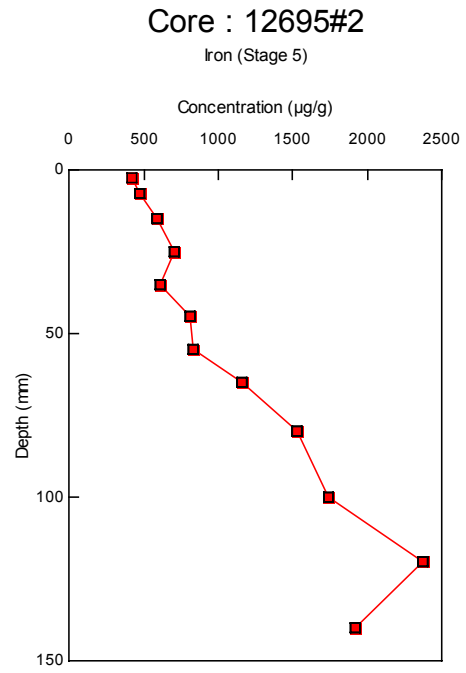


Fig. 5.6

Fig. 5.5-5.6. Down-core variation of Fe₄ and Fe₅ vs. depth in core 12695#2.

5.4. Calcium Carbonate content

The CaCO_3 contents of three cores were similar, gradually decreasing from ~65 to ~50% (w/w) to 100 mm, although below this depth there was some variability (Fig.5.7).

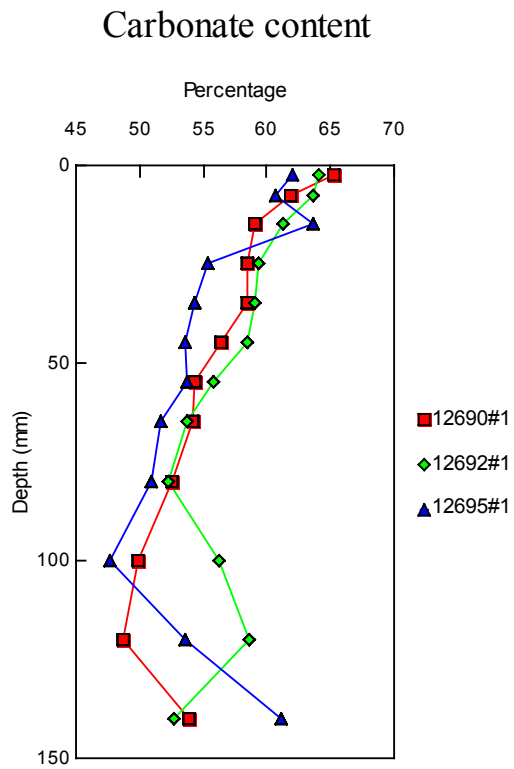


Fig.5.7

5.5. Total Organic Carbon (TOC) and C/N

In core 12690#1, TOC concentrations increased (~5-7%) to ~50 mm; below that depth, they decreased down-core. The average TOC concentrations in bottom unit (~5%) were lower than those of top unit of ~6% (Fig.5.8). C/N values were rather uniform (~8) except for a significant maximum (~13) in the 20-30 mm section.

Cores 12692#1 and 12695#2 showed complex behaviour, with some significant sub-surface maxima (Figs. 5.9 and 5.10, respectively). The average TOC concentration in core 12692#1 was higher in the bottom unit (~7%) than in top unit (~6%), whereas in core 12695#2 the average amounts (~5%) were equal in the top and bottom units. C/N values showed similar variability in both cores, particularly in 12695#2, although there was an overall increase down-core (Figs.5.9 and 5.10).

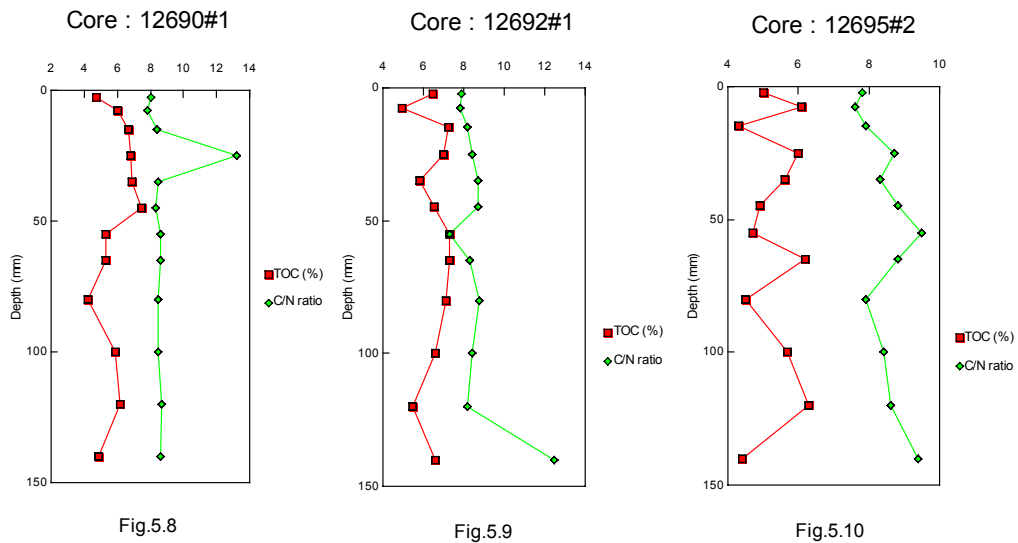


Fig. 5.8-5.10. Down-core variation of TOC, C:N vs. depth in core 12690#1, 12692#1 and 12695#2.

5.6. Hydrolysable amino acids (THAA) and carbohydrates (THCH)

The down-core profiles of THAA concentrations were variable; sub-surface concentration maxima were evident in all of the cores, particularly in the top sections (Figs.5.11-5.13).

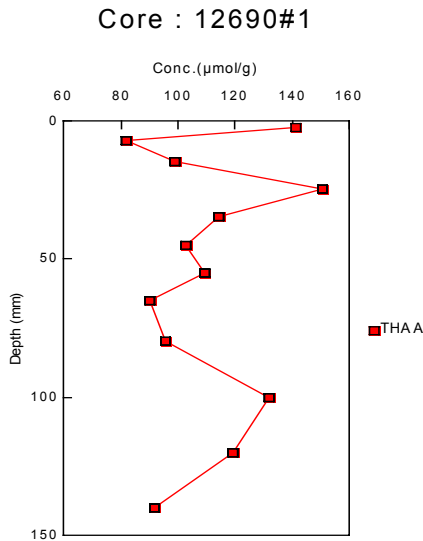


Fig.5.11

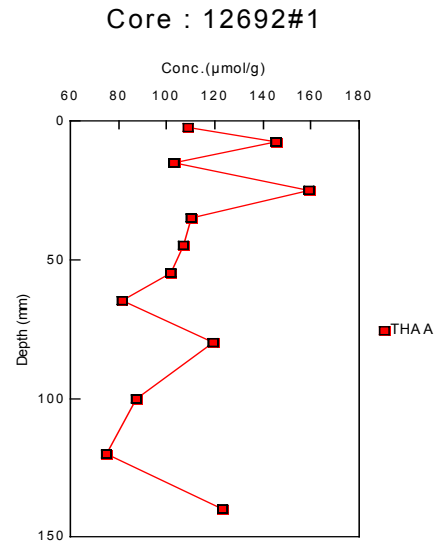


Fig.5.12

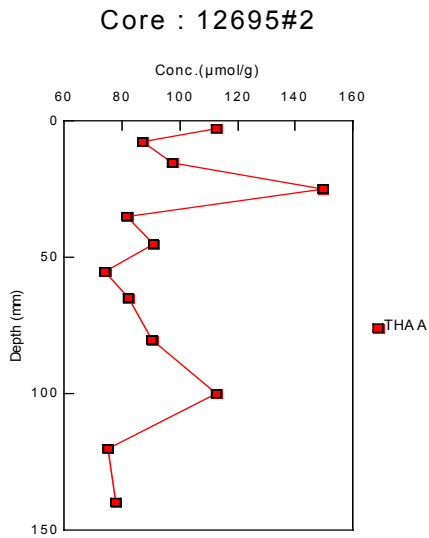


Fig.5.13

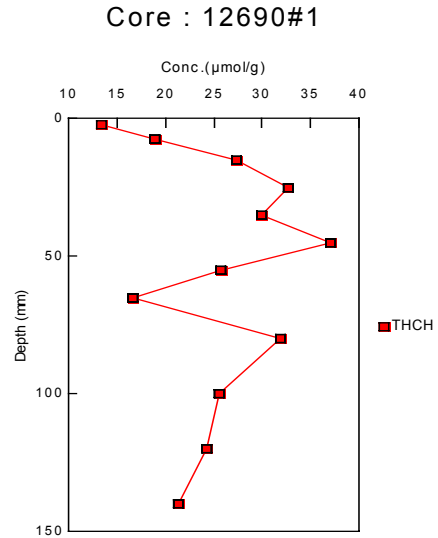
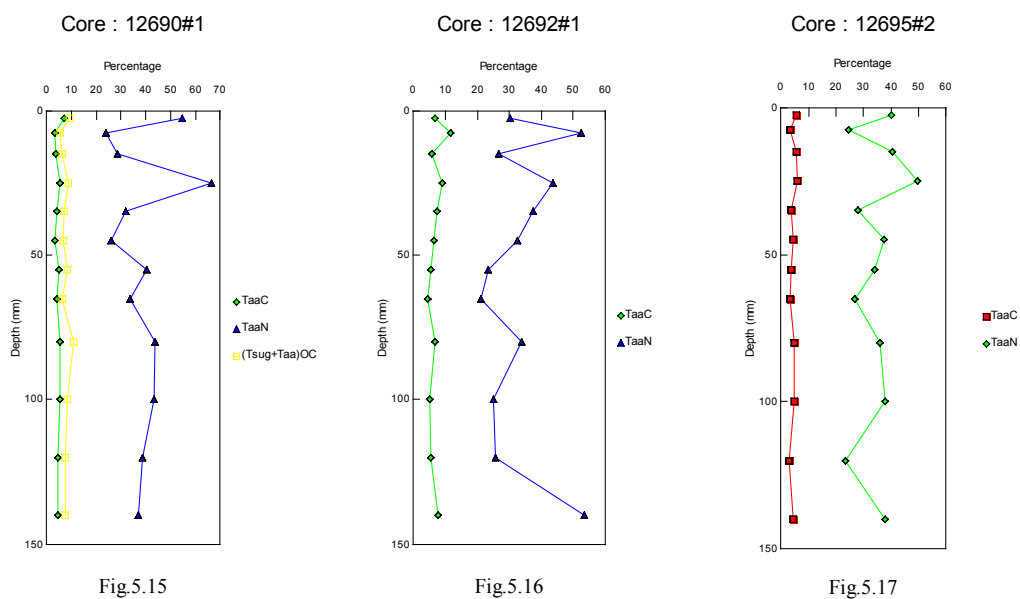


Fig.5.14

Figs. 5.11-5.14. Down-core variation of THAA, THCH vs. depth in cores 12690#1, 12692#1 and 12695#2.

Similar features were apparent in the down-core profiles once the THAA concentrations were normalised to TOC and TN as mole% TaaC and TaaN respectively (Cowie and Hedges, 1994), although these did not necessarily coincide with the maxima in absolute THAA concentrations. In all of the cores the %TaaN and %TaaC profiles behaved in a similar way (Figs.5.15-5.17).



Figs. 5.15-5.17. Down-core variation of %mole TaaC, TaaN and (Tsug.+Taa)OC in cores 12690#1, 12692#1 and 12695#2.

THCH were only determined in one of the cores (12690#1); levels in 12692#1 and 12695#2 were below detection, although it should be noted that in all of the samples analysed from this site, problems were encountered with an interfering component during the analyses. Unfortunately, lack of time precluded the development of different analytical methods (e.g. Pakulski and Benner, 1994).

In core 12690#1, the THCH concentrations were apparently lower (Fig.5.14) than those of the THAAs (Fig.5.17), but normalised values (%T_{sugar}) were similar, and did not vary significantly down-core (Fig.5.15).

5.7. DISCUSSION

The sediment samples studied in this section of the thesis were collected from the most intense part of the permanent OMZ at the Oman Margin. At the time of their collection, oxygen concentrations in overlying waters were $\sim 0.2 \text{ mL L}^{-1}$ (Gage, 1995) whilst, oxygen was rapidly depleted in the sediments themselves, which become reducing below the surficial layer overlying the sediments. Unfortunately, lack of time precluded a detailed examination of the bulk properties of the samples analysed in this study, however, data is available for replicates collected at the same site; this shows that the sediments were fine muds (mean particle size $29 \mu\text{m}$) of relatively uniform composition (Patience and Gage, personal communication). Radionuclides (namely ^{210}Pb) were also determined in cores from the same site; these show that the sediments are mixed, but only to a depth of 20-40 mm (Levin and Smith, personal communication). It should be noted that macrofaunal abundances were surprisingly high considering the low oxygen concentrations (12,000 individuals m^{-2} , dominantly polychaetes), hence the mixing of surficial sediments might be ascribed to bioturbation.

TOC contents of the sediments were significantly higher than at the abyssal site (6-8% vs <4% TOC, respectively), and amongst the highest at the Oman Margin (Smallwood, personal communication). C/N values (~ 8) are again typical of relatively “fresh” marine-derived OM (e.g. Jasper and Gagosian, 1990). This seems

to be confirmed by the high % Taa N values (Figs.5.15 to 5.17; Cowie and Hedges, 1994; discussed below). At first sight, therefore, it would be expected that the sediments are diagenetically active and a key question is “Does the solid state speciation of Fe and Mn reflect the potential diagenetic activity of the sediments?”.

5.8. Manganese

The non-detrital Mn solid state speciation determined in sediments from the most intense part of the OMZ at the Oman Margin was different from that in the abyssal cores.

According to Chester et al. (1994), the solid state speciation of the non-detrital Mn in sea water particulates is dominated by Mn₂ which makes up an average of ~ 40% of the non-detrital Mn and Mn₁, which makes up an average of ~20%. In contrast, ‘new’ oxides of Mn₃ are formed at the sediment surface as the down-column carriers are destroyed during oxic diagenesis. However, in the absence of an oxic layer, ‘new’ oxides will not be formed, and so will not be available to take part in the Mn ‘cycle’ where they would be utilized as secondary oxidants for the degradation of OM. From the present data, it is apparent that the Mn₃ does not take part in diagenesis, since it is absent. The Oman Margin cores therefore provide an example of a sedimentary environment in which ‘new’ Mn oxides do not form, and in which there are no ‘aged’ Mn₄ oxides. It is, therefore, of particular interest to determine if, in the absence of Mn oxides, the system switches to the use of Fe oxides; e.g. as it would have done if all the Mn oxides had been utilized as secondary oxidants. In other words, is the diagenetic sequence brought forward in the absence of Mn₃ and Mn₄ oxides?.

The virtual absence of non-detrital Mn in the present margin samples was nonetheless surprising. Since the sediments were collected at the most intense part of the OMZ, and as the sediments were reducing up to the surface, *i.e.* there is virtually no oxic layer present (Gage, 1995), then it might have been expected that no 'new' Mn₃ oxides/oxyhydroxides would have formed at the sediment/sea-water interface. Hence, no Mn would be available to be utilized in the Mn recycling trap in the interstitial waters, and there was no Mn enrichment as observed, for example, in the Madeira abyssal plain turbidites (Thomson *et al.* 1986; Middleburg and de Lange, 1988) or in the Oman Margin abyssal sediments (This study). The transport of Mn from shallow to deeper waters has been observed previously at the California Margin (Johnson *et al.* 1992) was ascribed to Mn reduction at the shallow stations, the dissolution of Mn in the porewaters, escape through the sediment-water layer to the water column and subsequent transport to deeper waters, where Mn re-precipitates. A similar scenario may explain the lack of Mn₃ in these sediments. However the absence of Mn₄ 'aged' oxides, which are presumable considerably more recalcitrant, was more striking.

It is unlikely that the sedimentary material supplied to the Oman Margin would be free of 'aged' Mn₄ oxides. For example, aeolian transport from the surrounding desert and arid regions is the major source of land-derived solids to the Oman Margin, and such desert-derived dusts contain as much as 50% of their ΣMn in non-detrital forms (see *e.g.* Chester *et al.* 1996, although in that study, no distinction was made between the various non-detrital speciation hosts). Some of this non-detrital Mn may be soluble in sea water, especially in the intense OMZ, so it is not possible without water column data to estimate what proportion of the Mn oxides

reach the sediment surface. However, if ‘aged’ Mn oxides were deposited it is evident that they have been destroyed, possibly by utilization as secondary oxidants.

All measurements made at the time of sample collection show that the sediments were indeed reducing at the 400 m site, probably within one or two mm of the surface (Meadows and Meadows, in Gage, 1995). To provide oxygen it is therefore, possible that the system switched to the ‘aged’ recalcitrant Mn₄ oxides and utilized these as secondary oxidants. This would have resulted in the release of dissolved Mn into the interstitial water which would have migrated upwards under a concentration gradient; however, in the absence of a surface oxic layer, and this dissolved Mn would have been released into the overlying sea water.

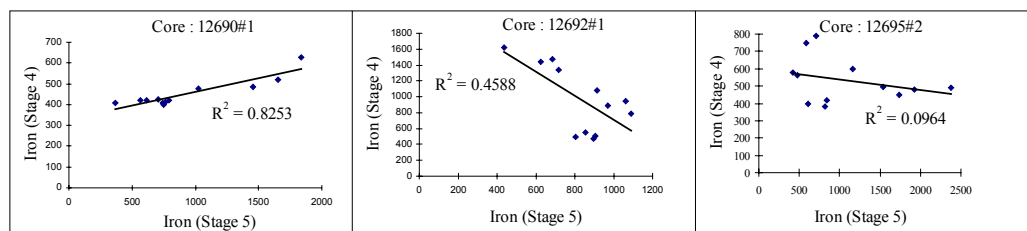
It is more difficult, however, to explain the lack of “organically-associated” Mn₅ in the margin sediments. In the sediments at the base of the Oman Margin “organically-associated” Mn made up as much as ~1% in core 12687#8 of the non-detrital Mn, although it was not detectable in core 12687#10. From the present data, therefore, no explanation can be offered for the absence of “organically-associated” Mn₅ in the sediments of the three Oman margin cores at the OMZ. The important point, however, is that there is a virtual absence of non-detrital Mn in the cores. It should be noted that Somayajulu *et al.* (1994) also found that manganese was extensively depleted in sediments collected at the Indian Margin of the Arabian Sea. The water overlying these sediments were also depleted in oxygen, whilst the sediments themselves were enriched in OM. The question which therefore arises is ‘Where non-detrital Mn is absent, is there evidence that Fe oxides have been utilized as secondary oxidants in the Oman Margin cores?’

5.9. Iron

The non-detrital Fe in the margin sediments was partitioned between ‘aged’ Fe₄ oxides and the “organically-associated” Fe₅; i.e. there are no ‘new’ Fe₃ oxides. In the sediments collected from the most intense part of the OMZ at the Oman Margin, the ‘aged’ Fe₄ oxides made up ~ 33%, 54% and 33% in the core 12690#1, 12692#1 and 12695#2 respectively and the “organically-associated” Fe₅ oxides each made up ~ 68%, 46% and 67% of the total non-detrital Fe in these cores.

The virtual absence of non-detrital Fe₃ oxides indicates that as for Mn, low levels of O₂ have precluded the formation of ‘new’ Fe₃ oxides (see Chapter 4). Hence no ‘new’ Fe oxides have been available as secondary oxidants. This is in contrast to the conditions at the abyssal site, where the oxidizing environment at the sediment-water interface resulted in high retention of upwardly diffusing iron and manganese and the formation of metal-enriched sediments.

The most striking feature of the data set is its variability, particularly in the down core profiles of Fe₄ (see Figs.5.1, 5.3 and 5.5). Furthermore, whereas in Core 12690#1, there is a significant linear relationship between Fe₄ and Fe₅ (Fig.5.18) in Cores 12692#1 and 12695#2 there is an inverse relationship (Figs.5.19 and 5.20, respectively), although this is tentative in the case of 12695#2.



significant at p <0.01

significant at p <0.02

not significant

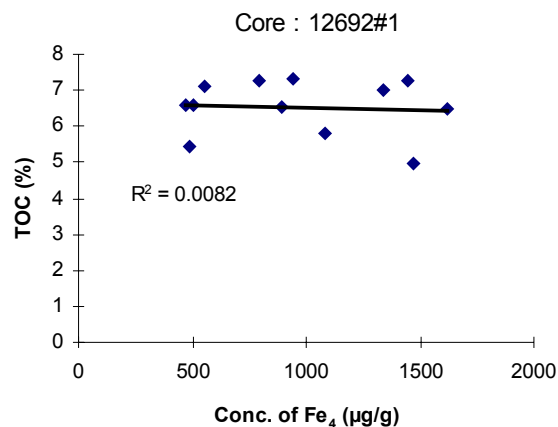
Fig. 5.18

Fig. 5.19

Fig. 5.20

Figs. 5.18-5.20. Relationship between Fe₅ vs. Fe₄ in core 12690#1, 12692#1 and 12695#2.

In Core 12692#1, there is a clear downcore decrease in the concentration of Fe₄ oxides. This tentatively suggests that there maybe some respiration of Fe₄ oxides, in other words that bacteria have utilised the recalcitrant ‘aged’ oxides as secondary oxidants. It is interesting to note that in this core, there is an inverse relationship between Fe₄ and Fe₅ and since the latter are probably associated with the sedimentary precipitation of sulphides (pyrite framboids being abundant in these sediments; Lallier-Verges, 1993), this may further imply some diagenetic modification of Fe₄. There is a clear evidence from the study of ODP Leg 117 of offshore Oman for bacterial sulphate reduction and fixation of pyrite with the presence of large proportion of organic sulphur (Lükage *et al.* 1996). However it should be noted that there is no clear relationship between Fe₄ and any OM parameter (Fig.5.21). Therefore, if microbially mediated reduction of Fe₄ oxides occurs in this core it does not significantly influence the composition of the OM. This may be due to the insensitivity of the “bulk” techniques used to analyse OM in these sediments, however any such hypothesis is purely speculative.



not significant

Fig. 5.21. Relationship between Fe₄ vs.TOC in core 12692#1.

In core 12690#1, there is a very strong linear relationship between Fe₄ and Fe₅. In this case, there was no overall decrease in TOC, TN, %TaaC or %TaaN, which might suggest that little/or no diagenesis has occurred, despite the high OM contents of the sediments. This seems unlikely, however, it is possible that the Fe₄ and Fe₅ profiles simply reflect the source strength of their inputs to the sediments. In Core 12695#2, there little or no relationship between Fe₄ ad Fe₅, and the core appears to be “intermediate” between 12690#1 and 12692#1.

5.10. Total organic carbon content of the sediments.

The total organic carbon contents of the cores were in the range 5-7%, whilst C/N values were ~8. There was again variability in the TOC down-core profiles (Figs.5.8 to 5.10). In one of the cores (#12690), there was down-core increase in TOC in the top unit from ~5% to 7%. Such a feature was not apparent in cores 12692#1 or 12695#2. This variability might be ascribed to historical changes in OM flux to the sediments (Bertrand *et al.* 1996), however in the absence of ¹⁴C ages, such a hypothesis

is difficult to assess. On the other hand the lack of correlation in TOC contents between the cores suggests that there may be other controls on the TOC contents, for example, sediment resuspension and deposition, mixing and slumping as well as settling of fresh OM.

The C/N values are consistent with relatively fresh plankton derived OM (Jasper and Gagosian, 1990; Macdonald *et al.* 1991). The C/N ratios did show increasing trend down-core in two of the cores namely 12692#1 and 12695#2 (Figs.5.9 and 5.10). Nitrogen containing compounds are less stable during diagenesis, hence the C/N values normally increases or, at least, remains constant with increasing age (*e.g.* Degens and Mopper, 1976; Bender *et al.* 1989). This suggests therefore, that at least in these cores there may have been some diagenetic modification of OM. On the other hand in core 12690#1, there is no down-core trend (there is a large spike at 20-30 mm). This apparent lack of distinct diagenetic signal (see also below hydrolysable amino acids and carbohydrates) is very surprising. For example, in sediments from the Peru Upwelling region, which are also organic rich, there is a distinct and relatively rapid loss of organic N (Patience *et al.* 1992; Lewis and Rowland, 1993), which is absent here. The explanation for this lack of diagenetic activity may lie in the nature of the OM itself. For instance, it is known that the OM in Peru margin sediments is well preserved and labile, however that in the Oman margin sediments significantly degraded (Emeis *et al.* 1991), possibly as a result of the long residence of the OM in the water column (Rao and Lamboy, 1994). The data accrued for hydrolysable amino acids and carbohydrates (one core only) in this study confirms the degraded nature of the OM in the Oman margin sediments.

5.11. Total hydrolysable amino acids and carbohydrates.

The absolute concentrations of THAAs were significantly higher in the surficial sediments from the 400 m site than at the abyssal site (141 vs 61 $\mu\text{mol g}^{-1}$ in cores 12690#1 and 12687#8 respectively), whilst those of THCH (only determined in one core, see above) were slightly lower (13 vs 24 $\mu\text{mol g}^{-1}$ respectively in the same cores). Mean concentrations in the whole sediment cores of both THAAs and THCHs, were both higher in the shallow vs abyssal cores. At first sight, this suggests a greater supply of OM rich in THAAs and THCHs to the sediments at the shallow site. However, when their concentrations are normalised to TOC as % TaaC and %Tsugars and THAAs concentrations to %TaaN (Cowie and Hedges, 1994; see Chapter 4) a different picture emerges (Figs. 5.15 to 5.17 and Tables C.1.6 to 1.8, Appendix C). Hence values of %TaaC and %Tsugars tend to be somewhat lower than those in the top layers of the abyssal sediments (Tables B.1.7 and B.1.8 in Appendix B). These mole% values are surprisingly low, considering the proximity of the sediments to the OMZ, and the extremely high productivity of the water column (Burkill et al. 1993). In fact, the %(Taa+Tsugars)OC values for 12690#1 (Fig. 5.15) are <10% in the surficial sediments, and are close to the values reported by Cowie and Hedges (1994) for oxidised turbidites from the Madeira Abyssal Plain, and are lower than those from the oligotrophic north Pacific (4990 m water depth, Lallier-Vergès and Alberic, 1990). This clearly underpins the suggestion that the sedimentary OM deposited at the Oman Margin is rather refractory, possibly due to its resuspension and deposition and its long residence time in the water column (Rao and Lamboy, 1994). Paradoxically, the %TaaN values for the same sediments are high (Fig. 5.15 to 5.17) and are more typical of coastal surficial sediments deposited

under anoxic conditions (Cowie and Hedges, 1994). It seems that the THAAs have been preferentially removed during sedimentation (see Lee and Wakeham, 1989), but that the remaining THAAs still account for a substantial proportion of the remaining organic nitrogen. Such a process must be distinct from that observed in the Peru Margin, where THAAs are removed with increasing sediment depth, at the same time as the nature of organic N changes from dominantly amino-acid N to quaternary N (Patience *et al.* 1992). It should be noted that in the latter case, the transformation of N probably occurs over thousands or more years in the sediment column. Absolute concentrations of both THAAs and THCHs vary considerably down-core and there are significant 'sub-surface' spikes, particularly in the top 40 mm of the sediments. ²¹⁰Pb data show that the sediments are mixed to this depth (Levin and Smith, personal communication), hence it is possible that these sub-surface maxima reflect bioturbation (Horsfall and Wolff, 1997, see Chapter 4). However, examination of %TaaC and %TaaN, show little overall change down-core. Once again, this suggests that any diagenetic removal of THAAs or THCHs is slow in these sediments.

As was the case at the abyssal site, there were **no** significant correlations between the OM parameters and the solid state speciation data for Fe and Mn (the latter being absent). Presumably Fe₄ oxides are too recalcitrant to be utilized in Fe respiration (see Fig.5.5). Organic matter diagenesis in sediments proceeds in order of decreasing energy production per mole of organic carbon oxidised (O₂ > manganese oxide ~ nitrate > iron oxide > sulphate). In order to understand the processes occurring in the Oman Margin, pore water data is necessary to confirm the involvement of nitrate reduction. However, in view of the absence of Mn₃ and Mn₄ oxides in these sediments and the apparent recalcitrance of the Fe₄ oxides, sulphate is the most likely available electron acceptors for diagenetic reactions to proceed.

There is some indirect evidence to support the importance of sulphate reduction. In the ODP Leg 117, drilled offshore Oman, the dissolved sulphate concentration in the pore water sediments decreased from values of 25 mmol/l to almost zero within the first 50 m, thus indicating an apparently large depth range for bacterial sulphate reduction. Most of the reduced sulphur produced by this processes was fixed in pyrite. In addition, the sediments also contain a large proportion of organic sulphur (Lükage *et al.* 1996). Methanogenesis may be important in deeper sediments, but methane will commonly accumulate only after sulphate becomes nearly depleted (Martens and Berner, 1977; Reeburg, 1980).

5.12. CONCLUSIONS

1. There was no detectable non-detrital Mn in these cores. This is attributed to the lack of Mn₃ new oxides precipitation in surficial sediments and to the reduction and export of any Mn₄ “aged” oxides.
2. The “organic-associations” of Fe₅ do not appear to have suffered diagenetic modification; *i.e.* the binding strength of the Stage 5 “organic-association” appears to be sufficiently strong to preserve the trace metals.
3. There are no other clearly defined relationships in the solid state speciation of ‘aged’ oxides of Fe₄ that can be defined as being diagenetically-mediated.
4. Differences in OM parameters were linked to the distinct compositions of the cores. Concentrations of TOC and TN, as well as THAA and THCH were lowest in the bottom unit. The sources of the OM throughout the cores were complex.
5. There was little apparent diagenetic modification of OM; Normalised concentrations of THAA and THCH suggest that the OM is degraded, prior to

transport to the sediments and that there is little diagenetic removal relative to increasing sediment depth.

6. Unlike the MAP (Sutton, 1996) there was ***no*** relationship between OM parameters and Mn (or Fe) solid state speciation, reflecting the absence of ‘new’ oxides from the sediments.