Biogeochemical processes at the sediment–water interface in a Northeastern Atlantic abyssal locality (Porcupine Abyssal Plain)

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Abstract

Temporal and spatial variability in the composition of suspended particulate material (SPM) was found at a Northeastern Atlantic abyssal locality on the Porcupine Abyssal Plain at a depth of 4850 m. Total SPM was distinctly higher in July 1997 than in March–April 1997 and October 1996. The 20 m of water immediately overlying the seabed was strongly influenced by resuspension and the suspended particulate matter was enriched with iron and manganese. Two water distinct layers, which were characterized by being enriched with SPM, Fe_p, Mn_p and Al_p, were encountered during all sampling periods at depths of 4000 m and 4800 m. The enrichment of SPM with biogenic elements such as Ba, Ca and Sr implies it has a high biogenic content. Increases were observed in the concentrations of these biogenic elements throughout the sampling period, which indicates that the biogenic content of the SPM was steadily increased. SPM content and element/aluminum ratios increased in the spring and summer of 1997 compared to autumn 1996, probably as a result of increases in primary productivity, coincidental increases in near-bottom current velocities and possibly other processes such as increases in bacterial activity and bioturbation. Authigenic formation of solid phases of Fe and Mn were also influencing the spatial variability. Chemical reactions involving organic carbon and oxygen, which lead to the incorporation of iron and manganese in various forms into sediments were deduced. It is proposed that there was formation of lepidocrocite (γ-FeOOH) in the presence of organic carbon and oxygen, and also that iron may also have been transformed into Fe_2O_3. Re-precipitation of Fe and Mn is strongly enhanced by their enrichment in the SPM in the bottom waters. The sediments predominantly consist of biogenic carbonates and can be characterized as foraminiferal ooze. The proportion of these biogenic carbonates proved to be higher in the more recent sediments, either as result of recent increases in total primary productivity or because of carbonate dissolution within the subsurface sediments. Parallel increases of Mn, Fe and carbonates in the sediment layers supports the idea that the metallic ions are being adsorbed on to calcite surfaces, rather than being co-precipitated in the carbonate phases. Reprecipitation of iron and manganese in other solid phases with the involvement of organic carbon (C_{org}) in the oxygen penetration zone is suggested. © 2001 Elsevier Science Ltd. All rights reserved.

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Contents

1. Introduction

This paper examines geochemical interactions between surface sediments and bottom waters. By examining the variability in the elemental composition of the sediments and suspended particulate matter, we have studied processes such as:

1. early diagenesis in the sediments and the preservation of the sedimentary record,
2. remineralization in the water column, and
3. fractionation during the adsorption of dissolved species onto particles and during particle–particle interactions.

These processes are of considerable importance and have been the subject of several earlier investigations (Hunter, 1983; Honeyman & Santschi, 1989; Nyffeler, Li, & Santschi, 1984).

Both the solubility and the distributions of metal ions are controlled by their interaction with complexing ligands. Reduction/oxidation processes can also switch their phase between being in solution and being in particulate form (Davis & Leckie, 1978; Martin & Knauer, 1984; Schindler, 1990; Martin, Fitzwater, Gordon, Hunter, & Tanner, 1993). Redox chemical species such as NO_3^-, NO_2^-, NH_4^+ and $PO_4^=$, are often responsible for changing the chemical state of the metal ions, and the REDOX conditions are also involved in many of the geochemical reactions. Bacterial activity can often accelerate these reactions (Stumm & Morgan, 1981; Nealson, 1978, 1983; Cowen & Silver, 1984; Emerson, Cranston, & Liss, 1979).

The distribution of oxygen, inorganic carbon, alkalinity and nutrients (nitrate, silicate and phosphate) in ocean waters are mainly controlled by biological processes such as photosynthesis and respiration. However, lateral and/or vertical mixing and advection play an important role in determining the chemical characteristics of seawater masses, and result in changes in the concentration levels of these chemical species.

The BENGAL study area, at 48°50′N, 16°30′W (Billett & Rice, 2001) the deep waters are flowing northwards, whereas flow in the surface mixed layer and at the thermocline is generally southwards (Reid, 1994). Rintoul (1988) suggested that the circulation of intermediate waters is stronger and northwards similar to the transport of deep waters.

Additionally the water mass characteristics are being affected by the northward flow of the Antarctic Bottom Water (AABW) and the Lower Deep Water (LDW) (McCartney, 1992). In 1996–1997 current meter observations showed that the flow rates 0.5 mab were quite slow, their mean velocity being just 3.5 cm/sec showing a maximum speed of 9 cm/sec. Mean flow rates at 15 and 140 mab were 5 cm/sec, and reached a maximum of 13 cm/sec (Vangriesheim, Springer, & Crassous, 2001).

At 48°N in the NE Atlantic downwelling in the upper part of the water column above 800 m results in strong vertical transfer, which is consistent with a general sinking resulting from evaporation from the surface. Macdonald (1998) gave an initial estimate of 5×10^{-4} cm s^{-1} for the vertical transfer between 36°N and 48°N, while the transfer rate resulting from abyssal upwelling is about 1×10^{-5} cm s^{-1}. From below 800 m to depths of about 4000 m, there was evidence of upwelling throughout the water column.

2. Methodology

2.1. Suspended particulate matter sampling, sample preparation and analysis

Sampling in the PAP area was conducted from the *Meteor* in October 1996 and RRS *Discovery* in March–April 1997 and July 1997 respectively. Water samples were collected using Niskin bottles mounted on a CTD rosette sampler. These water samples were filtered on board through pre-weighed Millipore membrane filters (0.45 μm pore size), using a vacuum pump. Any residual salts were removed from the filters by repeatedly rinsing with distilled deionized water, pH-adjusted (pH=8). The filters were oven dried for 12 h at 60°C, weighed, then leached for 4 h with 20 ml of a mixture of ultrapure 2 M HCl–1 M HNO$_3$ at room temperature. This dissolved the carbonates and the oxyhydroxide phases, the more resistant (e.g. Fe^{3+}) oxyhydroxides and the metal sulphides (Landing & Lewis, 1991; Landing & Bruland, 1987; Kenison Falkner et al., 1993).

The HCl/HNO$_3$ fractions were reduced individually to near-dryness in Teflon beakers on a hot plate and then redissolved in 5 ml of an ultrapure mixture of 0.5 N HCl and 0.1 N HNO$_3$. Aliquots of these samples were then analysed by graphite furnace atomic absorption spectrometry (Bishop, 1990; Loring & Rantala, 1992; Trocine & Trefry, 1988; Kenison Falkner et al., 1993).

Solutions for the determination of Al, Fe and Mn were diluted with triple-distilled water to bring the concentrations into line with the linear portion of the calibration curve; this provided better sensitivity. Aliquots of the samples were then analyzed and the final concentrations calculated by multiplying with the dilution factor. Multipoint calibrations were applied for all the elements studied. Working standards were prepared daily by diluting with triple-distilled water ready-to-use Merck stock standards. Blank samples were taken with every batch in the same way as samples, in order to check for any reagent effect. All blank samples yielded concentrations that were <5% of the average particulate metal concentrations. The precision was checked with replicate analyses and was better than ±4% for all elements studied. The analytical instrumentation consisted of a 2001 Perkin Elmer spectrophotometer, combined with the 701 HGA Graphite Furnace model. Pyro/platform tubes together with matrix modification were used to provide increased sensitivity for Al, Fe and Mn determinations; the operational parameters recommended by the manufacturer were applied.

2.2. Sediment sampling, sample preparation and analysis

Cores of the bottom sediments were collected using a multicorer. Immediately after their retrieval, the cores were transferred to a constant temperature laboratory (4°C), where they were sliced into horizons of 0–5, 5–10, 10–20, 20–30, 30–40, 40–50, 50–60, 60–100, 100–150 and 150–200 mm. The slices were transferred into plastic containers and frozen at −20°C. The sediment slices were freeze-dried and then

ground to a powder using a pestle and mortar prior to analysis. From each slice, a 0.5 g sample of ground sediment was placed in a beaker and 5 ml of 6 N HCl were added. The sample was covered with a watch glass and placed on a hot plate (70°C) for 3.5 h, until a yellow-orange colour developed.

This HCl-leaching isolates the silicate–aluminosilicate fraction of the sediments, by dissolving the carbonates; the interstitial water evaporates together with some colloidal iron and also removes elements from ion-exchange position. Also, the HCl dissolves manganese and iron crystalline oxides and partially attacks clay minerals including iron clay montronite (Cronan, 1976; Chester & Hughes, 1967).

The residue after the treatment with HCl consists of resistant silicates and aluminosilicates. The samples were cooled and then filtered through Millipore membrane filters (0.45 μm); the filtrates were made up to 25 mls. All reagents were of analytical grade obtained commercially from Merck. Samples were analyzed applying flame atomic absorption techniques (Loring & Rantala, 1992), using the Perkin Elmer 2001 atomic absorption spectrophotometer under working conditions recommended by the manufacturer.

Multipoint calibration was applied in all cases using working standards prepared daily by the dilution of ready-to-use Merck stock standards for atomic absorption spectroscopy. Replicate analyses showed the precision was better than ±5%.

Additionally, 0.5 g from each ground sediment sample was placed in a glass beaker and 10 mls of 25% v/v acetic acid was added and left at room temperature for 5 h. The suspensions were then filtered onto pre-weighed membrane dry filters and the filters were dried at 60°C until they reached constant weight. The weight difference was ascribed to calcium carbonate.

3. Results and discussion

Chemical analyses were carried out on both sediment and suspended particulate matter (SPM) samples collected from the PAP area. The results are shown in Tables 1–4. In order to study the behaviour of elements and the biogeochemical processes taking place at the sediment–water interface the data are presented in three different ways:

1. Vertical profiles of element concentrations are presented to establish the levels within the water column at which the geochemical reactions of interest are taking place.
2. Normalized data are presented to identify the origin of the elements analyzed.
3. The association between the different phases and sources are investigated in order to examine the geochemical behavior of the elements within the water column and in the Benthic Boundary Layer (BBL).

3.1. Vertical distribution, spatial variability and behaviour of particles at the Porcupine Abyssal Plain

The concentrations of suspended particulate matter (SPM) increased from autumn 1996 to spring and summer 1997. In spring 1997, the SPM contents ranged from 156.7 μg/l to 458.3 μg/l; these were in the same order of magnitude as the SPM contents reported by Chester and Stoner (1972) for North Atlantic. The minimum value of 200 μg/l reported by Thomsen and Van Weering (1998) for the N.W. European Continental Margin (Goban Spur) also lay within this range.

In summer 1997 the SPM contents ranged from 280 μg/l to 5590 μg/l. Maximum concentrations occurred 10 m above the bottom (mab), and minimum values occurred at 130 mab (Fig. 1). The highest value we observed of 5590 μg/l was about 50% lower than the maximum value of 10000 μg/l reported by Thomsen and Van Weering (1998) in the benthic boundary layer at the Goban Spur on the Northwest European Continental Margin. At the other sampling times, the maximum concentrations of SPM were at ~830 mab and minimum concentrations were at 20–40 mab (Fig. 2). Within 20 m of the seafloor, concentrations of

Table 1
Station references positioning and results of the SPM samples analyzed

Cruise and date of collection	Station reference	Coordinates	Water depth (m)	SPM (µg/l)	Fe (ng/l)	Mn (ng/l)	Al(ng/l)	Fe/Al	Mn/Al
Meteor 36	367	48°58'N 16°28'W	3300	21.16	111.11	4.23	95.77	1.16	0.04
October 1996	367		3800	32.79	180.33	4.92	56.28	3.20	0.09
Depth=4830 m	367		4000	138.89	340.29	6.94	102.08	3.33	0.07
	367		4700	24.47	204.54	12.06	103.85	1.97	0.12
	367		4750	41.90	268.57	10.48	98.67	2.72	0.11
	375		4770	89.47	268.42	12.89	108.16	2.48	0.12
	375		4790	44.77	97.01	9.14	89.74	1.08	0.10
	380		4800	22.06	163.60	11.76	92.83	1.76	0.13
	380		4810	42.03	169.88	12.96	94.22	1.80	0.14
	380		4820	26.67	178.33	9.50	65.50	2.72	0.15
Discovery 226	13077/61	48°50'N 16°30'W	3300	160.00	3283.33	27.83	439.67	7.47	0.06
March–April 1997	13077/67		3800	160.00	2683.33	25.50	476.17	5.63	0.05
Depth=4835 m	13077/77		4000	458.33	4255.95	59.82	1045.83	4.07	0.06
	13077/91		4700	208.70	2456.52	35.00	646.74	3.80	0.05
	13077/23		4750	207.02	3140.35	23.16	329.65	9.53	0.07
	13077/30		4775	332.07	1886.79	34.34	500.57	3.77	0.07
	13077/91		4800	250.00	2687.50	52.71	660.42	4.07	0.08
	13077/30		4805	156.67	850.00	12.67	183.33	4.64	0.07
	13077/30		4815	186.67	2683.33	30.67	424.33	6.32	0.07
	13077/30		4826	192.31	2596.15	33.85	371.35	6.99	0.09
Discovery 229	13200/92	48°50'N 16°30'W	4000	794.00	1100.00	11.30	63.70	17.69	0.18
July 1997	13200/37		4700	280.00	1900.00	15.30	54.60	34.34	0.28
Depth=4830 m	13200/37		4750	335.00	1700.00	23.40	134.90	12.26	0.17
	13200/34		4770	470.00	3400.00	20.10	63.20	53.52	0.32
	13200/34		4790	478.00	3200.00	44.40	167.10	18.93	0.27
	13200/30		4800	741.00	4900.00	48.30	381.00	12.90	0.13
	13200/11		4810	617.00	4800.00	38.10	502.80	9.48	0.08
	13200/12		4820	5590.00	10500.00	143.60	742.30	14.16	0.19

Table 2
Results of sediment cores analyzed

Core number	Depth (mm)	CaCO$_3$ (%)	Al (%)	Fe (%)	Mn (mg/kg)	Fe/Al	Mn/Al
12930/10	0–5	72.60	1.46	1.02	450	0.70	0.031
	5–10	72.23	1.42	1.05	450	0.74	0.032
	10–20	71.26	1.79	1.07	500	0.60	0.028
12930/18	0–5	73.65	1.67	1.03	449	0.62	0.027
	5–10	73.04	1.83	1.07	499	0.58	0.027
	10–20	73.00	1.55	1.07	499	0.69	0.032
12930/36	0–5	74.54	1.45	0.97	450	0.67	0.031
	5–10	72.93	1.53	1.02	450	0.67	0.031
	10–20	72.23	1.61	1.03	450	0.64	0.028
12930/49	0–5	73.76	1.29	0.97	447	0.75	0.035
	5–10	73.54	1.49	0.97	449	0.65	0.030
	10–20	72.76	1.54	1.02	499	0.66	0.032
12930/76	0–5	69.08	1.42	1.24	500	0.87	0.035
	5–10	69.79	1.58	1.17	499	0.74	0.032
	10–20	71.56	1.59	1.08	500	0.68	0.031
372	0–30	71.22	1.04	0.97	512	0.93	0.049
	30–60	70.85	1.09	1.04	512	0.95	0.047
373	0–30	71.11	1.48	1.04	536	0.70	0.036
	30–60	70.66	0.95	1.01	524	1.06	0.055
13077/65	0–5	n.a.[a]	0.96	1.05	500	1.09	0.052
	5–10	n.a.	1.37	1.08	518	0.79	0.038
	10–20	n.a.	1.57	1.10	509	0.70	0.032
13200/46	0–5	n.a.	1.08	1.11	504	1.03	0.047
	5–10	n.a.	1.00	1.13	503	1.13	0.050
	10–20	n.a.	1.29	1.05	503	0.82	0.039
54301/19	0–5	n.a.	0.37	0.82	520	2.23	0.014
	5–10	n.a.	2.48	0.79	512	0.32	0.021
	10–20	n.a.	2.70	0.80	485	0.30	0.018
54301/21	0–5	n.a.	0.44	0.70	518	1.58	0.012
	5–10	n.a.	1.19	0.67	538	0.56	0.045
	10–20	n.a.	0.67	0.72	536	1.08	0.080
13368/26	0–5	n.a.	1.90	0.63	504	0.33	0.026
	5–10	n.a.	1.52	0.55	485	0.37	0.032
	10–20	n.a.	0.64	0.70	515	1.09	0.080

[a] n.a. = not analyzed.

suspended particulate matter increased indicating the influence of resuspension. Surface sediments are strongly affected by resuspension, which in turn influences the chemical composition of the SPM. Microscopical examination of the bulk sediment samples showed that the sediments were predominantly composed of carbonates of biogenic origin. Well-preserved foraminifer tests were abundant and showed no signs of dissolution. A schematic model of the formation, transportation and transformation of SPM during its descent from the euphotic zone to the seabed is shown in Fig. 3.

The element/aluminum ratios for the particulates and the sediments increased from autumn 1996 to spring and summer 1997, possibly indicating that the supplies of fresh material derived from primary productions in the overlying surface layers were increasing. The increase of SPM concentration from March to July 1997 is consistent with the lowest mass flux measured was in early April 1997, whereas the maximum mass flux was observed in July 1997. The lower concentrations of SPM found in autumn 1996 were the consequence of the decline from the summertime SPM maximum, following the seasonal collapse of the Spring bloom (Vangriesheim, Springer, & Crassous, 2001).

Table 3
Station references and positioning of the sediment samples analyzed

Cruise	Station reference	Coordinates PAP area	Date of collection
Discovery 222	12930/10	48°50′N–16°30′W	August–September 1996
	12930/18		August–September 1996
	12930/49		August–September 1996
	12930/76		August–September 1996
Meteor 36	372	48°58′N–16°30′W	October 1996
	373		October 1996
Discovery 226	13077/65	48°50′N–16°30′W	March–April 1997
Discovery 229	13200/46	48°50′N–16°30′ W	July 1997
Challenger 135 C	54301/19	48°50′N–16°30′W	October 1997
	54301/21		October 1997
Discovery 231	13368/26	48°50′N–16°30′W	March 1998

The high SPM concentrations observed in July 1997 cannot be explained by the physical environmental regime. Current velocities at the PAP site were too low to cause resuspension (mean/maximum current speeds at 15 mab were 5 and 13 cm/sec respectively, and at 0.5 mab were 3.5 and 9 cm/sec respectively, Vangriesheim et al., 2001). Benthic storms (up to 27 cm/sec) were recorded at the nearby NOAMP site by Klein and Mittelstaedt (1992) but no such storms have been detected at the PAP site (Vangriesheim, 1988; Lampitt et al., 2001).

It is suggested that large amounts of particles derived from the surface production, scavenge SPM resulting in the observed maxima in the BBL. As the large particles sink to the bottom they disaggregated into smaller particles, which are more easily resuspended. As a result of the substantial input of phytodetritus material to the seabed in July 1997, the megafauna increased in abundance and reworked the detritus at the sediment surface very quickly (Billett et al., 2001; Lampitt et al., 2001; Kiriakoulakis et al., 2001). Thomsen and Flach (1997) suggested that the activity of benthic fauna boosts resuspension into the benthic boundary layer (BBL). The structure of the sediment in the PAP area shows low compaction, indicating rapid accumulation and/or high bioturbation. Bioturbation activity is most intensive in the upper 20 mm of the layer, which is in agreement with Thomson et al. (1987), who observed that signs of bioturbation were apparent within the upper 6 cm of sediments in the N.E. Atlantic.

An alternative explanation for the high SPM concentrations observed in July 1997 is that residence times in the BBL were high as a result of low settling velocities of POC. The high POC/TPM ratios under low flow conditions, indicate POC is more readily resuspended than the inorganic particles. The decrease in POC/TPM ratios together with the increase in CPE/POC ratios under conditions of increasing current velocity, shows that the lithogenic component of the surface sediments starting to be resuspended (Thomsen & Van Weering, 1998). The variability of element/aluminum ratios implies that the large organic aggregates with low lithogenic content were settling more slowly.

The Fe/Al and Mn/Al ratios were well above the aluminosilicate values of 0.5 and 0.01 respectively, implying that significant amounts of iron and manganese were present in chemical forms other than the aluminosilicates. Our data suggest that most of the particulates had originated from the primary production in the overlying euphotic zone. Table 5 lists the correlations between the elements in the suspended particulate matter. It shows that both iron and manganese concentrations were positively correlated with the concentrations of the biogenic elements, such as Ba, Ca and Sr. We conclude that the vertical and temporal variability of Fe and Mn were being controlled by the biological fluxes. Another fraction of SPM originates from the authigenic formation of amorphous iron–manganese precipitates. Their formation could be chemically controlled and may be boosted by bacteria activity (see below).

Table 4
Comparison of Porcupine Abyssal Plain (PAP) sediments and SPM samples in the Atlantic Ocean, with other study areas[a]

	Fe		Mn		Al		CaCO$_3$		SPM (μg/l)	
a	0.96%	n=12	490.77 mg/kg	n=12	1.21%	n=12	72.28%	n=7	–	
b	0.96%	n=12	494.95 mg/kg	n=12	1.45%	n=12	71.86%	n=7	–	
c	1.16%	n=109	539.09 mg/kg	n=109	1.39%	n=109	66.87%	n=59	–	
d	2262.68 ng/l	n=28	28.71 ng/l	n=28	287.40 ng/l	n=28	–		481.91	n=28
e	1.18%	n=15	147.00 mg/kg	n=15	–		–		–	
f	0.89–3.68%		200–2900 mg/kg		–		30–60%	–	–	
g	7.3%		0.6%		5.6%		78.7%		–	
h	5.0%		0.4%		9.0%		–		–	
i	–		–		–		–		200–10,000	
j	155.25 ng/l	n=10	7.21 ng/l	n=10	75.01 ng/l	n=10	–		8.5	n=10
k North Atlantic	–		–		–		–		121–1168	
k Irish Sea	–		–		–		–		1087–1260	
l	58–581 ng/l		0.60–22.80 ng/l		31–768 ng/l		–		–	

[a] a: this study, average for PAP surface sediments (0–5 mm); b: this study, average for PAP subsurface sediments (5–10 mm); c: this study, average for all PAP sediments; d: this study, average for all PAP suspended particulate matter (SPM) samples; e: Horowitz and Cronan (1976), average for HCl-soluble Deep Sea Drilling Atlantic Sediments; f: Lew (1981), average in marls from the Atlantic ocean; g: Shearme et al. (1983), average for Trans Atlantic Gear (TAG) surface sediments; h: Turekian and Imbrie (1966), average for North Atlantic Pelagic clays; i: Thomsen and Van Weering (1998); j: Trocine and Trefry (1988), average on background samples at 26°N on the Mid-Atlantic Ridge; k: Chester and Stoner (1972), North Atlantic–Irish Sea; l: Krishnaswami and Sarin (1976).
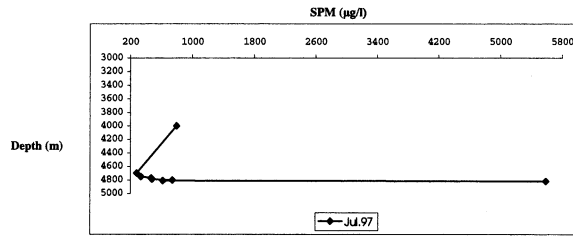
Fig. 1.   Vertical variability of suspended particulate matter (SPM) in the PAP area. July 1997.
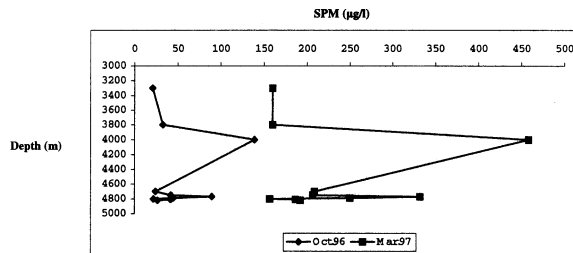

Fig. 2.   Vertical variability of suspended particulate matter (SPM) in the PAP area. October 1996, March–April 1997.

3.2. Biogeochemical approach of iron and manganese distribution

The chemical analysis of SPM indicates that concentrations of particulate iron tended to decrease close to the bottom in October 1996 and March 1997. In July 1997 the particulate iron concentrations were highest close to the seafloor and increased from 830 mab to 9 mab (Figs. 4 and 5), implying resuspension of sediments was influencing at least the lowest 60 m of the water column.

Between 60 mab and 800 mab there was evidence for a mixing zone in which both resuspended iron rich particles and amorphous iron precipitates were present. This is shown with the high Fe_p/Al_p ratios which are well in excess of the ratio of 0.5 typical of aluminosilicates. Otherwise the general trend for particulate Fe to increase from the sea surface down towards the bottom indicates that most of particulate iron is associated with organic particles and biological production and is being scavenged from the upper water column by sedimenting phytodetrital particles.

If this is the case then much of the particulate Fe in the lower water column originates from the release of iron originally incorporated in organic matter produced in the euphotic zone (Krishnaswami & Sarin, 1976). The synthesis of chlorophyll and nitrate reductase by phytoplankton requires sufficient concentrations of dissolved Fe, the majority of the exported Fe is derived from the lateral transport of particulate Fe (Martin et al., 1993).

A interesting feature of the water column at PAP is the occurrence of a layer enrichment with SPM at about 4000 m depth. This layer was observed during all sampling periods (October 1996, March–April 1997, July 1997). In both October 1996 and March–April 1997 the water in the layer was enriched with Fe_p and Al_p. The Al_p enrichment may be related to the scavenging of aluminium by biogenic particles. Yeats, Dalziel, and Moran (1992) reported that sorption onto the surfaces of living and dead diatoms in seawater was removing Al. However Mn_p was not as enriched as Fe_p in this layer. Additionally Fe_p/Mn_p ratios show tendency to increase with time. The Fe_p/Mn_p rose from 49 in October 1996, to 71 in March–April 1997, and then to 97 in July 1997. Another layer in which SPM, Fe_p and Al_p peaked was encountered at 4770 m in October 1996, at 4800 m in March–April 1997 and July 1997. The Fe_p/Mn_p ratios in this
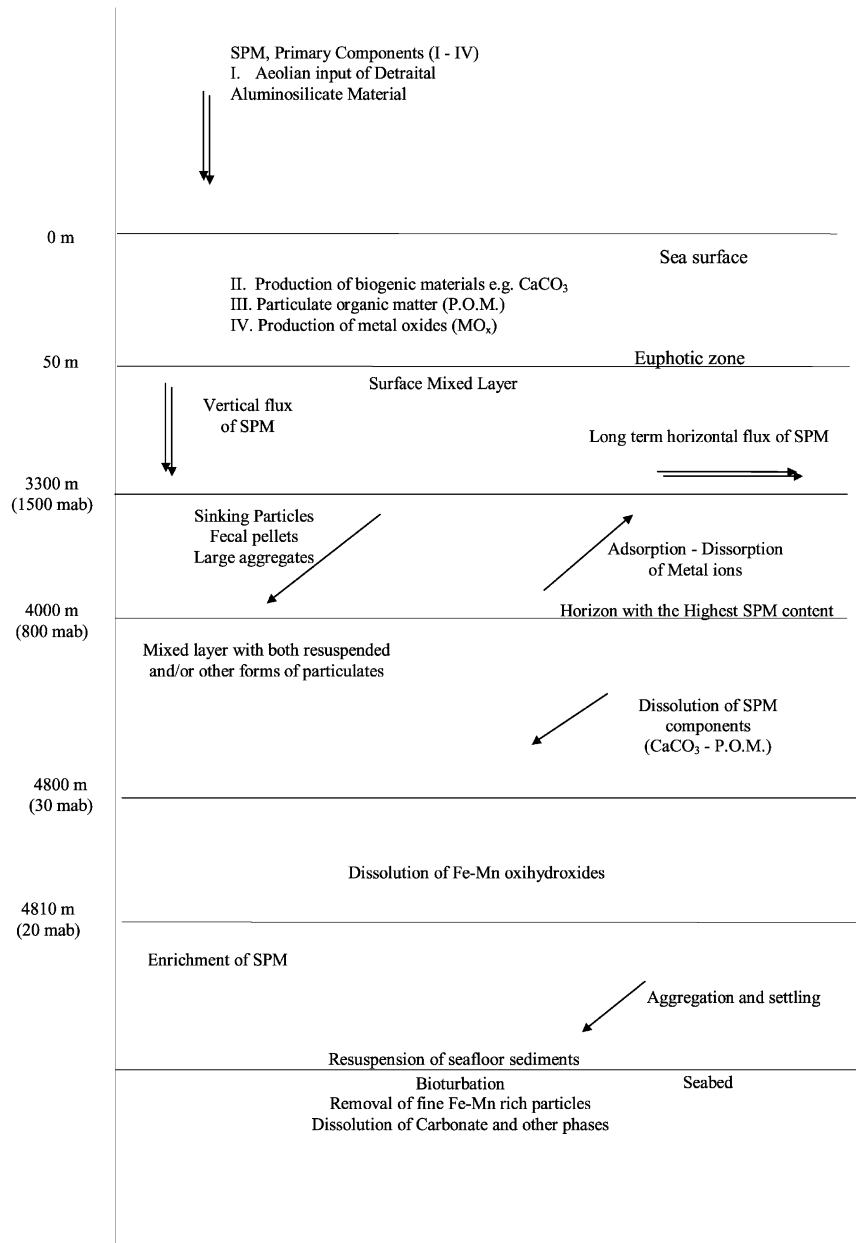
Fig. 3.   Schematic description of the processes taking place at the Porcupine Abyssal Plain (PAP) North Eastern Atlantic.

water layer increased with time from 20.8 in October 1996, to 51.0 in March–April 1997 and to 101.4 in July 1997.

Thus regardless of the origins of these two distinct layer, they appeared to have analogue sources for their SPM content. The strong biogenic influence on the constituents of the SPM, as discussed above, is also indicated by enrichment with biogenic elements such as Ba, Ca, and Sr. These enrichments were pronounced during March–April 1997 and July 1997 but less so in during the October 1996. We, therefore,

Table 5
Correlation coefficients among the element concentrations in suspended particulate matter samples collected from the PAP area

n=28	Al	Ba	Ca	Fe	Mg	Mn	Si	SPM	Sr
Al	1								
Ba	0.9546	1							
Ca	0.7969	0.9197	1						
Fe	0.9257	0.9299	0.8977	1					
Mg	0.7112	0.8623	0.9793	0.8057	1				
Mn	0.8772	0.9549	0.9535	0.9603	0.8869	1			
Si	0.5173	0.7099	0.8722	0.5843	0.9437	0.7083	1		
SPM	0.7864	0.9072	0.9951	0.8970	0.9782	0.9513	0.8697	1	
Sr	0.7959	0.9169	0.9986	0.9005	0.9792	0.9554	0.8694	0.9989	1
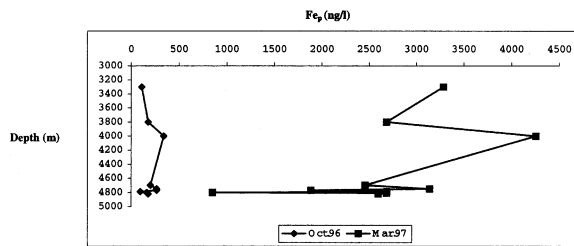
Fig. 4. Vertical variability of particulate iron (Fe_p) in the PAP area. October 1996, March–April 1997.
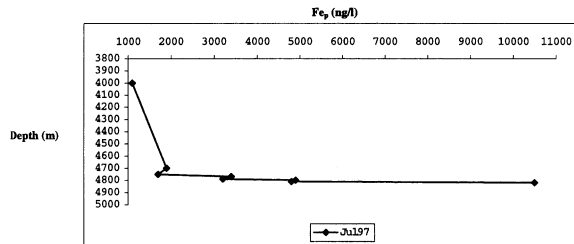
Fig. 5. Vertical variability of particulate iron (Fe_p) in the PAP area. July 1997.
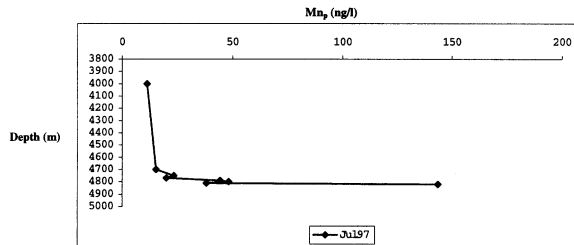
Fig. 6. Vertical variability of particulate manganese (Mn_p) in the PAP area. July 1997.

conclude that the increase in SPM in these layers observed in October 1996, March–April 1997 and July 1997 is directly related to increases in the primary productivity.

The concentrations of particulate manganese varied with depth and time of sampling. For example, Mn_p minima were observed at 20 mab in July 1997, at 30 mab in March 1997, and at 40 mab in October 1996 (Figs. 6 and 7). Similar patterns have been observed in the subtropical Pacific within the oxygen minimum
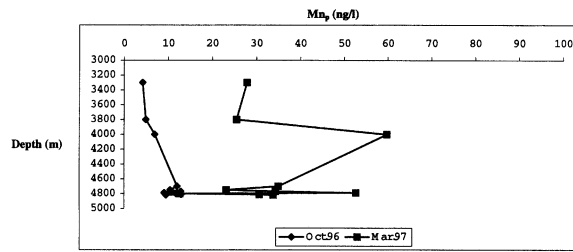
Fig. 7. Vertical variability of particulate manganese (Mn_p) in the PAP area. October 1996, March–April 1997.

layer (Martin & Knauer, 1984; Landing & Bruland, 1987) and also in the Aegean Sea (Voutsinou-Talia-douri, Varnavas, Nakopoulou, & Moriki, 1997).

The vertical profiles of manganese concentrations were high variable at PAP. The high Mn_p/Al_p ratios observed during all three sampling periods implies the presence of other forms of Mn_p. These other forms of manganese might be ions adsorbed onto the surfaces or bound within the matrices of calcium and aluminum particulates, manganese held within the lattices of minerals other than manganese oxides), and manganese within the cell contents of microorganisms, derived from the surface mixed layer. Thus, the high positive loadings of Mn_p with SPM and Fe_p are consistent with manganese being scavenged by the Fe phases and the organic aggregates in the seawater (Krishnaswami & Sarin, 1976). Manganese undergoes a dynamic redox cycle in seawater and the partitioning between dissolved Mn^{2+} and particulate MnO_x depends on the relative balance between oxidative and reductive reactions (Sunda & Huntsman, 1987).

Burdige and Nealson (1985); De Vrind, Boogerd, and De Long (1986) and Ehrlich (1980) suggested that in near surface waters, manganese reduction can be mediated, both directly and indirectly, by micro-organisms, while photochemical reactions result in the dissolution of particulate manganese through reduction (Sunda, Huntsman, & Harvey, 1983). As the organic matter sinks to deeper water and is decom-posed, it releases the manganese, resulting in the particulates becoming progressively manganese-poor. Re-oxidation of Mn^{2+} to Mn^{3+} or Mn^{4+} oxyhydroxides is relatively slow (Stumm & Morgan, 1981), but may be enhanced by bacterial activity (Nealson, 1978), a process that may be responsible for the enrichment of Mn_p and Fe_p in the well oxygenated deep waters of the NE Atlantic.

However, concentrations of Fe in the surficial sediment layer increased from 0.97% in October 1996 to 1.04% in April 1997 and 1.11% in July 1997. Manganese, however, was in higher concentrations in the top 5 mm of the sediment in October 1996 (536 mg/kg) than later in both April 1997 (500 mg/kg) and July 1997 (504 mg/kg) (Figs. 8–10).

Resuspension of seabed fine particles contributes to the Fe and Mn enrichment of SPM in the nepheloid layer. Bioturbation of the sediments enhances resuspension because it keeps the sediments loose by keeping it from compacting. Therefore Fe and Mn oxihydroxides as well as fine Al-rich particles are readily trans-ferred from the sediments back into the bottom waters. The increase in the Al content of SPM near the seabed parallels the increases in Fe and Mn and provides supportive evidence for such a process. The vertical profiles of Fe concentrations in the sediment cores showed that in many cases the surficial sediments contained less Fe than the subsurface sediments (i.e cores 12930/10, 18, 36, 49 and cores 372, 13077/65, 13200/46). This depletion may be a result of the removal of the Fe-rich fine particles during resuspension.

Both Mn and Fe were negatively correlated with $CaCO_3$ in the sediments indicating they are incorporated in chemical components other than the carbonate phase (Table 6). The surface sediment layer is subject to complex geochemical reactions; constituents derived from the water column are reacting with authigenic constituents, which is affecting not only their steady state conditions but are also changing the Eh/pH conditions. The Eh/pH variations in the pore waters–sediment system, are largely related to the oxidation of organic carbon by bacterial action. High concentrations of organic carbon in the surface sediments have
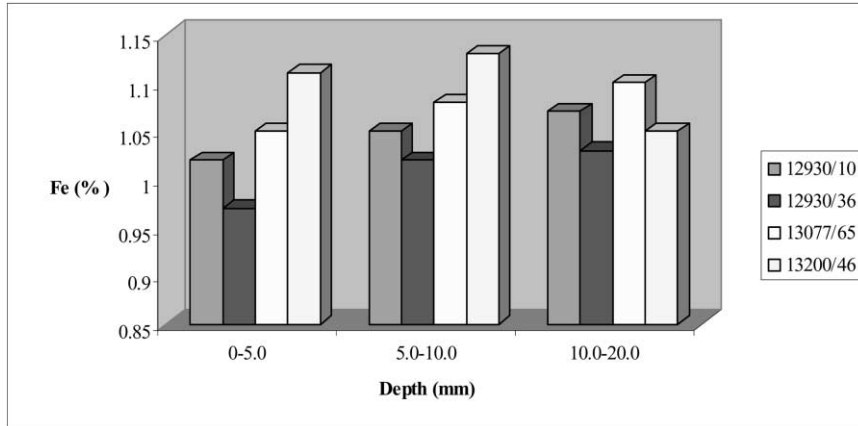
Fig. 8.   Variability of iron in sediment cores collected from the PAP area.
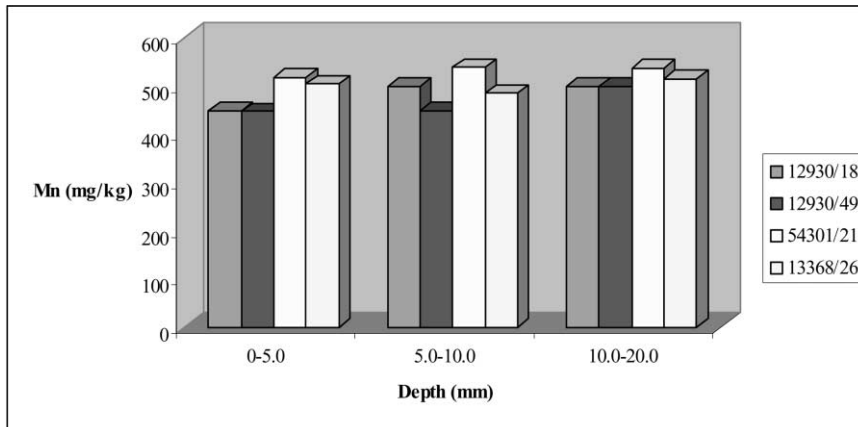

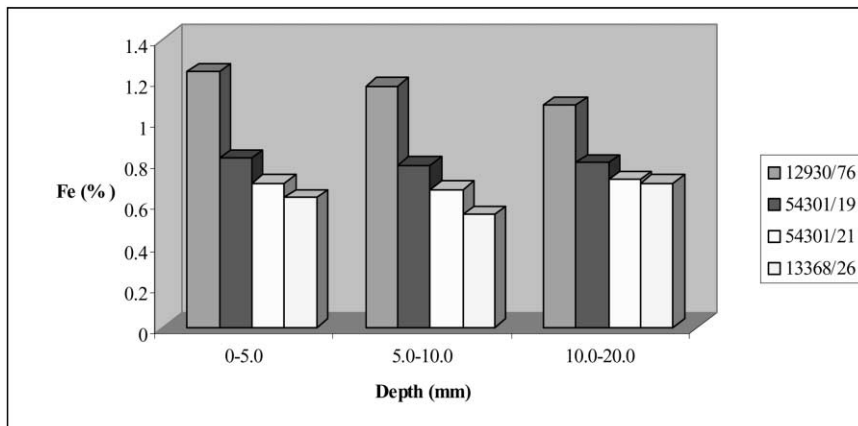Fig. 9.   Variability of manganese in sediment cores collected from the PAP area.

Fig. 10.   Variability of iron in sediment cores collected from the PAP area.

Table 6
Correlation coefficients among the element concentrations in sediment cores collected from the PAP area

$n=109$	$CaCO_3$	Ca	Si	Al-silicates	Mg	Fe	Mn	Ba	Al
$CaCO_3$	1								
Ca	0.999	1							
Si	0.058	0.058	1						
Al-silicates	−0.994	−0.994	−0.067	1					
Mg	−0.891	−0.891	0.042	0.877	1				
Fe	−0.966	−0.966	−0.016	0.941	0.864	1			
Mn	−0.967	−0.967	−0.132	0.960	0.815	0.938	1		
Ba	−0.886	−0.886	−0.085	0.855	0.733	0.920	0.877	1	
Al	−0.861	−0.861	−0.006	0.826	0.753	0.910	0.838	0.881	1

been found by a number of investigations (Heggie et al., 1987; Burdige & Homstead, 1994), and while high nitrate concentrations in the surficial sediment layer are associated with nitrogenous organic components (Balzer, 1989). The pore water analysis at PAP showed there were increase in nitrate, ammonia, silicate and alkalinity within the upper 2 cm of sediment that were inversely related to decreases in sediment C_{org}, phosphate and dissolved oxygen.

The interactions between Fe–Mn solid phases, Fe^{2+} and Mn^{2+} with organic matter and oxygen in the surface sediments and at the sediment water interface are affected by Eh and pH variations and additional sediment accumulation. These result either in the dissolution of Fe–Mn solid phases (cores 12930/10, 36 and cores 372, 10377/65, 13200/46), or in the formation of unstable amorphous Fe–Mn phases (colloidal Fe–Mn hydroxides), which are readily resuspended from the bottom. The hydrolysis equilibra of Fe^{2+} is strongly involved in these processes as described by the following reactions:

$$Fe^{2+} + OH^- = Fe(OH)^+ \tag{1}$$

$$Fe^{2+} + 2OH^- = Fe(OH)_2^0 \tag{2}$$

$$Fe^{2+} + 3OH^- = Fe(OH)_3^- \tag{3}$$

(Millero, Sotolongo, & Izaguirre, 1987).

In some cores (12930/76, 373, 54301/19, 54301/21, 13368/26), further oxidation of Fe^{2+} involving the Fe^{2+} chemical species, resulted in an increase of Fe concentration in the surface sediments.

$$2Fe(OH)^+ + \frac{1}{2}O_2 = Fe_2O_3 + 2H^+ \tag{4}$$

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3 \tag{5}$$

The availability of oxygen and hydrogen ions are controlling factors in these reactions.

In some other cases, the presence of organic matter (OM) appears to be influencing the degree of oxidation, altering the steady-state concentration of Fe^{2+} through the following reactions:

$$Fe^{2+} + OM + \frac{1}{4}O_2 = Fe^{3+} - OM \tag{6}$$

$$Fe^{3+} - OM \rightarrow Fe^{2+} + \text{oxidised OM} \tag{7}$$

(Miles & Brezonik, 1981).

Ferrous ions (Fe^{2+}) reprecipitate faster than Mn^{2+} ions, forming iron oxides–hydroxides. Under such conditions lepidocrocite (γ-FeOOH) surfaces can act as catalysts for the oxidation of Mn^{2+} and its removal from the pore water according to the following reaction:

$$FeOH + Mn^{2+} = FeOMn^+ + H^+ \tag{8}$$

(Sung & Morgan, 1981).

This process is very pronounced in sands and carbonates in which there is good ventilation with oxygen (Van der Weijden, 1975). The high positive loadings found between Fe and Mn concentrations in the factor analysis of the sediments constituents supports that the hypothesis that these geochemical processes were taking place.

The complete process suggested here is that first lepidocrocite (γ-FeOOH) is formed in the presence of organic carbon and O_2 according to the reaction:

$$2Fe^{2+} + \frac{1}{2}C_{org} + O_2 + 3H_2O = 2FeOOH + \frac{1}{2}CO_2 + 4H^+ \tag{9}$$

In highly oxidizing conditions some of the ferrous iron is transformed to Fe_2O_3 according to the reaction:

$$2Fe^{2+} + C_{org} + \frac{3}{2}O_2 + 2H_2O = Fe_2O_3 + CO_2 + 4H^+ \tag{10}$$

The existence of these reactions is feasible because reprecipitation of Fe is easier under highly oxidizing conditions (high Eh) (Bonatti, Fischer, Joensuu, & Ryndell, 1971; Emerson, 1985; Reimers, Kalhorn, Emerson, & Nealson, 1984). Organic matter facilitates the precipitation of Fe solid phases by adsorbing Fe^{2+} and re-precipitating under oxic conditions. A similar process been described to explain the formation of barite ($BaSO_4$) (Chow & Goldberg, 1960; Dehairs, Chesselet, & Jedwab, 1980). Thus organic carbon and oxygen can be seen to be important regulating factors, reaction (9), whereas reaction (10) leads to a more stable phase.

Once formed, the lepidocrocite then acts as a catalyst to intermediate stages in the formation of Fe_2O_3 and MnO_2 according to the reactions:

$$FeOH + Mn^{2+} = FeOMn^+ + H^+$$

(Sung & Morgan, 1981)
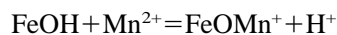
$$2FeOMn^+ + 2O_2 + H_2O = Fe_2O_3 + 2MnO_2 + 2H^+ \tag{11}$$
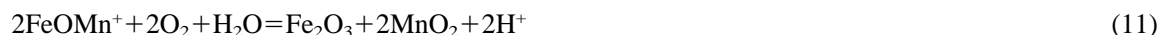
These geochemical reactions, involved in the re-precipitation of iron and manganese, may be boosted by microbial oxidation/reduction processes (Gebers & Hirsch, 1978; Nealson, 1983). The energy necessary for the microbial activation could be derived largely from the oxidation of organic matter and, in many cases, of nutrients. The role of bacteria in Eh changes is not direct. During their metabolism, they utilise inorganic constituents such as iron and manganese for their growth and reproduction. They cause variations, for example on the ferric:ferrous ion ratios, so that the

$$\text{Eh} = E_0 + \frac{RT}{n \cdot F} \cdot \ln \frac{\alpha \text{Fe}^{3+}}{\alpha \text{Fe}^{2+}} \tag{12}$$

may be changed. R is the gas constant; T is the absolute temperature; n is the number of electrons involved in the reaction; F is Faraday's constant and α is the activity of Fe^{3+} and Fe^{2+}

In the case of iron, Bruland (1983) suggested that a potential source is consistent with the electron transfer of Fe^{2+} and its transformation into Fe^{3+} in an oxic environment, as a result of the reaction:

$$\text{Fe}^{2+} - (e^-) = \text{Fe}^{3+} \tag{13}$$

Although the processes whereby bacterial metabolism is involved in metal precipitation is poorly known, we can assume that in the PAP area a combination of physicochemical and biogeochemical processes are responsible for the changes in the solid–soluble relationships. The growth of microorganisms can affect the potential conditions at a micro-scale and so can be responsible changes occurring between the two phases (Cowen & Silver, 1984; Cowen & Bruland, 1985).

3.3. The geochemical importance of $CaCO_3$ as a microenvironment for heterogenous reactions

The distribution of calcium carbonate in the sediment cores collected from PAP area shows that both the surface (mean 72.3%) and subsurface (mean 71.9%) sediments are rich in biogenic carbonate. The actual $CaCO_3$ contents ranged from 41.8% to 74.5%, which were close to the carbonate contents of 30–60% reported by Lew (1981) and 78.7% by Shearme, Cronan, and Rona (1983).

The vertical profiles of the $CaCO_3$ content show that it is highest in the surficial sediments and decreases slightly down core (Fig. 11). Sediments with a content of biogenic $CaCO_3$ content >60% are usually described as foraminiferal chalk oozes. Microscopical examination of bulk sediment samples showed that the majority of carbonate was indeed of biogenic origin and consisted mainly of skeletal remains of small organisms.

Three factors appear to have been controlling its vertical distribution:

1. Since higher concentrations of $CaCO_3$ were found in the surface rather than in the subsurface sediments, indicates that high primary productivity during the whole sampling period, but particularly prior to July 1997 had boosted the carbonate content. Such an increase is confirmed by both the increase in SPM
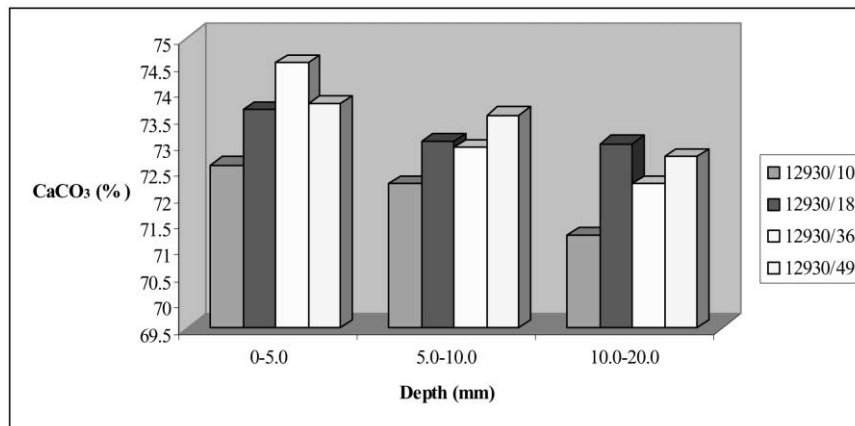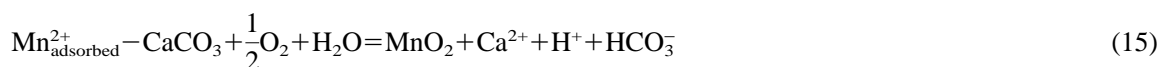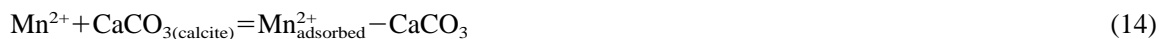

Fig. 11.   Variability of calcium carbonate in sediment cores collected from the PAP area.

and the increases in the concentrations of biogenic elements in the SPM (i.e. Ba, Ca, Sr) from October 1996 to March–April and through until July 1997.
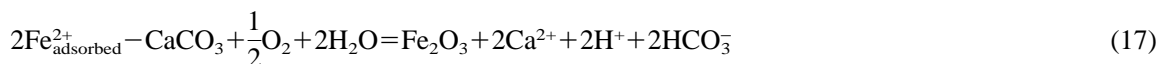
2. Any input of terrigenous sediments, in quantities sufficient to result in dilution of the biogenic components. The correlation coefficients between the concetrations of a variety of elements showed that the Al and Al-silicates contents were negatively correlation with the $CaCO_3$ content, confirming the antagonistic behaviour of these two constituents. In some cores (i.e. 12930/10, 12930/36, 13200/46, 372) there was a slight increase in Al content in the subsurface sediments relative to those at the surface. However it is unclear whether such lithogenic dilution was enough to account for the observed decrease in the $CaCO_3$ content of the subsurface sediments.

3. Another factor may be the in situ dissolution of $CaCO_3$. There was a negative correlation between $CaCO_3$, Fe and Mn (Table 6). We have therefore suggested that Fe and Mn are not incorporated in the carbonate phase but are co-precipitated as Fe–Mn oxides; hence the strong positive correlation found between Fe and Mn in the sediments analyzed. The correlation between Fe and Mn concetrations and those of Al could also be explained by the formation of coatings of Fe and Mn oxides on Al-silicate surfaces.

The main explanation for this could be that the Fe and Mn are being adsorbed onto the surfaces of $CaCO_3$ particles, which are then responsible for transporting the metals to the seabed, where they become buried in the sediments as a result of the sedimentation of $CaCO_3$ rather than the formation of rhodochrosite ($MnCO_3$) as suggested by (Sayles, 1981). After deposition on to the sediment interface, their redistribution depends upon the rate of calcite dissolution. If a high portion of the calcite dissolves, then the adsorbed Fe and Mn will be released because of the decline in $CaCO_3$ surface area, and may then re-precipitate in other solid phases.

In the deeper sediment the rate of dissolution of calcite as it is buried is consistent with the rate of increase of the iron and manganese content of the sediment with depth, resulting from authigenic precipitation and deposition of Fe and Mn in other phases, like stable oxides, rather than Fe–Mn carbonate phases (Martin & Knauer, 1984; Varnavas, 1988). The reactions involved in this oxidative uptake of Mn^{2+} could be as follows:
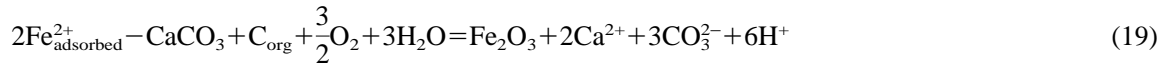
$$Mn^{2+} + CaCO_{3(calcite)} = Mn^{2+}_{adsorbed} - CaCO_3 \tag{14}$$

$$Mn^{2+}_{adsorbed} - CaCO_3 + \frac{1}{2}O_2 + H_2O = MnO_2 + Ca^{2+} + H^+ + HCO_3^- \tag{15}$$

And for Fe^{2+} could be as follows:

$$Fe^{2+} + CaCO_{3(calcite)} = Fe^{2+}_{adsorbed} - CaCO_3 \tag{16}$$

$$2Fe^{2+}_{adsorbed} - CaCO_3 + \frac{1}{2}O_2 + 2H_2O = Fe_2O_3 + 2Ca^{2+} + 2H^+ + 2HCO_3^- \tag{17}$$

Note the low demand of oxygen in Eqs. (15) and (17). In the deeper horizons within the sediment any oxygen needed could come from the reduction of nitrate in denitrification. Aerobic oxidation of organic matter is also responsible for $CaCO_3$ dissolution during diagenesis (Sayles, 1985). This will result in an increase in the alkalinity of the pore waters paralleled by an increase in the oxidation rate of organic carbon in the sediments and enhanced release of adsorbed Fe and Mn from calcite surfaces. Equations, which describe these processes, together with the increase in total carbonates in sediment from the PAP area and the authigenic formation of Mn oxides, could be as follows:

$$Mn^{2+}_{adsorbed}-CaCO_3+C_{org}+\frac{3}{2}O_2+2H_2O=MnO_2+Ca^{2+}+2CO_3^{2-}+4H^+ \tag{18}$$
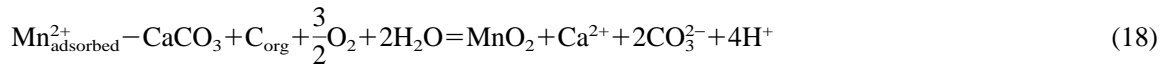
while for iron oxides could be:

$$2Fe^{2+}_{adsorbed}-CaCO_3+C_{org}+\frac{3}{2}O_2+3H_2O=Fe_2O_3+2Ca^{2+}+3CO_3^{2-}+6H^+ \tag{19}$$

Eqs. (18) and (19) lead to a higher demand for oxygen because there is simultaneous oxidation of Mn, Fe and C organic and we can assume that these reactions mainly take place in the subsurface sediment horizons. Additionally, the production of hydrogen ion (H^+) by the reactions described by Eqs. (18) and (19) is responsible for the presence of calcium in solution (Ca^{2+}) resulting to the observed increase in alkalinity.

4. Conclusions

The main biogeochemical processes taking place at the sediment–water interface on the Porcupine Abyssal Plain (PAP area) are described. The variability of manganese and iron concentrations in the upper sediment, implies that there is active resuspension of particles rich in Fe and Mn into the bottom waters. This resuspension is boosted by bioturbation. In the water column two distinctive layers of water have been identified during all three sampling periods (October 1996, March–April 1997 and July 1997) which are characterized by being significantly enriched with SPM, Fe_p, Mn_p, Al_p. These increased from October 1996 to July 1997 along with biogenic elements like Ba, Ca, Sr, which indicates the influence biogenic processes on the SPM constituents progressively increased during the period of observation. This was also consistent with the increased $CaCO_3$ content of sediments in the surficial sediments relative to the subsurface sediments. However, there may have been other factors, such as carbonate dissolution, which may have been responsible for the changes observed in the $CaCO_3$ sediment profiles.

The chemical reactions involving organic carbon that result in the incorporation of iron and manganese in various forms in the sediments in the oxygen penetration zone are deduced. The formation of lepidocrocite (γ-FeOOH) in the presence of organic carbon and oxygen is important, and some of the iron may also be transformed into insoluble Fe_2O_3. Organic carbon and oxygen are important limiting factors for these processes, while microbial action may also be involved.

Authigenic formation of iron and manganese oxides deeper within the sediment may involve the initial adsorption of Fe^{2+} and Mn^{2+} onto carbonate phases, their subsequent release back into solution following calcite dissolution and oxidation of organic carbon, and then re-precipitation. Resuspension of bottom sediments occurs which results not only in increases in the SPM content of the water in the BBL but also an enrichment with the manganese and iron of the suspended particulate matter.

Acknowledgements

the RV *Meteor* 36 leg 6 North Atlantic cruise for their help and their hospitality, as well as the chief scientists, the master, the crew and participants of the RRS *Discovery* and RRS *Challenger* BENGAL cruises.

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