

Abyssal plain
Interstitial water
Early diagenesis
Major cations
Sedimentation rate

Plaine abyssale
Eau interstitielle
Diagenèse
Alkalins
Taux de sédimentation

Chemical composition of interstitial water in cores from the Nares abyssal plain (Western North Atlantic)

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ABSTRACT

During the 1984 expedition with R. V. Tyro to the Nares abyssal plain, pore water was extracted from samples from 9 piston cores and 5 box cores. The collected pore water was analyzed on board ship for NO_2 , NO_3 , NH_3 , PO_4 , H_4SiO_4 , pH and alkalinity, and in our laboratory for alkali metals, Cl and SO_4 . The cores may be divided into "turbiditic" and "pelagic" cores. In the former, nitrate was depleted within a metre of sediment depth, whereas in the latter, nitrate concentration was relatively high right down to the bottom of the core. In the turbiditic cores, the reduction of iron- and manganese-oxides is the dominant diagenetic reaction; there is no discernible sulphate reduction. Ammonium is present throughout all the cores, but is below the detection limit in the bottom water samples. Phosphate concentrations in the pore water of the turbiditic cores show large variations with depth, probably in connection with redox conditions. The concentration of Ca^{2+} is higher and the concentration of K^+ lower in the pore water than in the bottom water; fluxes of $+0.25$ to $+1.2 \mu\text{M} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$ (Ca^{2+}) and of -0.2 to $-2.4 \mu\text{M} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$ (K^+) across the sediment-water interface have been calculated and are compared with published data. From the chloride/depth profile an estimate has been made of the very high sedimentation rates (approximately 45 cm/kyr) of the turbiditic sediments in the Nares abyssal plain,

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RÉSUMÉ

Composition de l'eau interstitielle dans des carottes de la plaine abyssale de Nares (Atlantique nord-ouest)

Au cours de la campagne 1984 du N. O. Tyro dans la plaine abyssale de Nares de l'eau interstitielle a été extraite des échantillons de 9 carottes « piston » et de 5 carottes « box ». Les eaux interstitielles obtenues ont été analysées à bord pour NO_2 , NO_3 , NH_3 , PO_4 , H_4SiO_4 , pH et alkalinité, et au laboratoire pour les alcalins, Cl et SO_4 . Les carottes peuvent être classées en carottes « turbiditiques » et « pélagiques ». Dans les carottes turbiditiques, le nitrate est consommé à une profondeur supérieure à un mètre dans le sédiment, tandis que dans la carotte "piston" pélagique la concentration de nitrate est relativement élevée jusqu'au fond de la carotte. Dans les carottes turbiditiques, la réduction des oxydes de fer et de manganèse est la réaction diagénétique dominante; il n'y a pas de réduction apparente de sulfate. L'ammonium est présent dans toutes les carottes mais à des concentrations inférieures à la limite de détection dans les échantillons d'eau de fond. Les concentrations en phosphate dans l'eau interstitielle des carottes turbiditiques montrent de grandes variations avec la profondeur; probablement liées aux conditions rédox. La concentration en Ca^{2+} est plus élevée, et la concentration en K^+ plus basse dans l'eau interstitielle que dans l'eau du fond de l'océan; des flux de $+0.25$ à $+1.2 \mu\text{M} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$ (Ca^{2+}) et de -0.2 à

$-2.4 \mu\text{M} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1} (\text{K}^+)$ ont été calculés et comparés avec des résultats publiés. A partir du profil chlorure/profondeur, une estimation a été faite des taux de sédimentation (environ 45 cm/kyr des sédiments turbiditiques dans la plaine abyssale de Nares),

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INTRODUCTION

During the 1984 expedition with R. V. Tyro, cores were collected from the central area of the Nares abyssal plain. In this area the sea floor is almost flat and water depths vary between 5850-5900 m (Duin, 1985). These depths are well below the CCD and therefore the sediments, apart from some turbidites, are almost carbonate depleted. Basically two sediment types have been described for the Nares abyssal plain: slowly accumulating brown pelagic clay and faster accumulating grey silty sediment, attributed to turbiditic deposition (Shiple, 1978). The grey sediment has been interpreted as material from distal turbidites from the Hatteras abyssal plain, situated immediately east of the Nares abyssal plain. The Vema Gap has been recognized as the main channel between the two plains (Tucholke, 1980). In the area to be considered here, this results in a major direction of transported turbiditic sediments from south-west to north-east (Kuijpers, 1985; Kuijpers, Duin, 1985).

Recent studies of the chemistry of interstitial water in sediments from the Madeira abyssal plain have shown that the extent of diagenetic processes and the related geochemistry is very dependent on the organic carbon content of the sediment (Thomson *et al.*, 1984; Colley *et al.*, 1984; Wilson *et al.*, 1985; de Lange, 1984a). In general, turbidites in the Madeira abyssal plain have a much higher organic carbon content than the pelagic sediments. Major differences can therefore be expected for the pore-water composition of either of these two types of sediments, provided the dimensions of the specific deposit are sufficiently large. Division of the recovered cores into "pelagic" and "turbiditic" (consist-

ing mainly of pelagic- and turbiditic sediments respectively) in fact yields distinct differences in pore-water geochemistry; this will be discussed below. The turbiditic sediments were generally recognized as green-to-grey silty clays; pelagic sediments by their brownish colour and clayey consistence. In the Nares abyssal plain a similar situation exists; however some cores of intermediate character were also encountered.

The lateral distribution of pelagic and turbiditic sediment in the Nares abyssal plain seems to be much more irregular: cores taken within a mile of each other from areas with no discernible difference in elevation can vary from pelagic (box core 84BC15) to turbiditic (piston core 84PC5; Fig. 1).

These facts are in sharp contrast with the common by held view of homogeneously distributed sediments in abyssal plains. From the piston cores available for geochemical sampling and pore water extraction, only one core (84PCM39) consisted mainly of pelagic sediment. This core was taken on a small abyssal hill approximately 200 m above the abyssal plain-sediments. Since the geochemical characteristics of all the turbiditic cores are very similar, only one piston core, namely 84PM1, will be discussed here, and will be compared to the pelagic piston core 84PCM39. In the remainder of the text and the figures, these cores will be referred to as 84P1 and 84P39.

SAMPLING/ANALYTICAL METHODS

During the 1984 expedition with R. V. Tyro to the Nares abyssal plain (Western North Atlantic), 9 piston cores and 5 box cores were selected for geochemical analysis; only two piston cores, representative of turbiditic and pelagic sediments respectively, will be discussed here. The turbiditic core (84P1) is from the plain itself, the pelagic core (84P39) from a nearby abyssal hill, approximately 200 m above the plain. The locations of the geochemically studied cores are indicated in Figure 1.

Deep-sea sediment for pore-water extraction must be handled extremely carefully if results are to be reliable. Great care must be taken in handling the samples and in controlling temperature and oxygen conditions during squeezing (Presley *et al.*, 1967; Mangelsdorf *et al.*, 1969; Bischoff *et al.*, 1970; Fanning, Pilson, 1971; Bray *et al.*, 1973; Horowitz *et al.*, 1973; Robbins, Gustinis, 1976; Loder *et al.*, 1978; Sayles, 1979; de Lange, 1984b).

Another possible source of error is caused by decompression as the cores are raised from the bottom of the sea to the surface; this may result in CaCO_3 precipitation (Murray *et al.*, 1980).

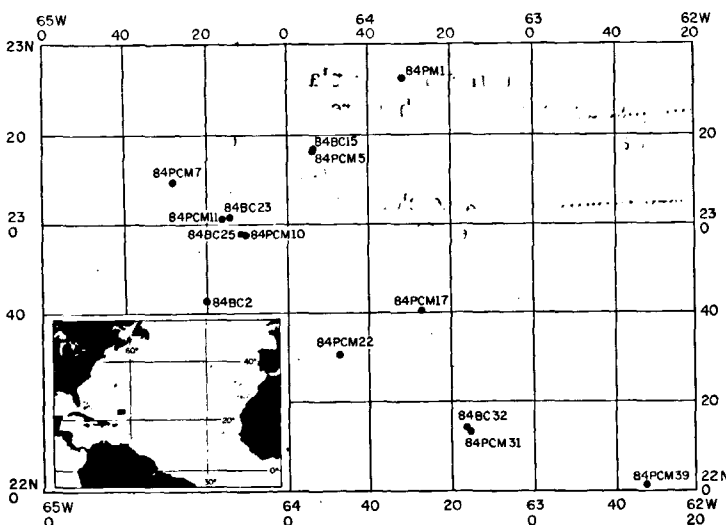


Figure 1
Sampling area during the 1984 cruise with R. V. Tyro to the Nares abyssal plain. Only the cores where pore water was extracted are indicated.

Table 1

Mean concentrations of 22 bottom water samples, taken at approximately 1 m above the sediment/water interface.

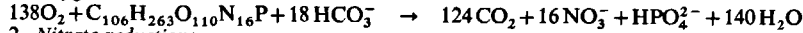
	NH ₃ (x)	NO ₂ ⁻ (x)	NO ₃ ⁻ (x)	HPO ₄ ²⁻ (x)	H ₄ SiO ₄ (x)	O ₂ (x)	Na ⁺ (')	Mg ²⁺ (')	K ⁺ (')	Ca ²⁺ (')	Cl ⁻ (')
st.d.	<1	<0.05	20.2	1.3	58.5	130	485	54.5	10.5	10.5	560
	-	-	.9	.2	.9	1	5	.9	.2	.2	.5

(x: concentration in µM; ': concentration in mM).

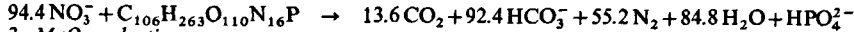
Table 2

Oxidation reactions of organic matter in marine sediments.

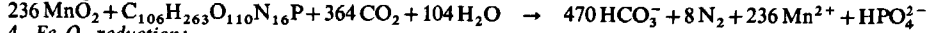
1. Oxygen reduction:



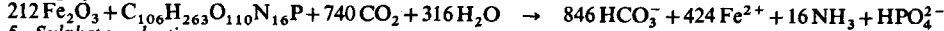
2. Nitrate reduction:



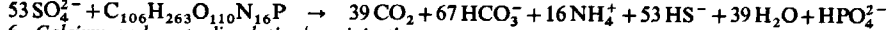
3. MnO₂ reduction:



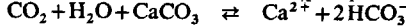
4. Fe₂O₃ reduction:



5. Sulphate reduction:



6. Calcium-carbonate dissolution/precipitation:



Contamination by oxygen and temperatures deviating from the *in situ* temperature can cause a large variation in the concentration of many elements in the pore water (Sayles *et al.*, 1973a; Gieskes, 1973; Sayles *et al.*, 1976; Shishkina, Tsvetkov, 1978; Masuzawa *et al.*, 1980). An adequate shipboard routine was thus developed in order to prevent these factors from causing possible deviations in the *in situ* pore-water concentration (de Lange, 1984b). This routine has been described in detail elsewhere (de Lange, 1984b), but will be briefly summarized here.

Immediately after collection of the core, the pvc liner is cut into 100 cm sections which are tightly sealed and stored horizontally at 3-4°C. Pore water extraction is started within 24 hours of core collection. The core-sections are split lengthwise into two parts; one part is immediately transferred into a high-purity nitrogen atmosphere (O₂ < 0.003%). Samples for pore water extraction are taken after removal of the top mm of sediment to remove any oxidation/contamination. The pressure-filtration of the sediment in Reeburgh-type squeezers (Reeburgh, 1967) takes place in a nitrogen-filled glovebox. The recovered pore-water samples were immediately sub-divided into three separate portions which were subsequently acidified and used for the determination of alkalinity and used for other shipboard analyses respectively. The shipboard analyses were started within 12 hours of the extraction of the pore water. The determination of alkalinity was done by a modified titration method (after Strickland, Parsons, 1968); pH in sediment (punch-in) and pore water was measured, and analyses of nitrite, nitrate, phosphate and ammonium were carried out. All nutrients were measured on a Skalar SA-400 AutoAnalyzer; ammonium was measured according to the phenol-hypochlorite method (Solorzano, 1969; Helder, de Vries, 1979), the other nutrients by a modified automated Strickland and Parsons method (1968). All on-board determinations were made in duplicate, the analyses of the major cations at the University of Utrecht laboratory in triplicate. The major cations were measured by flame atomic absorption spectrometry (Perkin-Elmer 2380), sulphate on an ion-chromatograph

(Amolex-1). The organic carbon content was determined partly by a standard sulphuric acid/dichromate oxidation (after Walkley, 1947; Kurmies, 1949; Sim, Haby, 1971), and by a volumetric method after Hartmann *et al.* (Hartmann *et al.*, 1971); the difference between the results of the two methods was negligible. The standard deviation was from 2 to 10% for an organic carbon content of 0.70 to 0.15%, respectively. Chloride was analysed by a potentiometric titration (McDuff, pers. comm. 1984), with a standard deviation of less than 0.1%. Oxygen was only determined in bottom water samples, according to the Winkler method (Strickland, Parsons, 1968; Grasshoff, 1976).

RESULTS

Bottom water analyses of 22 samples (Tab. 1) are in accordance with results published elsewhere for the Western North Atlantic (Broecker, 1983; Mantyla, Reid, 1983), with the exception of two samples (84P5 and 84P7) which probably suffered from on-board contamination. These data were omitted from the calculation of the mean bottom water values.

Nutrients and sulphate

Pore water profiles from sediments of the turbiditic cores from the Nares abyssal plain show changes that are just as dramatic as those reported for the Madeira abyssal plain (Kuijpers, 1982; de Lange, 1984a). The nitrate concentration in these cores generally diminishes very rapidly to a value close to zero within a sediment depth of one metre. This is in accordance with the expected high accumulation rates for this type of sediment. The process of nitrification (reaction 1 of Table 2) in the "turbiditic" cores is only visible in the top 5 cm of box cores (not shown in figure). In the pelagic core 84P39, this reaction occurs to a depth of at least 2 metres (Fig. 3), causing a steadily increasing nitrate concentration down to this depth. Such high nitrate concentrations are commonly found in slowly accumulating, pelagically deposited sediments (*e.g.* Suess *et al.*, 1980; Emerson *et al.*, 1980).

In all the turbiditic cores, nitrite concentrations (not shown in figure) were below the detection limit

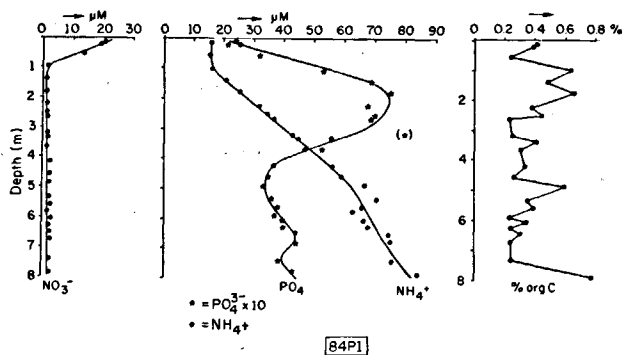


Figure 2
Nutrient concentration profiles in the pore water and organic carbon content in the solid phase of core 84P1. Arrows indicate bottom water values.

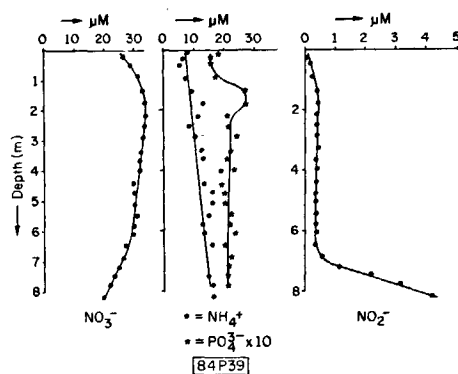


Figure 3
Nutrient concentration profiles in the pore water of core 84P39. Arrows indicate bottom water values.

($0.05 \mu\text{M}$) except at the sediment depth where nitrate concentration approaches zero and ammonium concentration starts to rise above $15 \mu\text{M}$. At this depth in core 84P1 (approximately 1 m), the nitrite concentration was slightly higher. However in the bottom part of core 84P39, the nitrite concentration rises to a much higher level, whereas the nitrate concentration is still considerable (Fig. 2, 3). Increased nitrite concentrations in either the seawater or sediment column have been explained both as an intermediate product in the oxidation of ammonium and the reduction of nitrate (Kiefer *et al.*, 1976; Suess *et al.*, 1980 and references herein).

The fact that the ammonium concentration in the turbiditic sediments already attains fairly high values in the top layers of the sediment is surprising. In the box cores, too, a fairly high concentration of ammonia ($10 \mu\text{M}$ on average) is found, whereas in the bottom-water samples, the concentration is always below the detection limit ($1 \mu\text{M}$). In view of the sampling and squeezing routine briefly described above, contamination due to sampling/squeezing does not seem very likely. It therefore appears that these relatively high ammonium concentrations in the presence of nitrate are genuine. Several possible sources may be considered, as will be discussed below.

In the published diagenetic models for marine interstitial waters (*e.g.* Froelich *et al.*, 1979), a regular increase of the phosphate concentration with depth in the sediment is assumed. However, in the turbiditic sediments of the Nares abyssal plain, the phosphate concentra-

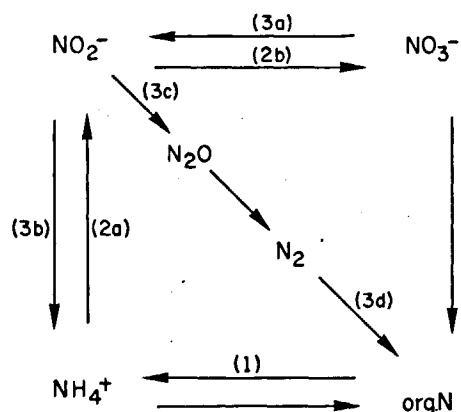


Figure 4
Nitrogen cycle during early diagenesis
1. decomposition of organic matter—see reaction 1 of Table 2.
2. nitrification—see reaction 1 of Table 2.
3. denitrification—see reaction 2 of Table 2.

tion/depth profiles show very distinct peaks (Fig. 2). This phenomenon was also found in the Madeira abyssal plain (Kuijpers, 1982; de Lange, 1984a).

In the Madeira abyssal plain, a close relationship was shown between the dissolved phosphate concentration and the organic carbon content of the solid phase (de Lange, 1984a). Such a relation appears also to exist in the Nares abyssal plain (Fig. 2), which indicates the importance of the organic carbon content of these sediments on the pore-water geochemistry.

The concentration of sulphate in the pore waters of Nares abyssal plain sediments remains constant with depth for all cores studied so far. This means that for those sediments down to a depth of at least 10 m, no reduction of sulphate occurs (Fig. 5). The high average sedimentation of core 84P1 (as discussed below) and the constant concentration of sulphate with depth in this core implies the availability of only a limited amount of organic carbon or a low decomposition rate of the organic material.

The sulphate concentrations for samples of core 84P39 have not been determined. But considering the relatively high nitrate concentration in the sediment at a depth of 8 m, the sulphate concentration is not expected to deviate from that found in sea water.

Major cations

During the early phase of diagenesis (*e.g.* reaction 1 of Tab. 2) the CO_2 that is formed reacts in the presence of solid-phase carbonate, according to reaction 6 (Emerson *et al.*, 1980). This results in an increase in Ca^{2+} concentration and alkalinity (Fig. 5, 6). Down to 1 metre in the sediment of core 84P1, reactions 1 and 2 (Tab. 2) are likely to be the only ones of importance. The alkalinity/ Ca^{2+} ratio of 2 : 1 according to reaction 6 of Table 2 (Emerson *et al.*, 1982) is in agreement with the ratio actually found in the topmost metre of the sediment column, after correction for the different diffusion coefficients of Ca^{2+} and HCO_3^- . Such a profile will only become visible when oxygen is available for the decomposition of the organic material. Decompression due to the raising of the core from the ocean floor

to the surface is a potential source of error in Ca concentration and alkalinity. The resulting loss of CO_2 can cause precipitation of CaCO_3 , which lowers the concentration of Ca^{2+} and alkalinity, and raises the pH (Murray *et al.*, 1980). In our shipboard data, no increase of either sediment (punch-in) or pore-water pH measurements is apparent. Therefore no major precipitation of CaCO_3 due to decompression seems to have occurred and will be excluded from the discussion hereafter. The reason for this lack of evidence of precipitation could be the low carbonate content of the sediment, thus avoiding the precipitation on seed crystals of CaCO_3 (Murray *et al.*, 1980).

A very regular but steady decrease of K^+ is apparent in the turbiditic sediments. No simultaneous change in the Mg^{2+} concentration was observed, whereas others have found large changes for Mg^{2+} (Sayles, 1979; 1981; Gieskes, 1973; Gieskes *et al.*, 1976; Gieskes, Lawrence, 1981; Manheim, 1976). Sayles (1979) finds an increase in the concentration of Mg^{2+} with sediment depth of almost the same magnitude as the increase in Ca^{2+} . A similar ratio of increase in the case of core 84P1 might remain invisible with our analytical resolution. An increase of only 0.3 mM of Mg^{2+} in this core is necessary to provide a charge balance of the major ions, if only minor changes in the concentration of Na^+ are assumed (*see also* Tab. 2a).

In core 84P39 containing mainly pelagic sediments, the Ca^{2+} concentration increases slightly with depth, and K^+ probably decreases slightly with depth. The data for K^+ as well as for Na^+ and Mg^{2+} in core 84P39 show too much scatter for any definitive conclusions to be drawn. The alkalinity/ Ca^{2+} ratio in this core is also close to 2 (Fig. 6).

Chloride

The chloride concentration in core 84P1 increases slightly with depth (Fig. 8). If the few sharp peaks (due to evaporation during squeezing) in the concentration/depth profile are omitted, a maximum value in the chloride concentration can be deduced at a sediment depth of 5 m or more. This maximum in the interstitial chloride concentration of this core may be attributed to the last glacial period, as will be discussed in more detail below. The chloride concentration/depth profile of core 84P39 is not shown. Due to the low sedimentation rate of the sediments in this core (*see below*), a glacial signal in the chloride concentration will have disappeared as a result of diffusion.

DISCUSSION

Nutrients

The concentration/depth profile of nitrite in the interstitial water of core 84P39 is interesting (Fig. 3), in that the concentration is slightly enhanced from 1 to 7 m but displays a major increase below the latter depth.

Nitrite is considered to be a possible intermediate product in the reduction of nitrate and in the oxidation of ammonium (Grundmanis, Murray, 1977; 1982; Gundersen, Mountain, 1973; Hartmann *et al.*, 1976; Kiefer *et al.*, 1976; Suess *et al.*, 1980; Anderson *et al.*, 1982; Helder W., 1983; Jahnke *et al.*, 1982; Olson, 1971; Fig. 4). Elevated nitrite concentrations at depths where a maximum nitrate reduction occurs have been explained as a kinetic intermediate between NO_3^- and N_2 (Emerson *et al.*, 1980). The slightly elevated nitrite concentration visible at a sediment depth of 1 to 7 m in core 84P39 could have the same origin. Oxidation of nitrite by oxygen keeps the nitrite concentration low

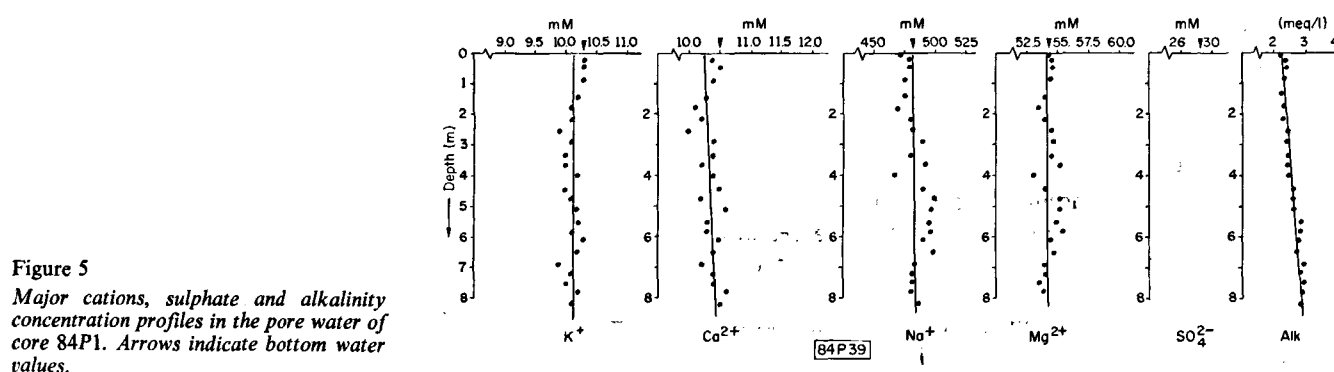


Figure 5
Major cations, sulphate and alkalinity concentration profiles in the pore water of core 84P1. Arrows indicate bottom water values.

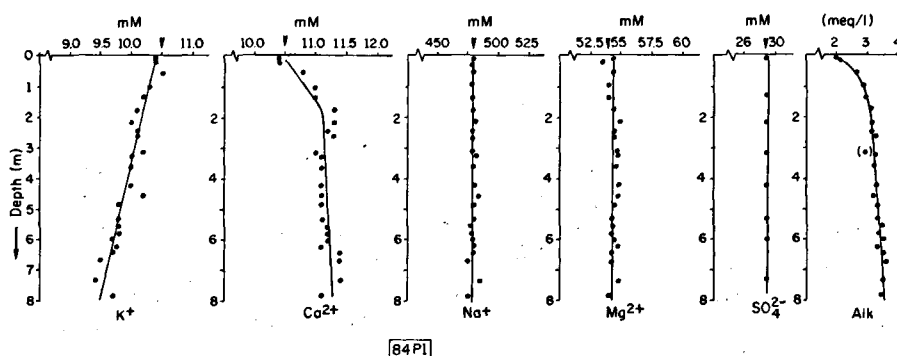


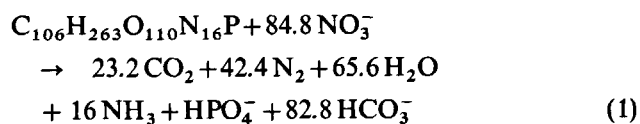
Figure 6
Major cations and alkalinity concentration profiles in the pore water of core 84P39. Arrows indicate bottom water values.

until the oxygen concentration in the pore water is almost depleted, presumably at 7 m. In the presence of low concentrations of both oxygen and organic matter in combination with a low porosity of the sediments of core 84P39, this intermediate product can apparently be present for a relatively long period of time.

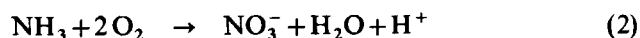
The relatively high concentration of ammonium (10 μM on average) found in the top layer of piston- and box-cores is unusual, compared with its concentration in the bottomwater samples: below the detection limit (<1 μM ; Fig. 2, 3; Tab. 2). As mentioned previously, contamination due to sampling/ squeezing is not very likely; different origins for this elevated ammonium concentration in the interstitial water from the top layer of the sediment will therefore be discussed.

During nitrification and denitrification (according to the overall reactions 1 and 2 of Tab. 2), no ammonium is formed, and considering the high nitrate concentration in core 84P39 no manganese/iron-oxide reduction is likely to occur above a sediment depth of 8 m. The ammonium could become available by an upward diffusion from more reducing parts of the core at depths lower than 8 m, or it could be formed in micro-environments in the top 8 m in which some iron/manganese-oxide reduction occurs. Such micro-environments with even some evidence of sulphate reduction have been observed in the Madeira abyssal plain sediments (Kuijpers, 1982). The extraction of exchangeable ammonium (Mueller, 1977) during squeezing of the sediment must also be considered as a possibility.

Another explanation for these relatively high ammonium concentrations is that the organic matter does not become completely oxidized during denitrification (equation 1):



In the presence of a sufficiently high concentration of oxygen, the ammonium is subsequently oxidized to nitrate (Fig. 4, equation 2).



It is possible that in sediments of low porosity (as is the case here) containing only minor amounts of oxygen, the ammonium formed in this reaction may remain in solution for a considerable time. The last possibility seems to be the most plausible, although with the data available at this time the other possibilities cannot be entirely excluded.

Phosphate concentration/depth profiles for interstitial waters from sediments from the Nares abyssal plain have distinct peaks (de Lange *et al.*, 1985), similar to those found in sediments from the Madeira abyssal plain (Kuijpers, 1982; de Lange, 1984a). In the latter area, a close relationship has been shown between the concentration of phosphate in the pore water and the organic carbon content of the solid phase (de Lange, 1984a). Such a relationship seems also to exist for sediments of the Nares abyssal plain (Fig. 2).

In contrast to the pelagic abyssal sediments, which normally contain only a very minor amount of "refractory" organic material, organic-rich turbidites have the potential to sustain a much higher rate of diagenetic reactions. Such reactions very soon exhaust the amount of oxygen (and of nitrate) available. Because of the high sedimentation rates, diffusion of oxygen into the sediment cannot keep pace with its consumption by diagenetic reactions; this results in suboxic conditions. Alternating layers of pelagic or turbiditic sediment low in organic carbon and organic-rich turbiditic sediment can therefore cause the highly fluctuating pore-water profiles of some ions (Fig. 2, 3), and can induce post-depositional migration fronts (Colley *et al.*, 1984; Sawlan, Murray, 1983; Thomson *et al.*, 1984; Tsunogai, Kusakabe, 1972; Wilson *et al.*, 1985). Phosphate concentrations in the Nares abyssal plain and in the Madeira abyssal plain are evidently most particularly affected by such conditions (Fig. 2, 3).

Major cations

Changes in the concentration/depth profiles of major cations in marine interstitial waters have been reported before (*e.g.* Gieskes *et al.*, 1976; Manheim, 1976). However, in the data presented here only the pore-water concentrations of Ca^{2+} and K^+ show a visible deviation from the sea-water concentration, whereas the concentrations of Mg^{2+} and Na^+ remain virtually constant. The relation between the change of the concentration of Ca^{2+} and the alkalinity of the interstitial water has been discussed.

The pore-water concentration of K^+ decreases steadily with depth in the turbiditic sediments, whereas in the pelagic core no decrease is visible (Fig. 5, 6).

Such a decrease in pore-water concentration of K^+ with depth in the sediment has been attributed to ion-exchange reactions on clay mineral surfaces and with interlayers (Powers, 1957; Presley *et al.*, 1973; Russell, 1970); but it might also be related to authigenic formation or diagenesis of clay minerals (Presley *et al.*, 1973; Manheim, 1976). Enrichment of K^+ in pore water from marine sediments has also been reported but, particularly in the case of the older data, no steps were taken to prevent warming up of the samples prior to or during the pore water extraction (Bischoff *et al.*, 1970; Bischoff, Ku, 1970; 1971; Mangelsdorf *et al.*, 1969; Sayles *et al.*, 1973a). It has been demonstrated that when the temperature during squeezing is 20°C higher than the *in situ* temperature, there is an increase of 20-28% in the concentration of K^+ in the extracted pore water (Sayles *et al.*, 1973b; Sayles, Manheim, 1975; de Lange, 1984a). However, K^+ enrichment has also been reported for samples from marine sediments that were cooled close to the *in situ* temperature during squeezing (Drever, 1971; Bischoff, Sayles, 1972; Hartmann *et al.*, 1976). Results from DSDP-cores do demonstrate that depletion rather than enrichment occurs in pore waters from marine sediments (Sayles *et al.*, 1973b; Waterman, 1973; Gieskes, 1975; Gieskes *et al.*, 1976; Gieskes, Lawrence, 1981). High K^+ depletion in pore water is found especially in continentally derived sediments. *In situ* sampled pore waters down

to a sediment depth of 2 m clearly show the same K^+ depletions, the magnitude being dependent on the amount of continental input (Sayles *et al.*, 1973b; Sayles, 1979). K^+ depletion in pore waters from the Brazil Basin correlates well with the continent-derived kaolinite content (Sayles, 1979). On the other hand, Sayles (1979) and Suess (Suess, 1976; 1982; Suess *et al.*, 1980) do find a Ca^{2+} enrichment, but not of the same relative magnitude as that found in this study. Perhaps the Ca^{2+} K^+ ratio found in the turbiditic sediments from the Nares abyssal plain is the result of two different reactions which accidently produce a 1 : 1 ratio. However, continentally derived brackish-water sediments deposited in the Norwegian Basin show similar concentration gradients for Ca^{2+} and K^+ (de Lange, 1983).

It seems likely that a K^+ decrease with depth (rather than a K^+ increase) is the normal situation (Sayles, 1979), especially when continentally derived sediments are deposited in a marine environment. If the relative decrease of K^+ for sediments deeper than 1 m is plotted against the relative increase of Ca^{2+} , then the same slope is found for all turbiditic cores (Tab. 3). The plot for core 84P1 is shown as an example (Fig. 7). The mean value of 1.00 ± 0.13 indicates a 1 : 1 exchange ratio for Ca^{2+} and K^+ . However, two different processes seem to govern the Ca^{2+} concentration in the pore water of core 84P1. First, as mentioned above, the diagenetically controlled dissolution of $CaCO_3$ causes a rapid increase in the Ca^{2+} concentration in the top two metres of this core. Exchange reactions, probably with the silicate fraction, *e.g.* clay minerals, seem to liberate some Ca^{2+} as well. A closer examination of Figure 2 indicates a relative change of approximately 1 : 2 in the concentrations of Ca^{2+} and K^+ in the depth interval from 2 to 8 m. During reduction of manganese-oxides/hydroxides at depths greater than 2 m in core 84P1 (de Lange, submitted), some $CaCO_3$ could precipitate again (Emerson *et al.*, 1980; 1982;

Table 2a

Concentration of ions from core 84P1, visualized in Figures 5 and 8, that were used in the flux calculations; all concentrations are in mM.

Core	Depth (cm)	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻
84P1	7-15	480	54.5	10.4	10.4	562.8
	17-27	477	53.5	10.4	10.4	563.6
	50-60	479	54.3	10.5	10.8	560.1
	97-106	478	54.1	10.3	11.0	558.7
	136-143	478	54.0	10.2	11.0	560.1
	174-182	479	54.4	10.1	11.3	560.0
	216-226	482	54.9	10.0	11.3	560.9
	247-257	478	54.5	10.1	11.2	561.1
	260-270	480	54.4	10.1	11.3	561.0
	315-323	479	54.7	10.2	11.0	562.3
	326-334	483	54.8	10.0	11.1	561.7
	363-370	481	54.6	10.0	11.1	562.0
	418-429	481	54.8	10.0	11.1	561.6
	454-465	484	54.8	10.2	11.1	570.8
	485-495	480	54.5	9.8	11.1	561.9
	529-540	479	54.3	9.8	11.1	562.3
	557-567	477	54.3	9.8	11.2	562.1
	581-592	478	54.2	9.8	11.2	562.5
	601-610	479	54.4	9.7	11.2	561.7
	623-632	480	54.7	9.8	11.1	563.1
	646-655	480	54.3	9.7	11.4	n.d.
	671-681	475	54.2	9.5	11.4	560.8
	736-747	484	54.8	9.4	11.4	563.7
	782-793	476	54.0	9.7	11.2	564.2

n. d. = not determined.

Table 3

$\Delta Ca^{2+} / \Delta K^+$ -slopes from turbiditic cores in NAP.

Core no.	Slope
84P01	1.26
84P05	0.94
84P10	0.95
84P11	0.90
84P22	0.97

Mean value 1.00 ± 0.13 .

Average equation: $\Delta K^+ = (1.00 \pm 0.13) \Delta Ca^{2+} - 0.04 \pm 0.17$.

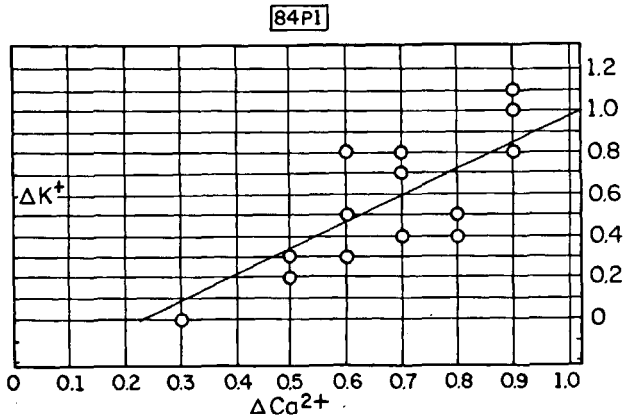


Figure 7

Plot of K^+ decrease versus Ca^{2+} increase in core 84P1 relative to the bottom water concentration, adapted to a first order polynomial; ($\Delta K^+ = (1.26 \pm 0.28) \Delta Ca^{2+} - 0.28 \pm 0.19$).

Sayles, 1981). This would cause a decrease in both alkalinity and the concentration of Ca^{2+} , neither of which was observed. Na^+ and Mg^{2+} will probably also take part in these exchange reactions, but if their change of concentration in pore water was similar to the change of concentration of Ca^{2+} and K^+ in the pore water (= 1 mM), then this change would not be detectable with the analytical techniques we used.

It can be stated conclusively that the changes in K^+ and Ca^{2+} concentration in the turbiditic cores of this area seem to be related in a 1 : 1 ratio (Fig. 6, Tab. 3). This apparent relation can be explained by two different processes: a diagenetic reaction involving Ca^{2+} , and a clay mineral exchange reaction where Ca^{2+} and K^+ participate in a 1 : 2 ratio. Participation of Mg^{2+} and Na^+ in the latter reaction cannot be ruled out.

Fluxes

Changes of concentration in the sediment result in fluxes of elements across the sediment-water interface. The diagenetic reactions in the sediment can have a major influence on the geochemical budgets of some of the major constituents of sea water. Fluxes of Ca^{2+} and K^+ across the sediment-water interface have been calculated on the basis of measured concentration gradients. The data of core 84P1, used in the calculations, and visualized in Figure 5, have been summarized in Table 2a.

In the present study, two different approaches have been used, one based on Manheim (1976) and the other on Sayles (1979; 1981). The obtained results have been compared with the results from Manheim and Sayles. Advection has been neglected in the calculations, but could be of some importance (Sayles, 1981). The method applied to the turbiditic piston core is in

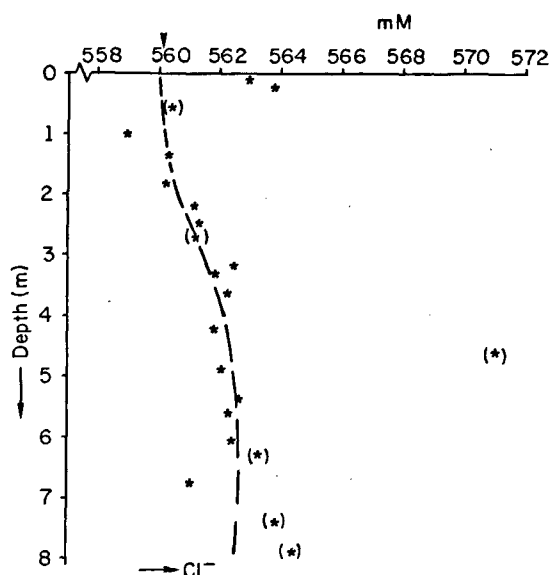


Figure 8
Chloride concentration profile of core 84P1. Arrow indicates bottom water concentration. Brackets indicate samples with low porosity, and therefore high evaporation due to a long squeezing time.

essence similar to that used by Manheim: a linear gradient is assumed in the topmost metre of the sediment. The expression used for the calculation of the fluxes for piston core and the similar linear derivation in the box cores is:

$$F_1 = -D_{\text{eff}} * (\Delta c / \Delta x), \quad (3)$$

where:

F_1 = flux calculated with the linear approach, a negative flux denoting a flux from the bottom water into the sediment;

D_{eff} = effective diffusion coefficient (this includes tortuosity) (in $\text{cm}^2 \text{s}^{-1}$);

Δc = concentration difference (in $\mu\text{M}/\text{cm}^3$); and

Δx = depth difference (in cm).

The same equation, but only for 20 cm of depth difference, has been used as an approximation for the calculation of fluxes in the two turbiditic box cores.

In the second approach, which is similar to that adopted by Sayles, a so-called analytical solution is used, which means passing to limit $x \rightarrow 0$ in equation 3. Then the following equation is obtained:

$$F_{\text{an}} = -D_{\text{eff}} * (\delta c / \delta x)_{x=0} \quad (4)$$

where

F_{an} = flux calculated using the analytical approach; and $(\delta c / \delta x)_{x=0}$ is the tangent of the analytical solution in $x=0$.

The analytical curve-fit extrapolation to the sediment-water interface should approach the value of fluxes across this interface more closely than the linear approximation of equation 3. However the method is also more sensitive to errors.

The two box cores in Figure 9 are considered to be representative of the real surface section of turbiditic sediments, for which core 84P1 has been taken as a typical piston core example. Samples were taken by subcoring in the box core taken with a $50 \times 50 \text{ cm}$ surface boxcorer; some compaction (up to 10%) during subcoring was inevitable. The increase of concentration

gradients thus caused leads to a 10% overestimate of calculated fluxes, but does not significantly change the results. Therefore a correction for this compaction will not be included in the calculations.

Although the gradient of K^+ in core 84P1 suggests a linear decrease with depth, a closer look at the near surface layer, as found in a box core, indicates much higher non-linear gradients, close to the sediment-water interface (Fig. 9). In the present work, the estimate of the fluxes for Ca^{2+} and K^+ in the piston cores is very similar to the average data given by Manheim (1976) (Tab. 4). However if high resolution data from surface sediments are taken into account, there can be up to a tenfold increase in the calculated fluxes. The estimated standard deviation for Ca^{2+} and K^+ in this work is 1%, which of course leads to relatively large uncertainties in the performed calculations. However, it is evident that the numbers obtained in the calculation of fluxes from elements involved in (diagenetic) reactions in the sediment depend largely on the method used in these calculations. The analytical approach probably gives the best estimate of fluxes across the sediment-water interface. The fluxes calculated by the analytical method in this study are much higher than those from Sayles (1979). Compaction by a factor of 2-3, as found by others for small diameter cores (van Bennekom, Berger, 1984; Lebel *et al.*, 1982) can be ruled out.

Advection, especially in this area of high sedimentation rates probably cannot be excluded entirely. The turbiditic sediment in the Nares abyssal plain shows relatively large fluxes of K^+ and Ca^{2+} across the sediment-water interface. The pelagic sediment in this same area behaves quite differently, with only minor fluxes of both constituents across the sediment/water boundary.

Chloride

The chloride concentration increases slightly with depth (Fig. 8). The few sharp peaks can probably be attributed to on-board evaporation during squeezing. The highest deviation in Figure 8 represents a difference of only 1.5% with respect to the expected concentration. The increasing Cl^- concentration with depth in the

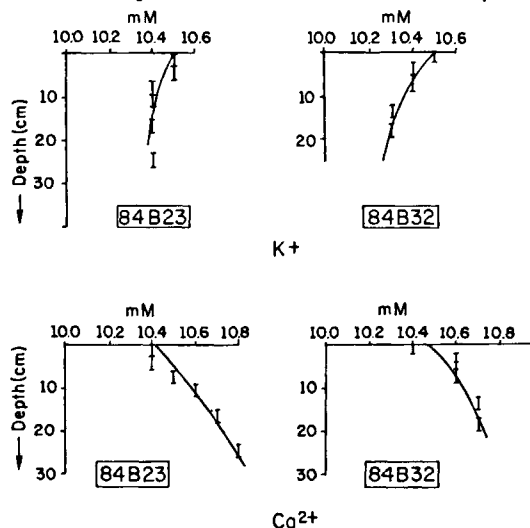


Figure 9
 K^+ and Ca^{2+} concentration profiles in two box cores (84B23 and 84B32). Vertical lines indicate depth range of sampling; arrows indicate bottom water concentrations.

Table 4
Calculated fluxes for K and Ca

	$D_{eff}(K^+)$ ($cm^2 \cdot s^{-1}$)	Flux(K^+) ($\mu M \cdot cm^{-2} \cdot yr^{-1}$)	$D_{eff}(Ca^{2+})$ ($cm^2 \cdot s^{-1}$)	Flux(Ca^{2+}) ($\mu M \cdot cm^{-2} \cdot yr^{-1}$)
Piston core (1)	4.3×10^{-6}	-0.22	1.7×10^{-6}	+0.23
84P1 (2)	5×10^{-6}	-0.20	2×10^{-6}	+0.25
Box core (lin) (2)	5×10^{-6}	-1.2	2×10^{-6}	+0.65
Box core (an) (2)	5×10^{-6}	-2.4	2×10^{-6}	+1.2
In situ (lin) (3)	$5-6 \times 10^{-6}$	-0.5	$1.9-2.3 \times 10^{-6}$	+2.5
In situ (an) (3)	$5-6 \times 10^{-6}$	-0.6	$1.9-2.3 \times 10^{-6}$	+3.0

(1)=Manheim 1976; (2)=this work; (3)=Sayles 1979 (mean values for samples from the Caribbean are used). (lin) in the case of box cores means a linear approach over 20 cm sediment depth; (lin) in the case of *in situ* pore water sampling means a linear approach over 5 cm sediment depth. (an) means the analytical curve-fit extrapolation to the sediment-water interface.

pore water originates from the last glacial period (ca. 18,000 yr B.P.) when large volumes of relatively fresh ocean water were fixed within polar ice-sheets, leaving the ocean water more saline (580 mM Cl^-) than at present (560 mM Cl^-) (Broecker 1982; McDuff, pers. comm.).

This glacial sea water was also incorporated in the sediments deposited during this period. However high sedimentation rates are necessary to keep this glacial signal visible despite diffusion since the time when the sediments were deposited. Apparently such a situation exists in the Nares abyssal plain, and the situation is even more favourable because of the low porosities of the sediments (20-50%).

It is easy to see from the chloride/depth profile that the bottom part of core 84P1 cannot be older than 18,000 years; this would indicate an average sedimentation rate of more than 45 cm/1000 yr!

A similarly high average sedimentation rate was deduced from sedimentological and seismic records for the same sediments by Kuijpers and Duin (Kuijpers, Duin, 1985; Duin, 1985; Kuijpers, 1985).

For core 84P39, taken on top of an abyssal hill and containing mainly pelagic sediments, high sedimentation rates are not very likely. Estimated sedimentation rates for pelagic sediments in the eastern part of the Nares abyssal plain are low (approximately 0.2-0.5 cm/kyr; Thomson *et al.*, 1984). If these low sedimentation rates hold for sediments of core 84P39, then a glacial signal will not be visible, as a result of diffusion.

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