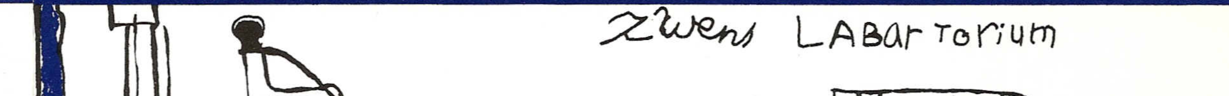
GEOLOGICA ULTRAIECTINA

Mededelingen van de
Faculteit Aardwetenschappen der
Rijksuniversiteit te Utrecht

No. 81

THE DISTRIBUTION OF NITROGEN ISOTOPES IN SEDIMENTS



S.O. SCHOLTEN

GEOLOGICA ULTRAIECTINA

Mededelingen van de
Faculteit Aardwetenschappen der
Rijksuniversiteit te Utrecht

No. 81

THE DISTRIBUTION OF NITROGEN ISOTOPES IN SEDIMENTS

CIP-GEGEVENS KONINKLIJKE BIBLIOTHEEK, DEN HAAG

Scholten, Sven Olaf

The distribution of nitrogen isotopes in sediments /
Sven Olaf Scholten. - [Utrecht : Faculteit Aardwetenschappen
der Rijksuniversiteit Utrecht]. - (Geologica Ultraiectina,
ISSN 0072-1026 ; no. 81)
Thesis Utrecht. - With ref. - With summary in Dutch.
ISBN 90-71577-35-X
Subject heading: nitrogen isotopes ; sedimentology.

THE DISTRIBUTION OF NITROGEN ISOTOPES IN SEDIMENTS

DE VERDELING VAN STIKSTOF-ISOTOPEN IN SEDIMENTEN

(MET EEN SAMENVATTING IN HET NEDERLANDS)

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE RIJKSUNIVERSITEIT TE UTRECHT
OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF.DR. J.A. VAN GINKEL,
INGEVOLGE HET BESLUIT VAN HET COLLEGE VAN DEKANEN
IN HET OPENBAAR TE VERDEDIGEN OP WOENSDAG
23 SEPTEMBER 1991 DES NAMIDDAGS OM 12.45 UUR

DOOR

SVEN OLAF SCHOLTEN
GEBOREN OP 18 JULI 1964, TE HILVERSUM

PROMOTOR: PROF.DR. R.D. SCHUILING
CO-PROMOTOR: DR. R. KREULEN

aan mijn ouders

If we see one goal clearly we may advance one step.
If we contemplate all goals at once we shall not advance at all.

John le Carré

VOORWOORD

Allereerst wil ik mijn co-promotor Rob Kreulen bedanken voor de fijne samenwerking en stimulerende discussies. Door zijn constructieve commentaren op mijn manuscripten lukte het mij op te schrijven wat ik eigenlijk bedoelde, waarbij tevens een sterke reductie van het aantal benodigde pagina's optrad.
Mijn isotopen-collega's Jan Meesterburrie, Anita van Leeuwen, Arnold van Dijk, Pier de Groot, Math Kohnen en Hans Eggenkamp bewezen dat het op een goed draaiend lab ook gezellig kan zijn.
Olaf Schuiling wil ik bedanken voor het kritisch doorlezen van mijn manuscripten en voor zijn optreden als promotor.

De volgende personen hebben op een of andere wijze aan mijn onderzoek bijgedragen: Geert-Jan de Haas, Bertil van Os, Jack Middelburg, Bas Dam, Nico van de Schuit, Giuseppe Frapporti, Paulien van Gaans, Simon Vriend, Gert de Lange, Pieter Kleingeld, Ad van Eerden, Paul Anten, Angelique Lesquillier, Vian Govers, Gijs Nobbe, Theo van Zessen, Chiel Eussen, Ineke Kalt, Sheila McNab, de medewerkers van de bibliotheek en de A.V.-dienst.
Hartelijk dank allemaal voor jullie hulp en vriendschap.

Een speciaal dankwoord richt ik tot de (kwarts-)glasblazers Bep Verwoert en Pieter Engels die altijd bereid waren om mij 'even tussendoor' te helpen.

Ik bedank de co-auteurs van de artikelen in dit proefschrift voor hun inbreng en diegenen die voor hun specifieke aandeel in de betreffende acknowledgements zijn genoemd.

Tenslotte bedank ik Lawrence Vriend en Hélène de Wit voor hun mooie bijdragen aan de vormgeving van dit proefschrift.

CONTENTS

Chapter I

Chapter II

Chapter III

Chapter IV

Chapter V

Chapter VI

Chapters 2 and 3 (combined) and 4 have been submitted to Geochimica et Cosmochimica Acta.
Chapter 5 has been submitted to Geology.
Chapter 6 has been submitted to AAPG-Bulletin.

CHAPTER I

SYNOPSIS

INTRODUCTION

This thesis deals with the behaviour of nitrogen in sediments. Nitrogen is a major constituent of the organic matter in sediments (*organic nitrogen*, N_{org}), but it is also present as inorganic nitrogen compounds (Fig. 1), in particular as ammonium which can be adsorbed to the sedimentary particles (*exchangeable nitrogen*, N_{ex}) or incorporated in the lattices of clay-minerals (*fixed nitrogen*, N_{fix}). Essential to this research is the method that was developed to separate the three nitrogen fractions in such a way that the isotopic compositions are preserved (**Chapter II**). The following chapters demonstrate that systematic changes occur in the distribution of the three nitrogen fractions, both during early diagenesis and during maturation of sediments. This introduction (**Chapter I**) accounts for the relationship between the following chapters and highlights some questions on the sedimentary nitrogen cycle that remain unanswered.

BIOLOGICAL NITROGEN CYCLE

Nitrogen in sediments originates from organic matter. For a better understanding of the processes leading to the observed sedimentary nitrogen distribution (discussed in the following chapters) an introduction to the major aspects of the biological nitrogen cycle is required (e.g. Delwiche, 1970; Sweeney et al., 1978; Helder, 1983; Berner and Berner, 1987). Atmospheric nitrogen (N_2) can only be taken up by certain micro-organisms, especially bacteria and algae, which convert it to organic nitrogen compounds (*biological fixation*). Only a minor fraction of the organic nitrogen is preserved in the soil or sediment, most of it is mineralized and biologically recycled. Organic compounds can be degraded to simple inorganic nitrogen compounds (*biological mineralization*) such as urea (NH_2CONH_2), nitrate (NO_3^-) and, most important the end product ammonium (NH_4^+).

Micro-organisms, in particular bacteria, are responsible for almost all major conversions in the biological nitrogen cycle, including processes such as *fixation*, *nitrification* ($NH_4^+ \rightarrow NO_3^-$) and *denitrification* ($NO_3^- \rightarrow N_2$). The inorganic nitrogen compounds, in turn, serve as nutrients for micro-organisms and plants (*assimilation*).

During the various processes in the nitrogen cycle, one of the two stable isotopes (^{15}N and ^{14}N) may be preferentially taken up by the organisms. This preferential isotope uptake results in a change in the $^{15}N/^{14}N$-ratio of the nitrogen compounds. The $^{15}N/^{14}N$-ratio is commonly expressed relative to a standard (atmospheric nitrogen, N_2) as $\delta^{15}N$-value (in ‰). Fractionation of nitrogen isotopes occurs in particular during nitrification and denitrification processes whereas biological fixation and mineralization mostly have less effect on the nitrogen isotope distribution (e.g. Miyake and Wada, 1967; Sweeney et al., 1978, Mariotti et al., 1984).

Although most land plants obtain their nitrogen from nutrients derived from decomposed organic matter, biologically fixed atmospheric nitrogen is a major nitrogen source (i.e. external nitrogen contributor) of *terrestrial* organic matter. Terrestrial runoff of dissolved organic and inorganic nitrogen compounds is the major source of nitrogen into the *marine* environment, where nitrogen fixation occurs on a much smaller scale than on land (e.g. Delwiche, 1970; Berner and Berner, 1987). This difference in the major nitrogen sources of terrestrial and marine environments is reflected by the average isotopic composition of the organic nitrogen (Peters et al., 1978; Sweeney et al., 1978; Sweeney and Kaplan, 1980; Mariotti et al., 1984; Owens et al., 1989): Terrestrial organic matter generally has low $\delta^{15}N$-values which lie close to the isotopic composition

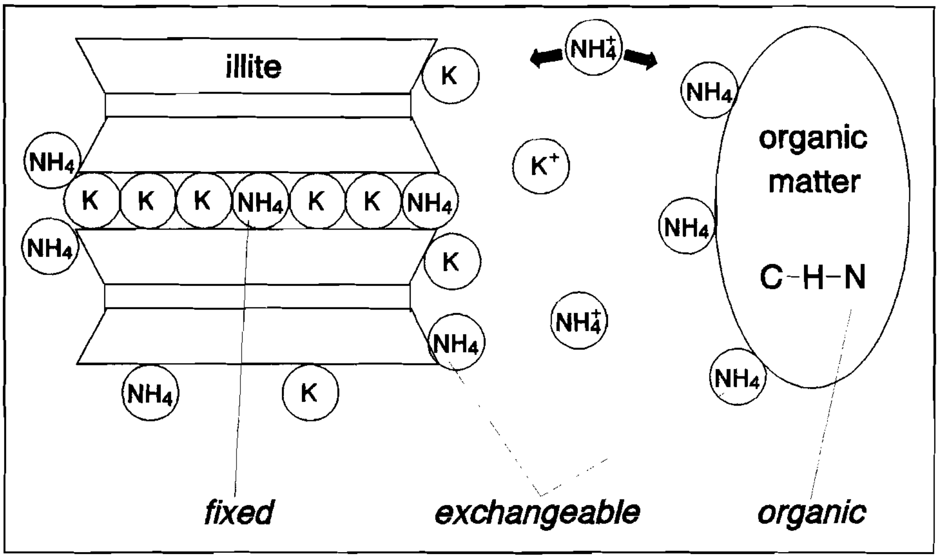


Figure 1. Schematic representation of the three nitrogen fractions (afer Williams et al., 1989). See text for explanation.

of atmospheric nitrogen ($\delta^{15}N_{air}$ = 0 ‰). Marine organic matter, on the other hand, has higher $\delta^{15}N$-values as a consequence of the uptake of nutrients that have fractionated isotopic compositions (7-10 ‰). Variations in the nitrogen isotopic composition of organic matter may occur on a local scale as a result of factors such as environmental pollution, fertilization, lack of nutrients or the presence of large populations of specific organisms (e.g. algal blooms).

THE ISOTOPIC COMPOSITION OF ORGANIC NITROGEN IN SEDIMENTS

The above mentioned relation between the nitrogen isotopic composition and the environment has only been demonstrated in particulate organic matter in the water column and in recently deposited organic matter. So far, no reports exist of a systematic relation between nitrogen isotopes and the environment of deposition in sediments that have undergone significant alteration. Why is it that the original biological trend of increasing $\delta^{15}N$-values of organic matter from terrestrial to marine environment seems to be lost in sediments?

The amount and the (chemical composition) of organic matter that is deposited and preserved in the sediments depend on various factors such as primary productivity, sedimentation rate, chemical conditions (redox potential, acidity) and microbial activity. Most of the organic matter that is deposited will be consumed by the organisms that live in the sediment. *Early diagenesis* is defined as the changes that occur soon after deposition of the sediments. Early diagenetic alteration of organic matter is largely controlled by microbial activity. **Chapter III** reports on the effect of bacterial oxidation on the isotopic composition of nitrogen and carbon in two homogeneously deposited turbidites from the Madeira Abyssal Plain. Only the upper parts of these turbidites were affected by oxidation, whereas the lower parts remained under reducing conditions. This provides a unique opportunity to study the effect of the early diagenetic oxidation of marine sediments without the obscuring effects of vertical changes in composition of the precursor organic matter.

Breakdown under oxidizing conditions caused a 75% decrease in the organic matter content of the turbidites. It was found that both the C/N-ratios and the $\delta^{13}C$-values of the organic matter are significantly lower in the oxidized layers. The isotopic composition of organic nitrogen shows a more complex behaviour with varying $\delta^{15}N$-values in the two turbidites. These changes in C/N- and isotope ratios are attributed to the selective decomposition of organic compounds. Organic matter is a complex mixture of numerous organic compounds with different C/N-ratios, different isotopic compositions and different resistance against bacterial attack. This mixture is selectively decomposed by micro-organisms leaving an isotopically altered residue in the sediment (e.g. Spiker and Hatcher, 1984; Macko et al., 1987; Freeman et al., 1990). Protection of nitrogen-bearing compounds (e.g. amino-acids, proteins and their derivatives) by clay minerals such as smectites can enhance the selective preservation of organic nitrogen, with subsequently decreasing C/N-ratios (Weiss, 1969; Müller, 1977; Hedges and Hare, 1987).

Ammonium is formed upon decomposition of organic matter. Part of this ammonium is sorbed to the charged surfaces of clay-minerals (*exchangeable ammonium*) and can easily be replaced by other cations (Ca^{2+}, Mg^{2+}, K^+) or newly formed ammonium (NH_4^+). Therefore, this exchangeable ammonium is believed to represent the isotopic composition of the most recently decomposed organic matter in a sediment. The differences in $\delta^{15}N_{ex}$-values of the oxidized and unoxidized turbidite layers are good evidence for the isotopic differences of selectively decomposed organic nitrogen compounds (**Chapter III**).

FIXED NITROGEN AS A PALAEO-ENVIRONMENT INDICATOR

Illite and montmorillonite are the major potassium-bearing clay minerals. Ammonium can be built into the interlayers of these clay minerals at the same position as potassium. The bonding of this *fixed ammonium* is strong and replacement by other cations will only occur at very slow rates. The amount of fixed nitrogen relative to the clay-content of a sediment may be a primary effect in which case it depends on the availability of NH_4^+ during formation of the clay minerals. Upon early diagenesis, NH_4^+ can be built into the interlayers of already existing clay minerals in which case the fixed nitrogen content depends on both the availability of NH_4^+ and other cations in the sediment pore-water and on the exchange rates of ammonium with other cations. The amount of ammonium in the sediment pore-water is related to the presence of organic matter and the rate at which the organic matter is being decomposed by micro-organisms. Under oxidizing conditions the ammonium content of pore-waters is much lower than in anoxic sediments (e.g. DeLange, 1988). Contrary to organic matter, clay minerals are not affected by bacterial oxidation and, thus, the fixed nitrogen content and $\delta^{15}N_{fix}$-values hardly decrease in the oxidized layers of the Madeira Abyssal Plain turbidites (**Chapter III**). An observed decrease in N_{fix}-content results from exchange with other cations, in particular potassium.

It is concluded that the isotopic composition of fixed nitrogen is largely determined by the organic nitrogen compounds that have been decomposed after deposition of the sediment, during the initial stages of early diagenesis.

Pursuing this line of reasoning, the question can be asked if the isotopic composition of fixed nitrogen preserves the environmental signature of sediments that have already undergone early diagenetic alteration? To find an answer to this question, samples from a wide variety of sediments ranging from terrestrial to deep-sea environments were studied (**Chapter IV**). It appears that the isotopic composition of *organic nitrogen* in these samples shows no relationship with the environment of deposition. This is probably the result of early diagenetic changes whereby a large part of the original organic matter has been decomposed and the environmental signatures, i.e. the original $\delta^{15}N_{org}$-values, have been lost. The *fixed nitrogen* isotope ratios, however, are clearly related with the sedimentary environment. $\delta^{15}N_{fix}$-values increase regularly going from terrestrial to marine clays in the North Sea, and deep-sea sediments from the Atlantic Ocean have still higher $\delta^{15}N_{fix}$-values. This trend in the isotopic composition of fixed nitrogen is similar to the trend in particulate and recent organic matter that was described earlier in this chapter.

The mechanism of preservation of the original environmental signature by the fixed nitrogen isotope ratio is not yet understood. The most likely explanation is that ammonium is built into the interlayers fairly soon after the deposition of the clay minerals when there are still vacant sites in the mineral lattice to be occupied. Once the large monovalent cations (K^+ and NH_4^+) are fixed into the interlayers, they will not readily be replaced by other cations. Therefore, the isotopic composition of fixed nitrogen is probably created during the initial stage of early diagenesis. As a consequence, the organic nitrogen compounds that were decomposed at this diagenetic stage to form NH_4^+ must have had the environment's specific isotopic signature that is preserved by fixed nitrogen. Further research is needed to study the nature of this labile organic nitrogen fraction and to find answers to the questions such as: Where does this organic matter come from? What organisms formed it? At what rate is the ammonium fixed by the clay minerals? Under which conditions may the fixed nitrogen signature be lost?

The isotopic composition of fixed nitrogen was used to determine the environmental settings of core samples from Pleistocene sediments in the Southern

North Sea (**Chapter V**). This research was connected to a major project of several European geological surveys, aiming to get more insight into the development of sedimentary settings in the Southern North Sea area during the Pleistocene. Environmental interpretation of soft sediment cores is often difficult when fossils are lacking and sedimentary structures were lost during the drilling process. On the basis of the fixed nitrogen isotope ratios of the clay-minerals, a distinction can be made between sediments which were deposited under terrestrial, deltaic and marine conditions. The environmental interpretations based on nitrogen isotope data agree very well with the interpretations based on sedimentological and palaeontological observations.

These results clearly illustrate the potential of the $\delta^{15}N_{fix}$-method as an indicator of sedimentary environment. Further investigation must show if equally specific nitrogen isotope systematics exist in other sedimentary settings. Different isotopic compositions may in particular be encountered in special (restricted) environments such as tidal flats and anoxic basins with their specific biota.

THE EFFECT OF MATURATION ON THE N-DISTRIBUTION IN OIL-SHALES

In the foregoing paragraphs the attention was focused on early diagenetic alterations where the distribution and isotopic compositions of the nitrogen fractions are mainly determined by microbial activity. Upon burial of the sediments, however, *thermal degradation* of organic matter becomes predominant. The increasing pressure causes compaction of the sediments and the elevated temperatures promote re-mineralization of the clay minerals. The effect of this *maturation* on the nitrogen distribution in two NW European shales is discussed in **Chapter VI.**

Oil is formed upon maturation of organic-rich shales. During the initial stage of maturation, light hydrocarbons are released which have lower $\delta^{13}C$-values than the residue. With increasing temperature more complex organic compounds are released whereas a residue of increasingly insoluble polycondensated organic compounds (*kerogen*) remains in the shales. As a result of the expulsion of isotopically light hydrocarbons, the kerogen in mature shales has higher $\delta^{13}C$-values than the kerogen in immature shales. The organic nitrogen content decreases upon maturation; this however does not seem to affect the nitrogen isotope ratios of the kerogen. Oils from the North Sea which are related to the Kimmeridge shales show similar $\delta^{15}N$-values as their source rocks. Deviating isotopic compositions of organic nitrogen occur only in advanced mature shales that have lost most of their organic matter.

The similarity in nitrogen isotopic compositions of oils and source rocks can be useful for oil - source rock correlations, on the condition that different types of source rocks have different δ^{15}N-values. The Posidonien Schiefer were deposited under shallow marine conditions and have a small range in $\delta^{15}N_{org}$-values. The Kimmeridge shales have more variable $\delta^{15}N_{org}$-values which are probably related to the varying environmental conditions of deposition of these sediments. An extremely high $\delta^{15}N_{org}$-value (+17.7‰, unpublished data) was found for a sample from the Green River shales which were deposited in lacustrine environments and consist of organic matter derived from algae and microbial lipids (Tissot and Welte, 1984). Future study on source rocks and related oils must demonstrate the reliability of nitrogen isotopes for oil - source rock correlation.

Clay minerals become unstable with increasing temperature and pressure and, as a consequence, they will recrystallize during the burial of sediments. A major change in clay mineralogy during the maturation of shales is the transition from smectite to illite (*I/S-transition*) by a process which involves isomorphic substitution of Si^{4+} by Al^{3+} and the uptake of K^+ in the interlayers (Weaver, 1989). Simultaneous to the uptake of potassium, ammonium can be fixed in the interlayers of the newly formed I/S. This causes a considerable increase (more than five times) of the fixed nitrogen contents of the clays during maturation. The fixed ammonium is derived from decomposing organic matter (oil formation) which has fairly constant δ^{15}N-values. Therefore, the isotopic composition of fixed nitrogen approaches the isotopic composition of the organic nitrogen in shales with increasing degree of maturation. This explains why immature shales have varying $\delta^{15}N_{fix}$-values that probably reflect isotopic differences in the original sediments, whereas mature shales have consistent isotopic compositions of fixed nitrogen that can be used as an indicator of the origin of the degraded organic matter.

Other questions that need yet to be answered are:
- Why does fractionation of the organic nitrogen isotope ratios mainly occur during early diagenesis and not during maturation of sediments? Could it be that the decomposition of organic matter by microbial activity is more selective than thermal breakdown of organic matter?
- At what stage of maturation is the environmental signature lost that was initially present in the fixed nitrogen isotope ratio of early diagenetic sediments? The changes in $\delta^{15}N_{fix}$-values must be related to the recrystallization of the clay minerals, but it is still

unclear if the NH_4^+ that was initially present in the interlayers of the clay minerals remained fixed or was replaced during recrystallization.

SUMMARY

The results from this thesis elucidate some of the major processes involved in the sedimentary nitrogen distribution, although much research on the sedimentary nitrogen cycle still needs to be done.

During early diagenesis the nitrogen isotopic composition of organic matter can be altered strongly through microbial activity (oxidation). An environmental signature, however, remains preserved in the fixed nitrogen isotope ratios. As a result, the $\delta^{15}N_{fix}$-values in a sediment can be successfully used as an indicator of the palaeo-environmental setting.

Thermal degradation (maturation) has only little effect on the nitrogen isotopic composition of organic matter. Oils have $\delta^{15}N$-values similar to their rocks. Therefore, $\delta^{15}N$ may be useful to correlate oils with their source rocks. Recrystallization of the clay minerals upon maturation causes an increase in the fixed nitrogen content of shales. The fixed nitrogen content of the clays can be used as a maturity-indicator. In mature shales, the isotopic composition of this fixed nitrogen is similar to the $\delta^{15}N$ of the decomposed organic matter.

References

Berner E.K. and Berner R.A. (1987) The global water cycle. Prentice-Hall, New Jersey. pp. 397.

De Lange G.J. (1988) Geochemical and early diagenetic aspects of interbedded pelagic/turbiditic sediments in two N. Atlantic Abyssal Plains. Ph.D. dissertation, Univ. of Utrecht.

Delwiche C.C. (1970) The nitrogen cycle. *Scientific American* **223**, 136-147.

Freeman K.H., Hayes J.M., Trendel J.M. and Albrecht P. (1990) Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. *Nature* **343**, 254-256.

Hedges J.I. and Hare P.E. (1987) Aminoacid adsorption by clay minerals in distilled water. *Geochim. Cosmochim. Acta* **51**, 255-259.

Helder W. (1983) Aspects of the nitrogen cycle in Wadden Sea and Ems-Dollard Estuary with emphasis on nitrification. Ph.D. dissertation, Univ. of Groningen.

Macko S.A., Estep M.L.F., Hare P.E. and Hoering T.C. (1987) Isotopic fractionation of nitrogen and carbon in the synthesis of aminoacids by microorganisms. *Chem. Geol. (Isot. Geosci. Sect.)* **65**, 79-92.

Mariotti A., Lancelot C. and Billen G. (1984) Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. *Geochim. Cosmochim. Acta* **48**, 549-555.

Miyake W. and Wada E. (1967) The abundance ratio of $^{15}N/^{14}N$ in marine environments. *Rec. Ocean. Works Japan* **9**, 37-53.

Müller P.J. (1977) C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* **44**, 765-776.

Owens N.J.P. (1985) Variations in the natural abundance of ^{15}N in estuarine suspended particulate matter: A specific indicator of biological processing. *Estuar. Coastal Shelf Sc.* **20**, 505-510.

Peters K.E., Sweeney R.E. and Kaplan I.R. (1978) Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr.* **23**, 598-604.

Spiker E.C. and Hatcher P.G. (1984) Carbon isotope fractionation of sapropelic organic matter during early diagenesis. *Org. Geochem.* **5**, 283-290.

Sweeney R.E., Liu K.K. and Kaplan I.R. (1978) Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In *Stable isotopes in earth sciences.* (ed. B.W. Robinson) *D.S.I.R. Bull.* **220**, 9-26.

Sweeney R.E. and Kaplan I.R. (1980) Natural abundances of 15N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chemistry* **9**, 81-94.

Tissot B.P. and Welte D.H. (1984) Petroleum formation and occurrence. 2nd ed. Springer Verlag, Berlin, 699p.

Weaver C.E. (1989) Clays, muds, and shales. *Developments in Sedimentology* **44**. Elsevier Sci. Publ. B.V., Amsterdam, 819p.

Weiss A. (1969) Organic derivates of clay minerals, zeolites and related minerals. In *Organic Geochemistry* (eds. G. Eglington and M.T.J. Murphy) pp. 737-781. Springer-Verlag.

Williams L.B., Ferrell R.E., Chinn A.W. and Sassen R. (1989) Fixed-ammonium in clays associated with crude oils. *Appl. Geochem.* **4**, 605-616.

CHAPTER II

PROCEDURES FOR ISOTOPE ANALYSES

S.O. Scholten and R. Kreulen
Department of Geochemistry, Institute of Earth Sciences,
University of Utrecht, P.O. Box 80021, 3508 TA Utrecht

MEASUREMENTS OF ISOTOPE RATIOS

Samples are converted to N_2 and CO_2 and the isotopic compositions are measured on a Sira 24 mass spectrometer. Isotopic compositions are expressed as:

$$\delta\ (‰) = \{(R_{sample} - R_{standard}) / R_{standard}\} \cdot 10^3 \qquad (1)$$

where δ is the per mil (‰) deviation from the standard, and R is the isotope ratio. The standards are atmospheric nitrogen ($\delta^{15}N$) and PDB ($\delta^{13}C$).

Sample preparation for total nitrogen, exchangeable (adsorbed) nitrogen, fixed nitrogen, organic nitrogen and organic carbon are as follows:

Total nitrogen (N_{tot})

About 0.2 g of dried sample is weighed and put into a quartz container. This container is placed in a quartz tube which contains CuO pellets at the bottom; the tube is evacuated and sealed. The quartz tube is then heated for 30 minutes at 1200°C at the position of the sample container in order to pyrolyse the sample. Next, the entire tube is placed in an oven and heated to 900°C (1 hour) in order to oxidize the sample with the oxygen that is released by the CuO at this temperature (combustion). Tests on lab standards (shales and coals) showed that the pyrolysis step prior to oxidation is essential for the complete conversion of organic matter to gas.

The gases that are released by the pyrolysis/combustion treatment are purified by means of Ag-wool (450°C, 30 minutes), to reduce nitrogen oxides to N_2-gas, and CuO (900°C, 30 minutes), to convert possible traces of CO to CO_2. The remaining gases are separated cryogenically and the N_2-gas is trapped on Porapak Q in a sample bottle cooled with liquid nitrogen. N_2-yields are determined manometrically and the isotopic compositions are measured. Precision of yield measurements is better than 5% at the

95% confidence level and standard deviation of the $\delta^{15}N$-values is less than 0.2 ‰. All samples are measured at least in duplicate.

Exchangeable nitrogen (N_{ex})

Exchangeable nitrogen is defined as ammonium that dissolves upon shaking the sample with a KCl-solution (Bremner, 1965b).

About 3 g of dried sample is shaken for 60 minutes with 20 ml (2M) KCl-solution. 0.1 g MgO-powder is added, after which NH_4^+ in the solution is converted to NH_3. Thereafter, the solution is distilled and the NH_3-gas is trapped in 20 ml (0.025N) H_2SO_4-solution. Using a more concentrated H_2SO_4-solution might lead to isotope fractionation (Fiedler and Proksch, 1975). The distillation is stopped 5 minutes after the first condensed water reaches the H_2SO_4-solution (total distillation time is about 30 minutes). To prevent cross-contamination (Newman, 1966), the apparatus is cleaned between each sample by distillation of ethanol and double distilled water. After the precipitation of ammonium sulphate, the salt is converted to N_2-gas by adding an LiOBr/LiOH-solution:

$$(NH_4)_2SO_4 + 3LiOBr + 2LiOH \rightarrow Li_2SO_4 + 3LiBr + 5H_2O + N_2 \qquad (2)$$

The N_2 gas is separated cryogenically and nitrogen yields and isotopic compositions are measured. In spite of the low concentrations of exchangeable ammonium in most samples, the reproducibility of both N-yields and $\delta^{15}N_{ex}$-values is satisfactory: precision of yield measurements is about 5.0% at the 95% confidence level and standard deviation of $\delta^{15}N_{ex}$-values is 0.15 ‰. Because only limited amounts of sample were available, no duplicate runs were done on exchangeable nitrogen. In cases of low N_{ex} content (< 15 ppm) not enough sample was available to yield measurable amounts of nitrogen for the measurement of $\delta^{15}N_{ex}$. The distillation procedure was tested regularly in between sample runs on an $(NH_4)_2SO_4$ lab standard ($\delta^{15}N$ = -6.21 ‰, S.D. = 0.05 ‰). Analyses of standards obtained from the International Atomic Energy Agency yielded satisfactory isotope data: $\delta^{15}N$ = 0.38 ‰ (S.D. = 0.05 ‰) for N1 and $\delta^{15}N$ = 20.05 ‰ (S.D. = 0.03 ‰) for N2. Small quantaties of these standards were measured so that NH_4^+-yields would be similar to those extracted from the samples.

Fixed nitrogen (N_{fix})

NH_4^+ built into the crystal-lattice of minerals (in particular clays, micas and feldspars) is called fixed nitrogen (N_{fix}).

About 1 g of sample is reacted for 2 hours with a KOBr/KOH-solution (Bremner, 1965b) and subsequently boiled vigorously for 5 minutes to remove the nitrogen formed by oxidation of organic matter. Thereafter, the sample is shaken for 1 hour with 10 ml (2N) KCl-solution to release exchangeable nitrogen. After centrifuging (30 minutes) and rinsing with distilled water, the residue is shaken for 24 hours with 20 ml HF/HCl-solution (5N HF/1N HCl) to release inorganic (fixed) nitrogen. The solution is distilled after the addition of 20 ml (10N) KOH_{aq} to release NH_3 and further treated as described under N_{ex}. Precision of the measurements of fixed nitrogen content is better than 2.0%, standard deviation of the $\delta^{15}N_{fix}$-values is better than 0.1 ‰. All samples are measured at least in duplicate. The analytical procedures were tested on an artificially made tobelite ($NH_4Al_2Si_3AlO_{10}(OH)_2$) with known nitrogen content and known isotopic composition (2.7 wt%N_{fix}, $\delta^{15}N = 1.4$ ‰). In addition, the method for fixed nitrogen extraction was tested on a natural ammonium-bearing biotite (0.056 wt%N_{fix}, $\delta^{15}N = 8.1$ ‰). The results were similar to those obtained after destruction of the same biotite using a high-frequency induction oven technique to release N_2. Artificial mixtures were made of clay mineral free organic matter (torbanite) with the above mentioned tobelite and biotite standards. Analyses of these mixtures showed that organic matter does not interfere with the $\delta^{15}N_{fix}$-determination and that the analytical procedure is reliable.

Organic nitrogen (N_{org})

Organic nitrogen contents are calculated by subtracting fixed and exchangeable nitrogen from total nitrogen:

$$X_{org} = X_{tot} - (X_{fix} + X_{ex}) \tag{3}$$

in which X stands for concentration of nitrogen.

Similarly organic nitrogen isotope ratios are calculated by combining mass balance (formula 3) with isotope balance:

$$\delta^{15}N_{org} = \frac{\{X_{tot} \cdot \delta^{15}N_{tot} - (X_{fix} \cdot \delta^{15}N_{fix} + X_{ex} \cdot \delta^{15}N_{ex})\}}{X_{org}} \tag{4}$$

Since in most samples N_{ex} contributes only a small fraction of the total nitrogen (< 3%), the calculation of N_{org} content and $\delta^{15}N_{org}$-value depends primarily on N_{tot} and N_{fix}. Therefore, in most cases simplified versions of formulas 3 and 4 can be used, leaving exchangeable nitrogen out of the formulas. Precision of the calculated organic nitrogen content is better than 6% and standard deviation of $\delta^{15}N_{org}$ is less than 0.3 ‰. These error estimates were calculated using the Gaussian Law of propagation of errors.

Organic carbon (C_{org})

Before the carbon content and carbon isotope ratio of the organic matter can be determined, the sample has to be carbonate-free. In particular the α-turbidite samples (chapter III) contain carbonate that is difficult to dissolve in 100% phosphoric acid. Therefore, samples are treated with 6N HCl instead of phosphoric acid, in a way similar to that described by Jasper and Gagosian (1990). It should be mentioned that this treatment may also remove some hydrolysable organic carbon (Spiker and Hatcher, 1984), but this fraction is thought to be rather small compared to total organic carbon. The dried residue is then combusted with CuO at 900°C in a closed circulation system at 0.2 atm. oxygen pressure and the released CO_2-gas is cryogenically separated from the other gases; carbon yields are determined manometrically. Precision of yield measurements is better than 5% and standard deviation of the $\delta^{13}C$-values is less than 0.1 ‰.

COMMENTS AND DISCUSSION OF THE ANALYTICAL PROCEDURES

- N_2-gas is trapped on Porapak Q at -196°C prior to the measurement of the nitrogen isotopic composition. Major advantage of Porapak Q is that at room temperature the N_2-gas is released completely and ready for isotope measurement, whereas N_2-gas trapped on a molecular sieve (-196°C) is only released completely after subsequent heating. Experiments varying the freezing times of small amounts of N_2-gas (±0.2 ml) showed that after 10 minutes freezing reliable yields and reliable isotopic compositions are obtained (Fig. 1).

- Several methods to release total nitrogen were tested on two samples. The samples were a marl (SE 27) collected in Calabria (Italy), and the organic residue left after treating the marl with HF/HCl solution. Table 1 shows the N-yields and $\delta^{15}N$-

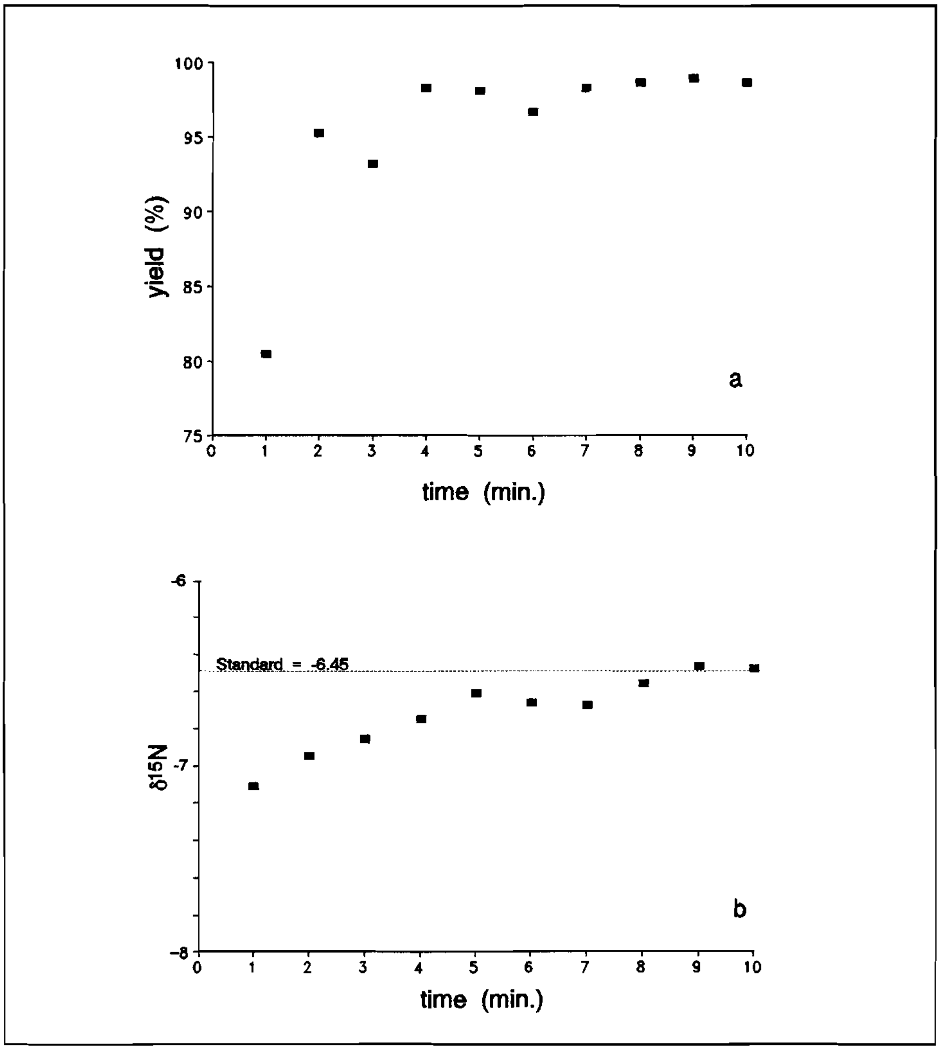


Figure 1. (a) Yields and (b) isotopic compositions ($\delta^{15}N$) of a standard nitrogen gas trapped on Porapak Q after various freezing times.

values of these samples obtained by different methods.

First method is Kjeldahl-destruction in concentrated sulphuric acid (465°C) (Bremner, 1965a) using selenium (Merck; Selenreaktions-gemisch zur Analyse) as a catalyst. Nitrogen was converted to ammonia and separated from the solution after digestion as described earlier. From the results in Table 1 it can be concluded that

Table 1. Results from the tests on methods to release nitrogen from two samples (see text for explanation). S.D. = standard deviation, precision at the 95% confidence level.

sample	method	n exp.	N content wt%	precision %	$\delta^{15}N$ ‰	S.D. ‰
total	Kjeldahl	12	0.068	7.8	3.4	1.1
total	induction	4	0.053	12.3	6.2	0.9
total	pyr/comb	4	0.100	4.1	3.0	0.1
organic	Kjeldahl	9	0.025	9.8	3.3	0.4
organic	pyr/comb	3	0.029	2.7	2.8	0.2

reproducibility of both yield and $\delta^{15}N$-values is not satisfactory. Jacobs (1978) suggested that loss of ammonia (vaporisation) may occur during the digestive procedure or that ammonia may not be released completely due to insufficiently high temperatures, inadequate periods of digestion or use of an unsuitable catalyst. Another disadvantage of the Kjeldahl-method is the incomplete release of ammonium from the inorganic mineral lattice during digestion. Especially in samples containing relatively high amounts of fixed ammonium (e.g. shales!) total N-yields can be much too low when the Kjeldahl-method is used.

The second method to release nitrogen was the thermal cracking of the sample by rapid heating (1500°C) in a high frequency (h.f.) induction oven. The experiments were done in a closed quartz tube under vacuum. The released gases were converted to CO_2 and N_2 by oxidation with O_2 from CuO (900°C) and cryogenically separated. Yields and $\delta^{15}N$-values show poor reproducibility (Table 1) and from mass-scans it could be seen that part of the nitrogen was oxidized, particularly to NO, which contributes to the yields and also interferes with the isotope ratio measurement. Condensation of organic compounds outside the hot spot of the h.f. induction oven was observed, which resulted in incomplete extraction.

Best reproducible results on total nitrogen were obtained using the combined pyrolysis/combustion method described on page 2.

If the gases formed upon combustion are not treated with Ag-wool, but only purified by undersaturated CuO (900°C), then most nitrogen oxides, except for N_2O, will already be reduced during the slowly cooling of the CuO. Ag-wool (450°C) completely reduces the remaining nitrogen oxides to nitrogen (N_2) without changing the isotopic composition, nor does it reduce CO_2 to CO which could otherwise interfere with the nitrogen isotope analyses. However, it should be kept in mind that only limited amounts of nitrogen oxides can be reduced with the Ag-wool (due to its limited surface area) and that quantities of nitrogen oxides might lead to incomplete reduction.

- Before the distillation of exchangeable ammonium, a small amount of MgO is added to the solution to prevent contamination by alkali-labile organic-N compounds which could interfere with the determination of ammonium (Bremner, 1965b; Bremner and Keeney, 1966).

Table 2. Precipitation of $(NH_4)_2SO_4$ from an aqueous solution by means of freeze-drying or evaporation under a continuous N_2-flow (40°C).

method	n exp.	N-yield %	S.D. %	$\delta^{15}N$ ‰	S.D. ‰
N_2-flow, 40°C	3	98.0	2.0	-6.0	0.12
freeze-drying	2	99.5	0.5	-5.9	0.11

- Table 2 compares two methods to precipitate $(NH_4)_2SO_4$ from an aqueous solution. A standard solution of $1.00 \cdot 10^{-3}$ M $(NH_4)_2SO_4$ was made and the salt was precipitated either by freeze-drying of the solution or by evaporation under a continuous N_2-flow in an oven at 40°C. Both methods produce good yields and $\delta^{15}N$-values, and both were used during this study (evaporation: Chapter V, freeze-drying: Chapters III, IV and VI).

- Since LiOBr is a rather unstable compound, it should be kept in a strongly alkaline medium (LiOH) and stored in a refrigerator (Fiedler and Proksch, 1975). If too large an excess of sulphuric acid is used in the hypobromide reaction (2), bromine may be formed according to the reaction:

$$Br^- + OBr^- + 2H^+ \rightarrow H_2O + Br_2 \tag{5}$$

- Fixed ammonium is extracted with HF/HCl-solution. Stevenson (1962) reported that the HF/HCl-solution does not deaminate organic nitrogen compounds and dissolves less than 5 percent of the organic carbon in shale samples. Thus, ammonium yields after acid treatment of shales can be considered as completely derived from fixed ammonium in the mineral lattices. However, the early diagenetic samples described in Chapters III, IV and V contain recent (easily hydrolysable) organic matter which could interfere with the N_{fix}-determination. Therefore all samples are first treated with KOBr/KOH-solution which removes the soluble organic nitrogen compounds.

References

Bremner J.M. (1965a) Total nitrogen. In *Methods of soil analysis, Part 2. Agronomy 9* (ed. C.A. Black), pp. 1149-1178. Americ. Soc. Agron., Madison, WI.

Bremner J.M. (1965b) Inorganic forms of nitrogen. In *Methods of soil analysis, Part 2. Agronomy 9* (ed. C.A. Black), pp. 1179-1237. Americ. Soc. Agron., Madison, WI.

Bremner J.M. and Keeney D.R. (1966) Determination and isotope-ratio analysis of different forms of nitrogen in soils. 3: Exchangeable ammonium, nitrate and nitrite by extraction- distillation methods. *Soil Sci. Soc. Proc.* **30**, 577-582.

Fiedler R. and Proksch G. (1975) The determination of 15N by emission and mass spectrometry in biochemical analyses: a review. *Anal. Chim. Acta* **78**, 1-62.

Jacobs S. (1978) The determination of nitrogen in biological materials. In *C.R.C. Critical reviews in analytical chemistry* **1978**, 297-322, C.R.C. Press Inc., Cleveland.

Jasper J.P. and Gagosian R.B. (1990) The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta* **54**, 1117-1132.

Newman A.C.D. (1966) The distillation of ammonia for isotopic analysis. *Chem.Ind.* **1966**, 115-116.

Spiker E.C. and Hatcher P.G. (1984) Carbon isotope fractionation of sapropelic organic matter during early diagenesis. *Org. Geochem.* **5**, 283-290.

Stevenson F.J. (1962) Chemical state of the nitrogen in rocks. *Geochim. Cosmochim. Acta* **26**, 797-809.

CHAPTER III

EARLY DIAGENETIC CHANGES IN NITROGEN AND CARBON ISOTOPES OF MARINE SEDIMENTS

S.O. Scholten and R. Kreulen
Department of Geochemistry, Institute of Earth Sciences,
University of Utrecht, P.O. Box 80021, 3508 TA Utrecht

ABSTRACT

Oxidation during early diagenesis has had a profound effect on the nitrogen and carbon isotopic compositions of two organic-rich turbidites from the Madeira Abyssal Plain. The isotopic compositions of three nitrogen fractions were studied: fixed nitrogen (NH_4^+ in clay minerals), exchangeable nitrogen (adsorbed NH_4^+) and organic nitrogen.

Oxidation of the turbidites caused a 75% decrease in the organic matter content. C/N-ratios after oxidation were lower than before oxidation. This change is attributed to the preservation of nitrogen compounds by clay minerals or to the presence of oxidation-resistant nitrogen compounds. Upon oxidation, the isotopic composition of organic carbon changes from -20 ‰ to -23 ‰. This indicates that the remaining resistant compounds in a marine sediment have more negative isotopic compositions. $\delta^{15}N_{org}$-values show a more complex behaviour upon oxidation. This is also reflected by the $\delta^{15}N_{ex}$-values, exchangeable nitrogen being directly derived from the decomposing organic matter. It is concluded that the precursor organic matter must have had a rather inhomogeneous nitrogen isotopic composition, possibly related to the limited availability of this nutrient in the food-chain, and that $\delta^{15}N_{ex}$-values correspond to the most recently decomposed organic compounds.

Fixed nitrogen in the unoxidized layers has $\delta^{15}N$-values in the narrow range from 5.6 ‰ to 5.8 ‰. Oxidation causes a 20% decrease in fixed nitrogen but $\delta^{15}N_{fix}$-values show only a small decrease, namely to ≈5.2‰. The fairly constant isotopic composition of N_{fix} rules out rapid isotope exchange with N_{org} or N_{ex} in the sediment. $\delta^{15}N_{fix}$ is believed to reflect the (possibly fractionated) cumulative isotopic composition of decomposing organic nitrogen under anoxic conditions.

The results indicate that care should be taken if the isotope values of organic carbon or nitrogen are used as indicators of the provenance of sediments, since early diagenetic alterations of the organic matter may change the isotopic composition and lead to misinterpretations.

INTRODUCTION

The effect of oxidation on the isotopic composition of organic carbon and organic, fixed and exchangeable nitrogen in marine sediments is described. The study was done on two originally homogeneous turbidites, covered by pelagic intervals, from the Madeira Abyssal Plain (north-east Atlantic Ocean). After their deposition, the upper parts of these turbidites were altered by oxidation, the lower parts remaining under reducing conditions (Buckley and Cranston, 1988). Because the turbidites were originally homogeneous, one is unlikely to encounter the uncertainties that are associated with diagenetic oxidation processes in sediments that are continuously deposited. The choice of the samples also eliminates changes with varying degrees of bioturbation, bacterial activity, etc. Therefore, this sample set provides a unique opportunity to study the diagenesis of marine sediments without the obscuring effects of vertical changes in the composition of the precursor organic matter or minerals.

Concentrations and isotopic compositions of carbon and nitrogen in soils and sediments have been studied extensively (e.g. Delwiche, 1970; Sweeney et al., 1978; Peters et al., 1978; Létolle, 1980; Showers and Angle, 1986; Dean et al., 1986; Macko et al., 1987; Jasper and Gagosian, 1989). Much less is known about the behaviour of the isotopes of carbon and nitrogen during early diagenesis (e.g. Sweeney and Kaplan, 1980; Spiker and Hatcher, 1984).

Stable isotope ratios of organic carbon (C_{org}) and organic nitrogen (N_{org}) may be used as indicators for the provenance of organic matter in sediments provided that no major changes in isotopic composition occurred during early diagenesis. The aim of this study is to investigate to what extent $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ change during early diagenesis, with special emphasis on oxidation. In this connection, the effect of oxidation on the C/N-ratios of organic matter was studied.

To obtain a better understanding of the behaviour of nitrogen upon diagenesis, one also needs to consider the changes that occur in the concentration and isotopic composition of inorganic nitrogen. Inorganic nitrogen in marine sediments occurs mainly in two forms: (1) exchangeable nitrogen (N_{ex}), ammonium adsorbed to minerals and organic matter and (2) fixed nitrogen (N_{fix}), ammonium bound into the crystal-lattice of minerals. The changes that occur upon the oxidation of these two inorganic nitrogen fractions are discussed and their relation to organic nitrogen will be considered. This study attempts to find out whether isotope ratios of organic and inorganic nitrogen remain constant upon oxidation during early diagenesis and whether they can provide a tool for the determination of sediment provenance.

SAMPLE LOCATIONS AND DESCRIPTION

Samples used in this study were collected from sediment cores of the Madeira Abyssal Plain (M.A.P.) in the north-east Atlantic Ocean (Fig. 1). The late Quaternary sediments in this area consist of thick (up to 5 m) turbiditic sequences interlayered with thin (3 to 15 cm) pelagic sediments. The stratigraphy of the Madeira Abyssal Plain sediments and

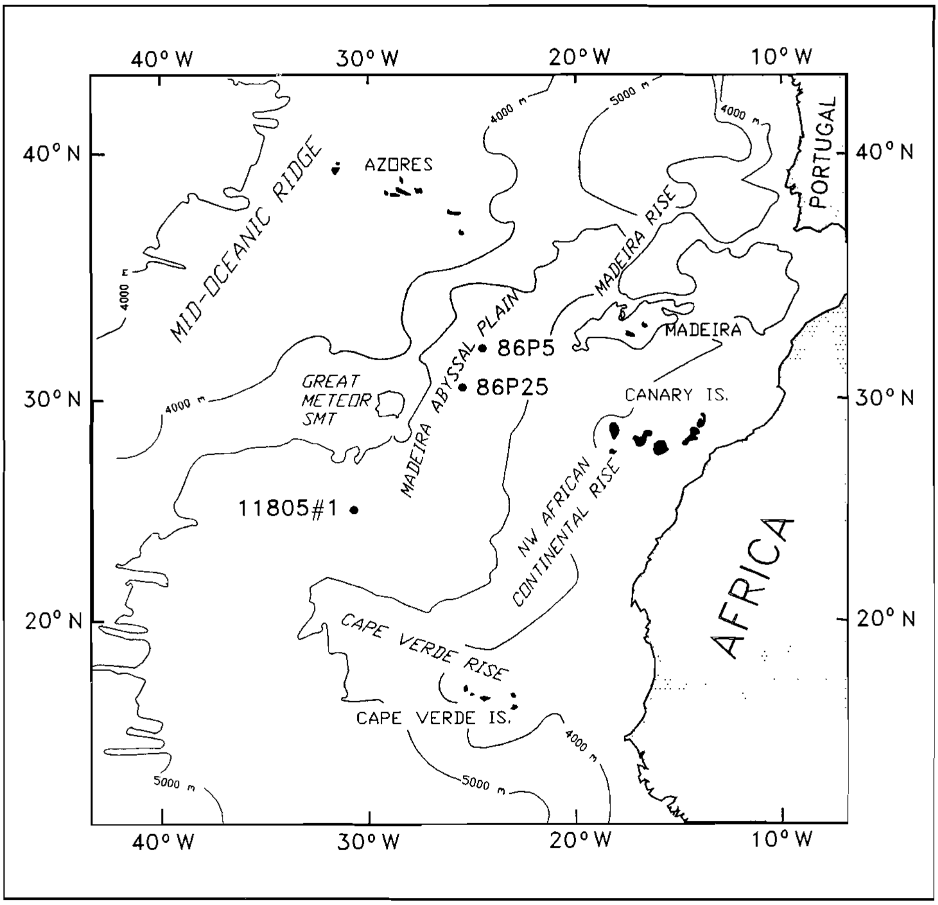


Figure 1. Map of the north east Atlantic Ocean showing sampling locations.

their lateral correlation has been described by (e.g.) Weaver and Kuijpers (1983), Kuijpers et al. (1984), Weaver and Rothwell (1987). These authors suggested that the turbidites were deposited during glacial-interglacial transitions, when sedimentation rates were high, and spread out over distances of up to several hundreds of km.

On the basis of geochemical characteristics which reflect their source areas, three major turbidite types can be recognized in the M.A.P. sediments: organic-rich, volcanic, and calcareous turbidites (De Lange et al., 1987; Middelburg and De Lange, 1988). Organic-rich turbidites, which are the subject of this study, are derived from the NW African margin and contain more than 0.3% C_{org}, about 50% carbonate, the remainder being predominantly quartz and clays. The mineralogical composition within the turbidites is homogeneous and only the silt content increases to some extent close to the bed (McCave and Jones, 1988).

A sharp oxidation front occurs in the turbidites, representing the penetration depth of oxygen diffusing from the bottom water. Deposition of pelagic sediments followed by the deposition of a new turbidite stopped the oxygen diffusion and preserved the original composition of the turbidites below the oxidation front (Wilson et al., 1985; Thomson et al., 1987; Buckley and Cranston, 1988). Above the oxidation front, where suboxic conditions (Berner, 1981) prevailed since oxygen diffusion was terminated, up to 80% of the organic matter is degraded and lost (Prahl et al, 1989). Simultaneously, about 10% of the calcium carbonate is lost.

For this study, samples from three different cores were examined which had been collected by the Dutch Geological Survey (RGD) and the Institute of Oceanographic Sciences (IOS): Cores 86P5 (32°2.50'N, 24°12.50'W) and 86P25 (30°44.23'N, 25°22.45'W) at 5400 m water depth and Core 11805#1 (25°40.2'N, 30°56.3W) at 6000 m water depth (see Fig. 1). Sampling methods have been described in detail by De Lange (1988). The cores were stored in a refrigerated dark room (4°C). Prior to analyses, three samples of the f-turbidite were taken from both core 86P5 and core 86P25; two samples were from below the oxidation front and one was an oxidized sample. The f-turbidite has an age of 140±12 kyr (Buckley and Cranston, 1988). From core 11805#1 five samples were taken of a turbidite layer which has not yet been designated and will be called α-turbidite in this paper. Two samples are from the oxidized layer, one sample is from the oxidation front and two samples are unoxidized (Table 1).

The localities of cores 85P5 and 86P25 are more than 200 km apart. Core 11805#1 was collected some 1000 km further to the south of the other two cores; this

Table 1. Concentrations and isotope ratios of nitrogen and organic carbon (n.d. = not determined). wt%K_2O and wt%Al_2O_3 determined by ICPES.

core	interval	depth cm	nr	K_2O wt%	Al_2O_3 wt%	N_{tot} wt%	$\delta^{15}N_{tot}$ $^{o}/_{oo}$	N_{fix} ppm	$\delta^{15}N_{fix}$ $^{o}/_{oo}$	N_{ex} ppm	$\delta^{15}N_{ex}$ $^{o}/_{oo}$	N_{org} wt%	$\delta^{15}N_{org}$ $^{o}/_{oo}$	C_{org} wt%	$\delta^{13}C_{org}$ $^{o}/_{oo}$	C/N molar
86P5	ox	704-714	6054	1.59	9.44	0.047	-1.1	94	5.4	11.6	n.d.	0.036	-2.8	0.22	-23.0	7.0
	unox	751-761	6056	1.34	8.39	0.120	4.5	96	5.8	29.1	7.4	0.107	4.3	1.04	-20.2	11.3
	unox	772-782	6057	1.36	8.50	0.140	1.9	99	5.7	26.7	7.3	0.127	1.5	1.00	-20.1	9.2
86P25	ox	780-789	6204	1.26	9.33	0.056	0.4	88	5.0	10.3	n.d.	0.046	-0.5	0.24	-21.9	6.2
	unox	855-868	6208	1.05	8.22	0.135	3.9	110	5.6	30.9	7.4	0.121	3.7	1.13	-20.2	10.9
	unox	905-916	6210	1.00	8.12	0.160	2.6	97	5.7	25.0	7.2	0.148	2.3	1.15	-20.2	9.1
11805#1	ox	87-95	26968	1.65	9.50	0.050	3.0	115	5.4	8.7	n.d.	0.038	2.3	0.24	-23.0	7.3
	ox	105-112	26967	1.61	9.12	0.068	4.1	101	5.2	n.d.	n.d.	0.058	3.9	0.44	-21.5	8.8
	front	114-120	26966	1.59	8.84	0.115	3.8	107	5.1	22.5	-3.4	0.102	3.8	0.85	-20.8	9.7
	unox	122-131	26965	1.64	8.84	0.116	3.4	120	5.8	24.5	2.2	0.102	3.1	1.00	-20.4	11.5
	unox	152-162	26964	1.63	8.76	0.121	2.3	120	5.7	24.5	2.9	0.107	1.9	1.00	-20.1	11.0

gave us the opportunity to compare the isotope geochemistry of different turbidites (with probably different provenance) and to examine the effect of oxidation on their respective isotopic compositions. Core 11805#1 is located in a small basin only connected with the M.A.P. by a narrow channel. From other geochemical data it has been concluded that the α-turbidite is not related to the f-turbidite (J. Ebbing, pers. com.).

RESULTS

Concentrations and stable isotope ratios of organic carbon, total nitrogen and the organic, exchangeable and fixed nitrogen fractions are shown in Table 1. Also shown in Table 1 are K_2O and Al_2O_3 contents, which serve to correlate fixed nitrogen contents with clay-mineral contents (after Müller, 1977).

Upon oxidation, 76 - 79% of the organic carbon and 59 - 66% of the organic nitrogen is removed. This corresponds to a shift in C/N-ratios from 9.1 - 11.5 (molar ratio) in the unoxidized layers to 6.2 - 8.8 in the oxidized layers.

Organic carbon isotope ratios of samples below the oxidation front fall within a narrow range (-20.4 ‰ $< \delta^{13}C_{org} <$ -20.1 ‰). In all three cores, oxidation lowers $\delta^{13}C_{org}$ significantly (down to -23.0 ‰). Organic nitrogen isotope ratios behave differently: $\delta^{15}N_{org}$-values of unoxidized turbidites show a fairly large spread from 1.5 ‰ to 4.3 ‰. $\delta^{15}N_{org}$-values of the f-turbidite decrease considerably upon oxidation (-0.5 ‰ and -2.8 ‰), whereas $\delta^{15}N_{org}$ of oxidized α-turbidite samples (2.3 ‰ and 3.9 ‰) remain similar to the isotope values of the unoxidized samples.

Exchangeable nitrogen contents are fairly constant below the oxidation front (about 25 ppm N_{ex}) and decrease considerably upon oxidation (to less than 12 ppm N_{ex}). Owing to the limited amount of sample available, the $\delta^{15}N_{ex}$-values of oxidized samples could not be determined.

Below the oxidation front, fixed nitrogen concentrations lie within a narrow range, with 96 - 110 ppm N_{fix} in samples from the f-turbidite and 120 ppm N_{fix} in the α-turbidite. About 10% of the N_{fix} fraction is lost through oxidation; this corresponds to a 20% decrease in the N_{fix}/Al_2O_3-ratio. It is noteworthy that unoxidized samples from both the f-turbidite and the α-turbidite have very constant $\delta^{15}N_{fix}$-values of 5.7 ±0.1‰. The oxidized samples show slightly lower $\delta^{15}N_{fix}$-values between 5.0 ‰ and 5.4 ‰.

Total nitrogen contents decrease upon oxidation from 0.116 - 0.160 wt% to 0.047 - 0.068 wt%. Inorganic nitrogen (N_{fix} and N_{ex}) makes up less than 15% of total nitrogen in samples below the oxidation front and more than 20% in the oxidized samples. Therefore, $\delta^{15}N_{tot}$ mainly reflects the isotopic composition of organic nitrogen: $\delta^{15}N_{tot}$-values for unoxidized turbidite layers range from 1.9 ‰ to 4.5 ‰ and decrease in the oxidized layer of the f-turbidite (0.4 ‰ and -1.1 ‰), whereas in the oxidized layer of the α-turbidite no change is found (3.0 ‰ and 4.1 ‰).

Summarizing, oxidation decreases the contents of organic carbon and nitrogen (N_{org}, N_{ex} and N_{fix}) in all fractions. $\delta^{13}C_{org}$ and, to lesser extent, $\delta^{15}N_{fix}$ decrease upon oxidation; $\delta^{15}N_{org}$ decreases in the f-turbidite but remains constant in the α-turbidite. $\delta^{15}N_{ex}$ is not measured in the oxidized samples because of the low N_{ex} contents.

DISCUSSION

The changes in total nitrogen content and isotopic composition that occur upon oxidation result from the behaviour of the separate nitrogen fractions (N_{org}, N_{ex} and N_{fix}). Therefore, the three nitrogen fractions will be discussed separately here.

Organic carbon and organic nitrogen

Oxygen and nitrate originally present in the pore water during deposition of the turbidites was rapidly consumed by decomposition of the most labile organic matter; thus the original composition of the sediment could for the most part be preserved (cf. Wilson et al., 1985). Further oxidation has only taken place in the top layer of the turbidites as a result of oxygen and nitrate diffusing downward from the sediment-water interface into the sediment (Wilson et al., 1985; Thomson et al., 1987; Buckley and Cranston, 1988). As a result of this oxidation, both organic carbon and organic nitrogen contents decrease (Fig. 2a). Above the oxidation front, as much as 76 - 79% of organic carbon and 59 - 66% of organic nitrogen has been removed. The C/N-ratios in the unoxidized turbidite layers of 9.1 - 11.5 (molar ratios) (Fig. 2b) are in the range of living marine organic matter in zones of deep-water upwelling at low latitudes like the African continental slope (Rashid, 1985). However, changes in the composition of particulate organic matter in the water column before sedimentation and changes that occurred upon sedimentation before the material was remobilized and the turbidite was deposited may have altered the original C/N-ratios considerably. The contribution of terrestrial organic matter from the NW African coast is probably small compared to the input of marine organic matter that is due to the high primary productivity (of phytoplankton

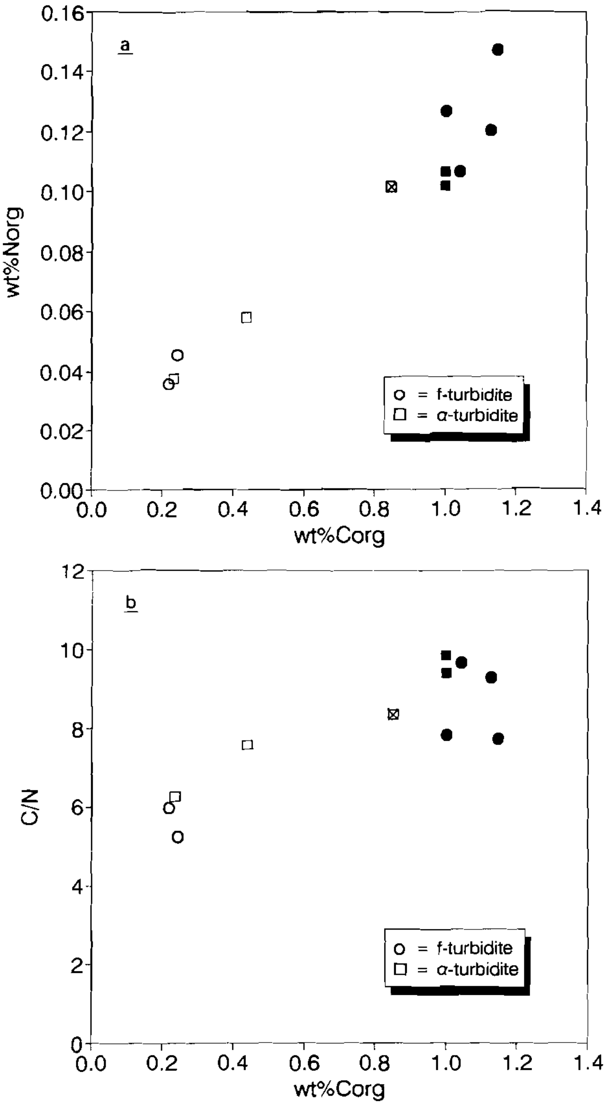


Figure 2. Relation between organic carbon content (wt%C_{org}) and (a) organic nitrogen content (wt%N_{org}), (b) C/N-ratios (wt%/wt%) in oxidized (open symbols) and unoxidized (closed symbols) samples from Madeira Abyssal Plain turbidites. Crossed symbols indicate samples from the oxidation front.

and marine plants) caused by upwelling nutrient-rich deep-water off the coast. The low C/N-ratios (≈10) in the unoxidized turbidite layers are an indication that the organic matter is predominantly of marine origin, though Meybeck (1982) demonstrated that C/N-ratios of particulate organic matter in major world rivers also lie between 8 and 10 (wt ratio) and a terrestrial component in the turbidite samples can therefore not be ruled out.

A small but significant decrease in the C/N-ratios upon oxidation can be observed (Fig. 2b). C/N-ratios below the oxidation front lie between 9.1 and 11.5, whereas oxidized samples have lower ratios ranging from 9.7 in the oxidation front of the α-turbidite down to 6.2 in the oxidized layer of the f-turbidite from which about 75% of the organic matter has disappeared. This indicates that the organic nitrogen compounds are better preserved against oxidative breakdown than on average the organic matter. The preservation of organic nitrogen can be the result of the protection of nitrogen-bearing compounds (e.g. amino-acids, proteins and their derivatives) by clay minerals such as smectites, montmorillonites (Weiss, 1969; Müller, 1977; Hedges and Hare, 1987). It can also reflect the presence of more stable nitrogen compounds such as hetero-cyclic compounds, aliphatic amines, etc. Taking into consideration that organic matter is a mixture of a wide variety of organic compounds, some of which are much more stable than others, it is not surprising that C/N-ratios change during organic matter breakdown. The very homogeneous character of the turbidites from the Madeira Abyssal Plain (McCave and Jones, 1988; De Lange, 1988) ruled out sorting as a possible explanation for changing C/N-ratios.

A relation is found between $\delta^{13}C_{org}$ and the organic carbon content (Fig. 3): the oxidation of 76 - 79% of the organic carbon content results in a decrease of $\delta^{13}C_{org}$ from -20 ‰ to -23 ‰. We assume that the $\delta^{13}C_{org}$-values of samples below the oxidation fronts represent the isotopic composition of the precursor organic matter. The value of -20 ‰ then indicates a predominantly marine origin with only trace amounts of terrestrial input (e.g. Peters et al., 1978; Dean et al., 1986; McArthur, 1989). This is in line with the low C/N-ratios (between 9.1 and 11.5) in these samples, which also indicate a predominantly marine provenance of the organic matter.

The lower $\delta^{13}C_{org}$-values of the oxidized samples demonstrate a shift towards isotope values which are commonly found in sediments with input of terrestrial organic material (Dean et al., 1986; Jasper and Gagosian, 1989). If we were to interpret only the $\delta^{13}C_{org}$-values of oxidized samples one might therefore come to the conclusion that terrestrial organic matter contributed a considerably larger fraction to the turbidites than can be concluded from the data on the unoxidized turbidite samples. This possibility is not pursued further here, since more data on the organic geochemistry (biomarkers) of

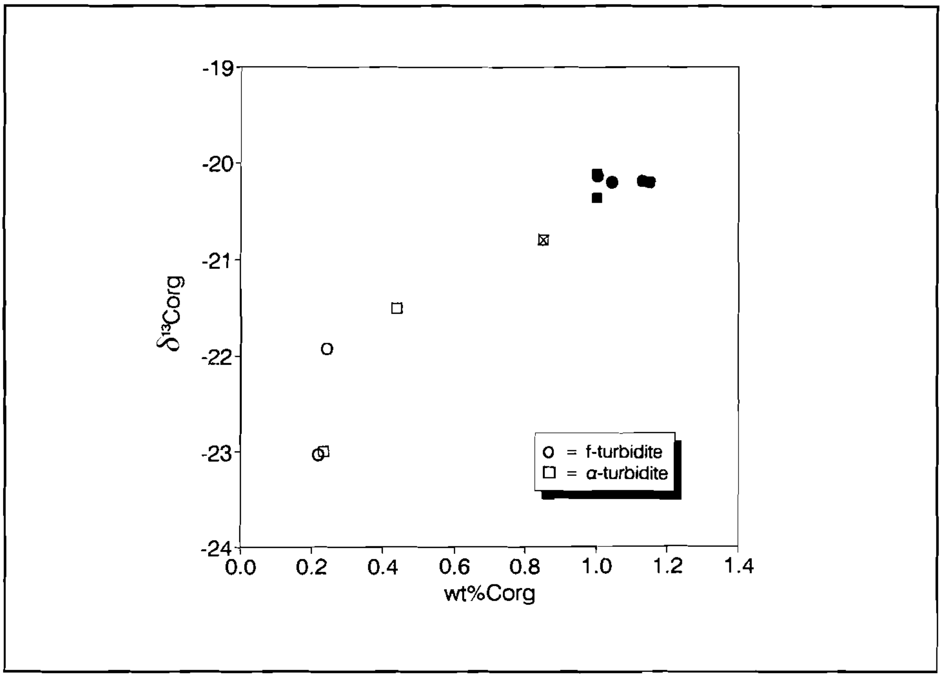


Figure 3. Relation between organic carbon content (wt%C_{org}) and isotopic composition (δ13C_{org}). See Fig. 2 for symbol explanation.

these samples are needed to prove the presence of terrestrial organic compounds (Prahl, pers. comm.). From carbon isotope studies on marine sapropel, Spiker and Hatcher (1984) reported differences of up to 14 ‰ between the lipids and humin in this algal, sapropelic sediment. Due to microbial alterations, the δ^{13}C-values of individual branched and cyclic hydrocarbons from the Messel Shale range between -20 ‰ and -75 ‰ (Freeman et al, 1990). Spiker and Hatcher (1984) concluded that during early diagenesis ^{13}C-enriched carbohydrates are lost, which decreases $\delta^{13}C_{org}$, by as much as 4 ‰. Similarly, the observed decrease in $\delta^{13}C_{org}$ of the turbidites could be the result of the preservation of organic carbon compounds with lower isotopic compositions than the average δ^{13}C of the organic matter in the turbidites. McArthur (1989) found that samples in the M.A.P. α-turbidite show no change in isotopic composition after 31% of their organic carbon content has been oxidized. This indicates that changes in $\delta^{13}C_{org}$-values are not directly proportional to the degree of oxidation of organic matter; the behaviour is probably related to the distribution of isotopes in the various organic carbon compounds (e.g. Freeman et al., 1990).

The isotopic composition of organic nitrogen is not constant in the unoxidized layers of both turbidites. In contrast with the carbon isotopes, a relatively wide range (cf. Table 1 and Fig. 4) of $\delta^{15}N_{org}$-values between 1.6 ‰ and 4.4 ‰ is found, which must be caused by variations in $\delta^{15}N_{org}$ of the organic nitrogen compounds:

(1) As a result of isotope fractionation in the nitrogen cycle, organic matter shows variations in $\delta^{15}N$. A main source of organic nitrogen in soils is $N_{2(g)}$ from the atmosphere, which has been fixed by microorganisms and certain plants. Air has a $\delta^{15}N$-value of 0 ‰, but the isotopic compositions of the nitrogen compounds may undergo fractionation through biosynthetic fixation and in particular, upon decomposition, nitrification and denitrification. Similar processes contribute to variations of $\delta^{15}N_{org}$ in the marine environment, although this nitrogen is mainly derived from runoff of terrestrial organic matter; upon decomposition of this organic matter, ammonia is formed, which can be nitrified by bacteria. This nitrate has average $\delta^{15}N$-values of

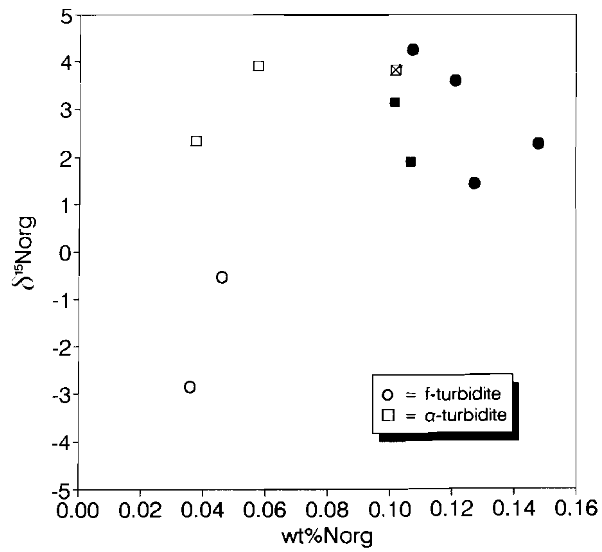


Figure 4. Relation between organic nitrogen content (wt%N_{org}) and isotopic composition ($\delta 13N_{org}$). Note that $\delta^{15}N_{org}$-values of samples from the f-turbidite decrease upon oxidation, whereas they remain fairly constant in samples from the α-turbidite (see Fig. 2 for symbol explanation).

7 - 10 ‰ (Peters et al., 1978) and will be consumed rapidly by microorganisms. To some extent, dissolved atmospheric nitrogen can also be fixed by microorganisms in the euphotic zone (Sweeney and Kaplan, 1980), though Altabet (1988) questions whether there is uptake of N_2 and suggests NO_3^- as the principal source of new nitrogen in the euphotic zone of the Sargossa Sea. As a result of its different nitrogen sources, marine organic matter is on average isotopically heavier than terrestrial organic matter.
(2) Nitrogen is often a limiting factor in the production of organic matter by photosynthesis (Delwiche, 1970) and consequently, organisms will be less selective in their uptake of nitrogen-compounds than in the case of carbon. Therefore, $\delta^{15}N$ of organic compounds in living organisms may show considerably more variation than $\delta^{13}C$.
(3) Even in the case where an isotopically homogeneous nutrient is available, large fractionations between the different major molecular compounds within a single organism may occur. For instance, Macko et al. (1987) found differences of up to 13 ‰ for the nitrogen isotopic composition of isolated amino acids in blue-green algae. It is thought that these isotope fractionations between amino acids are associated with the metabolic pathways in their synthesis.

It is evident that $\delta^{15}N$ of organic matter in the sediments depends very much on the provenance of the compounds and on environmental factors. After deposition, early diagenetic changes under anoxic conditions may also cause shifts in isotopic composition. The observed range of $\delta^{15}N_{org}$-values in the unoxidized turbidite layers must be caused by a combination of these factors.

Unlike $\delta^{13}C_{org}$, the isotopic composition of organic nitrogen does not change systematically with oxidation of the turbidites. Whereas $\delta^{15}N_{org}$ in the oxidized layer of the f-turbidite decreases to an average value of -1.7 ‰, the oxidized layer of the α-turbidite has an average $\delta^{15}N_{org}$-value of 3.1 ‰, which is in the same range as $\delta^{15}N_{org}$ in the unoxidized layer (Fig. 4). This seemingly erratic behaviour of the isotopic composition of organic nitrogen as a result of oxidation, combined with the large spread of $\delta^{15}N_{org}$-values in the unoxidized turbidite layers, can probably best be explained by a very heterogeneous isotopic composition of the nitrogen compounds (Macko et al., 1987). Therefore, the isotopic composition of organic nitrogen in the turbidites is believed to depend largely on the relative stabilities of the nitrogen compounds, on the metabolic pathways in the synthesis of the nitrogen compounds, on the limited availability of this nutrient in the biological foodchain and consequently to a certain extent on differences that result from the provenance of the compounds.

Exchangeable nitrogen

Oxidation causes a drop in the exchangeable nitrogen (NH_4^+) content from ≥25 ppm to about 10 ppm (Table 1). N_{ex} occurs as ammonium, either adsorbed to the surface of clay minerals or adsorbed to organic matter (Boatman and Murray, 1982). Upon oxidation, ammonium adsorbed to the surface of clay minerals can be replaced by monovalent cations (in particular potassium) and oxidized to nitrate (NO_3^-). When organic matter is oxidized, part of the adsorbed ammonium will be released and also oxidized to NO_3^- (nitrification). Hence, the decrease in exchangeable nitrogen may result from changes in clay mineralogy and changes in the composition of organic matter.

The isotope ratios of the f-turbidite samples below the oxidation front ($\delta^{15}N_{ex}$ = 7.2 ‰ and 7.4 ‰) differ considerably from those of the α-turbidite samples ($\delta^{15}N_{ex}$ = 2.2 ‰ and 2.9 ‰). In contrast, the isotope ratios of fixed nitrogen are very similar in these samples, namely between 5.6 ‰ and 5.8 ‰ (cf. Table 1). Therefore, isotope exchange between adsorbed and fixed ammonium will probably not take place at high rates, otherwise the $\delta^{15}N_{fix}$-values would vary corresponding to the changing $\delta^{15}N_{ex}$-values. Thus, N_{fix} is ruled out as the main source of N_{ex}.

It is more likely that the exchangeable nitrogen originates from the breakdown of organic nitrogen compounds and that the $\delta^{15}N_{ex}$-values reflect variations in the isotopic composition of the decomposed organic nitrogen compounds (N_{dec}). The isotopic composition of the organic matter that has been removed from the turbidites upon oxidation ($\Sigma\delta^{15}N_{dec}$) can be calculated by a mass balance (Table 2). $\Sigma\delta^{15}N_{dec}$ of the α-turbidite is 3.6 ‰, whereas the f-turbidite has a much higher value of 5.3 ‰. This corresponds to the isotopic compositions of exchangeable nitrogen in the turbidites

Table 2. Average isotopic composition of nitrogen in oxidized, unoxidized and decomposed organic matter.

	f-turbidite		α-turbidite	
interval	wt%N	$\delta^{15}N$	wt%N	$\delta^{15}N$
oxidized	0.041	-1.7	0.048	2.5
unoxidized	0.126	3.0	0.105	3.1
$\Sigma\delta^{15}N_{dec}$	0.085	5.3	0.057	3.6

(2.6 ‰ and 7.3 ‰ respectively). $\delta^{15}N_{ex}$ and $\Sigma\delta^{15}N_{dec}$ are considerably higher than $\delta^{15}N_{org}$ in the f-turbidite, but they are similar to $\delta^{15}N_{org}$ in the α-turbidite where the isotopic composition of organic matter has hardly changed upon oxidation. Exchangeable nitrogen must therefore be derived from decomposing organic matter. Provided that N-isotopes of the N_{ex}-fraction can be exchanged easily, the variable isotopic composition of decaying organic matter can cause large variations in $\delta^{15}N_{ex}$. Thus, the very low $\delta^{15}N_{ex}$-value of -3.4 ‰ in the oxidation front of the α-turbidite may reflect the isotopic composition of certain decomposing organic compounds with low $\delta^{15}N$-values.

Fixed nitrogen

Fixed nitrogen corresponds to NH_4^+ incorporated in the interlayers of the (clay-)mineral lattices at the monovalent cation site (Müller, 1977). Mineralogic variations in the samples, in particular clay contents and clay mineralogy, contribute to changes in N_{fix}-concentration. Therefore the N_{fix}-concentrations in Fig. 5 are expressed relative to Al_2O_3-contents. Fig. 5 shows that oxidation results in a small reduction in the NH_4^+/Al_2O_3-ratio (about 20%) in both turbidites. Also, minor changes in the K_2O/Al_2O_3-ratios occur, though no coinciding relations with the N_{fix}/Al_2O_3-ratios are found in either turbidite. Replacement of ammonium ($r_{NH_4^+}$ = 1.43 Å) by potassium (r_{K^+} = 1.33 Å) is the most likely mechanism causing the decrease in N_{fix}/Al_2O_3-ratio. In addition, early diagenetic alterations in clay-minerals may contribute to the observed changes of fixed nitrogen and potassium relative to alumina. More detailed study of the clay-mineralogy will be needed to explain these differences between the α- and f-turbidite.

All turbidite samples below the oxidation front have very similar $\delta^{15}N_{fix}$-values (5.7 ‰ ±0.1 ‰). This is not surprising since organic nitrogen and exchangeable nitrogen show considerable variations in isotopic composition. Exchangeable nitrogen can easily be removed from the organic matter or clay mineral surface and is believed to reflect the isotopic composition of the organic compounds that are currently being decomposed. Transfer of exchangeable nitrogen from the mineral surface into the mineral lattice will only take place at slow rates and will depend on the availability of free monovalent cation sites. This uptake of N_{fix} at a low rate probably levels out the brief fluctuations in the isotopic composition of decomposing organic matter. Thus, fixed nitrogen may reflect the isotopic composition of the cumulate of decomposed organic matter, whereas exchangeable nitrogen reflects the most recently decomposed organic matter. $\delta^{15}N_{fix}$-values do not necessarily represent an unfractionated average $\delta^{15}N$ of the decomposed

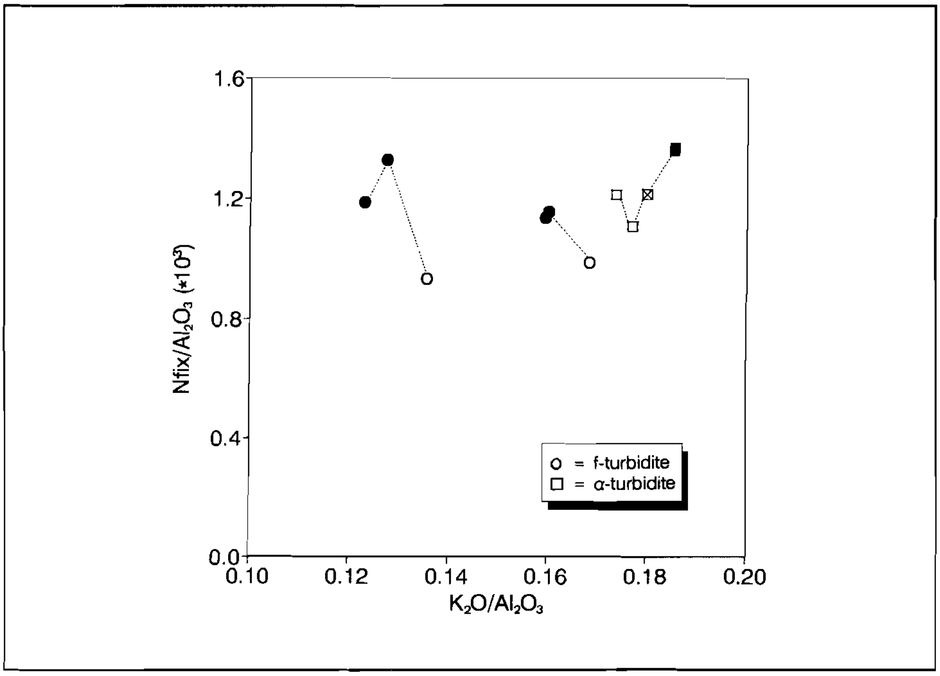


Figure 5. Plot of N_{fix}/Al_2O_3-ratio versus K_2O/Al_2O_3-ratio. Dotted lines connect samples from the same cores (see Fig. 2 for symbol explanation).

organic matter, since fixed nitrogen is only a minor fraction of the total amount of decomposed organic nitrogen. Small fractionations could also occur during uptake of NH_4^+ into the mineral lattice.

The $\delta^{15}N_{fix}$-values between 5.6 ‰ and 5.8 ‰ coincide remarkably well with the calculated $\Sigma\delta^{15}N_{dec}$-value of 5.3 ‰ in the f-turbidite (Table 2). Though this value represents the average isotopic composition of organic matter that was decomposed *upon oxidation*, it could be similar to the $\delta^{15}N$-values of the more labile organic compounds under anoxic conditions. In the α-turbidite, however, $\delta^{15}N_{fix}$ is 5.8 ‰ whereas $\Sigma\delta^{15}N_{dec}$ is considerably lower (3.6 ‰). This shows that it is probably an over-simplification to use $\Sigma\delta^{15}N_{dec}$-values calculated following oxidation to explain the isotopic composition of fixed nitrogen. Because NH_4^+ concentrations decrease drastically upon oxidation, it seems likely that $\delta^{15}N_{fix}$ depends mainly on the isotopic composition of the organic matter decomposed under anoxic conditions, either in the turbidites or (at an earlier stage) in the sediments where the turbidites originate.

The oxidized turbidite layers contain 20% less N_{fix}/Al_2O_3 than the layers below the oxidation front; this decrease is accompanied by a small decrease in $\delta^{15}N_{fix}$-values from 5.7 ‰ to 5.2 ‰ (Fig. 6). Possible explanations for the change in $\delta^{15}N_{fix}$ are:

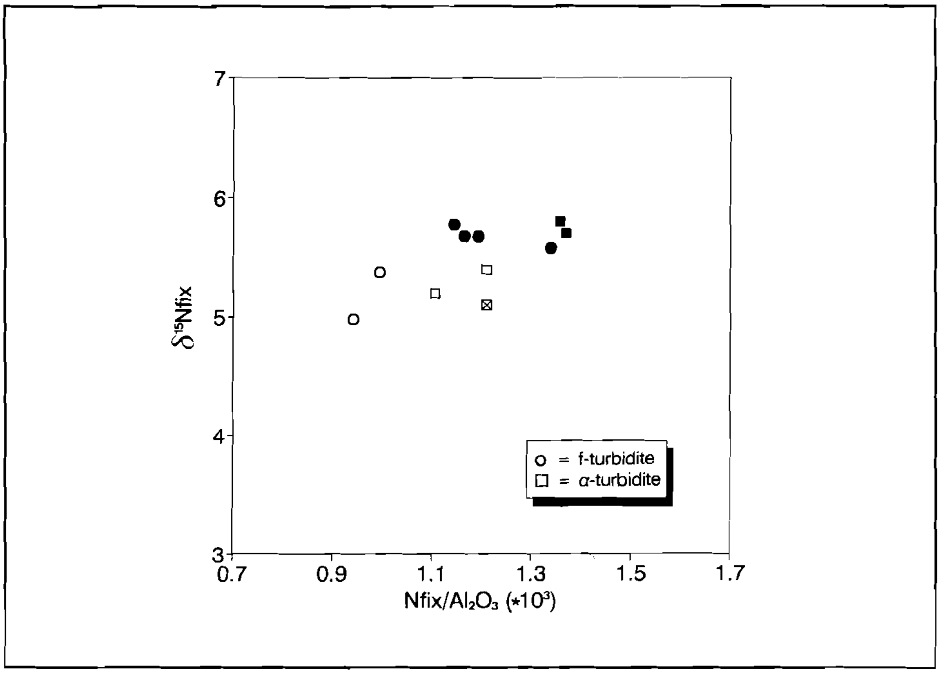


Figure 6. Relation between N_{fix}/Al_2O_3-ratio and isotopic composition of fixed nitrogen ($\delta^{15}N_{fix}$). Unoxidized samples (closed symbols) have similar isotope values with 5.6 ‰ $\leq \delta^{15}N_{fix} \leq$ 5.8 ‰. Upon oxidation, $\delta^{15}N_{fix}$ decreases slightly by ±0.5‰ (open symbols).

(1) Fixed nitrogen is released from the mineral lattices upon oxidation; this may be caused by cation exchange or changes in the mineral lattices.

(2) If it is assumed that under oxidizing conditions no fixed nitrogen is built into the mineral lattices since only a little (exchangeable) NH_4^+ is available, then the difference in $\delta^{15}N_{fix}$ can also result from simultaneously continuing uptake of NH_4^+ in the unoxidized layers. By means of mass and isotope balances one can calculate the isotopic composition of the nitrogen fraction that was fixed in the unoxidized layers while oxidation took place in the top layers: $\delta^{15}N$ of this fraction is on average 7.7 ‰. This coincides well with $\delta^{15}N_{ex}$ in the unoxidized layers of the f-turbidite (7.3 ‰), but the low $\delta^{15}N_{ex}$-values of the α-turbidite (2.6 ‰) contradict such an explanation.

Since in both turbidites the concentrations and isotopic compositions of fixed nitrogen behave similarly upon oxidation, the first explanation seems the most likely, though a combination of processes may have taken place: increasing fixed nitrogen content and $\delta^{15}N$ in the unoxidized layers, while fixed nitrogen was simultaneously removed above the oxidation front.

CONCLUSIONS

The organic matter in the two turbidites studied is predominantly of marine origin. This can be concluded from the low C/N-ratios and the $\delta^{13}C_{org}$-values in the unoxidized layers, though these sediments were probably already subject to changes before being deposited as turbidites. Oxidation of the upper part of the turbidites lowers the $\delta^{13}C$ of organic carbon considerably. This means that $\delta^{13}C$ is not homogeneous in all organic carbon compounds and that the organic compounds which are released upon oxidation have on average higher $\delta^{13}C$-values than the residue. Hence, it will only be possible to estimate sediment provenance from $\delta^{13}C$-values in recent sediments that have not undergone major diagenetic changes.

Organic nitrogen also decreases upon oxidation, though at a lower rate than carbon. Thus, C/N-ratios decrease in the oxidized parts of the turbidites. The preferential preservation of nitrogen compounds is most probably the result of protection by clay minerals and/or because upon oxidation the organic nitrogen compounds have, on average, more stable compositions than the carbon compounds in the remainder.

Unlike $\delta^{13}C$ of organic carbon, the isotopic composition of organic nitrogen is very inhomogeneous within the unoxidized layers of the turbidites. The variable $\delta^{15}N_{org}$-values may be the result of (1) isotope fractionation during the formation of the organic compounds and (2) the limited availability of nitrogen in the food-chain, which leads to uptake of nutrients with strongly deviating nitrogen isotopic composition. Thus, the organic compounds within a single species may already show a variable isotopic composition of nitrogen. Differences in $\delta^{15}N_{org}$ of the turbidites may also depend on the provenance of the organic matter.

$\delta^{15}N_{ex}$ depends strongly on the $\delta^{15}N$ of decomposed organic matter, since it can be exchanged easily. Consequently, the observed wide range in the isotopic composition of exchangeable nitrogen in the unoxidized samples results from the breakdown of organic matter with variable $\delta^{15}N$-values. The consistency between $\Sigma\delta^{15}N_{dec}$ and $\delta^{15}N_{ex}$ in the two turbidites strongly supports the assumption that exchangeable nitrogen reflects the $\delta^{15}N$ of decomposed organic matter.

Considering the wide ranges of $\delta^{15}N_{org}$- and $\delta^{15}N_{ex}$-values, the isotopic composition of fixed nitrogen is remarkably constant in the unoxidized layers of the turbidites. A possible explanation for this is that ammonium exchange between the fixed and exchangeable fractions proceeds at slow rates, otherwise $\delta^{15}N_{fix}$ would vary more. Therefore, the $\delta^{15}N_{fix}$-values reflect the possibly fractionated average isotopic composition of exchangeable nitrogen and consequently of decomposing organic nitrogen under anoxic conditions when ammonium is present as exchangeable nitrogen adsorbed to the mineral surfaces and dissolved in the pore water of the sediment. The slow uptake of ammonium into the mineral lattice will prevent large variations in $\delta^{15}N_{fix}$ when the isotopic composition of exchangeable nitrogen fluctuates upon the decomposition of inhomogeneous organic matter.

Upon oxidation, the isotope values of fixed nitrogen decrease only slightly, although N_{fix}-concentrations relative to Al_2O_3 decrease by 20%. It can be concluded that the fixed nitrogen isotopes must be homogeneously distributed in the clay-minerals. The small shift in $\delta^{15}N_{fix}$ is caused by cation exchange or changes in the mineral lattices upon oxidation and continuing uptake of ammonium in the unoxidized layers of the turbidites.

It is proposed that the measurement of the $\delta^{15}N_{fix}$ is an alternative method for determining the provenance of a sediment, since it reflects the average isotopic composition of the organic nitrogen that has decomposed since the sediment was deposited.

Acknowledgements

We are grateful to J.A.N. Meesterburrie for technical and analytical assistance. We thank the Rijks Geologische Dienst (RGD), the Institute of Oceanographic Sciences (IOS) and particularly, J. Ebbing and G.J. de Lange for providing core samples and data of ICP-analyses. The valuable contributions of P.F.M. van Gaans, B. van Os and S.P. Vriend are gratefully acknowledged. We thank A. van Eerden for preparing the tobelite and G. Frapporti for drawing the map. H.G.M. Eggenkamp and J.J. Middelburg carefully read the manuscript and suggested many improvements. Suggestions made by F.G. Prahl and two anonymous reviewers led to major improvements in the paper. Miss S. McNab is thanked for linguistic and stylistic advice. The mass spectrometer was partly financed by the Netherlands Organization for the Advancement of Pure Research (ZWO). S.O. Scholten was supported by funds of Koninklijke/Shell Laboratories (KSEPL) in Rijswijk, the Netherlands.

References

Altabet M.A. (1988) Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean. *Deep-Sea Res.* **35**, 535-554.

Berner R.A., (1981) A new geochemical classification of sedimentary environments. *J. Sed.Petrol.* **51**, 359-365.

Boatman C.D. and Murray J.W. (1982) Modeling exchangeable NH_4^+ adsorption in marine sediments: Process and controls of adsorption. *Limnol. Oceanogr.* **27**, 99-110.

Buckley D.E. and Cranston R.E. (1988) Early diagenesis in deep sea turbidites: The inprint of paleo-oxidation zones. *Geochim. Cosmochim. Acta* **52**, 2925-2939.

Dean W.E., Arthur M.A. and Claypool G.E. (1986) Depletion of ^{13}C in cretaceous marine organic matter: source, diagenetic or environmental signal? *Mar. Geol.* **70**, 119-157.

De Lange G.J. (1988) Geochemical and early diagenetic aspects of interbedded pelagic/turbiditic sediments in two N. Atlantic Abyssal Plains. Ph.D. dissertation, Univ. of Utrecht.

De Lange G.J., Jarvis I. and Kuijpers A. (1987) Geochemical characteristics and provenance of late Quarternary sediments from the Madeira Abyssal Plain, N Atlantic. In Geology and Geochemistry of Abyssal Plains (Eds. P.P.E. Weaver and J. Thomson) *Geol. Spec. Publ. 31*, pp. 147-165.

Delwiche C.C. (1970): The nitrogen cycle. *Scientific American* **223**, 136-147.

Freeman K.H., Hayes J.M., Trendel J.M. and Albrecht P. (1990) Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. *Nature* **343**, 254-256.

Hedges J.I. and Hare P.E. (1987) Aminoacid adsorption by clay minerals in distilled water. *Geochim. Cosmochim. Acta* **51**, 255-259.

Jasper J.P. and Gagosian R.B. (1989) Glacial-interglacial climatically forced ^{13}C variations in sedimentary organic matter. *Nature* **342**, 60-62.

Jasper J.P. and Gagosian R.B. (1990) The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta* **54**, 1117-1132.

Kuijpers A., Rispens F.B. and Burger A.W. (1984) Late Quarternary sedimentation and sedimentary processes on the Madeira Abyssal Plain, eastern North Atlantic. *Meded. Rijksgeol. Dienst* **38**, 91-118.

Létolle R. (1980) Nitrogen-15 in the natural environment. *In Handbook of environmental isotope geochemistry, Vol. 1A, The terrestrial environment*, (eds. P. Fritz and J.C. Fontes), pp. 407-433. Elsevier.

Macko S.A., Estep M.L.F., Hare P.E. and Hoering T.C. (1987) Isotopic fractionation of nitrogen and carbon in the synthesis of aminoacids by microorganisms. *Chem. Geol. (Isot. Geosci. Sect.)* **65**, 79-92.

McArthur J.M. (1989) Carbon isotopes in porewater, calcite and organic carbon from distal turbidites of the Madeira Abyssal Plain. *Geochim. Cosmochim. Acta* **53**, 2997-3004.

Meybeck M. (1982) Carbon, nitrogen and phosphorus transport by world rivers. *Amer. J. Sci.* **282**, 401-450.

McCave I.N. and Jones K.P.N. (1988) Deposition of ungraded muds from high-density non-turbulent turbidity currents. *Nature* **333**, 250-252.

Middelburg J.J. and De Lange G.J. (1988) Geochemical characteristics as indicators of the provenance of Madeira abyssal plain turbidites. A statistical approach. *Oceanol. Acta* **11**, 159-165.

Müller P.J. (1977) C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* **44**, 765-776.

Peters K.E., Sweeney R.E. and Kaplan I.R. (1978) Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr.* **23**, 598-604.

Prahl F.G., De Lange G.J., Lyle M. and Sparrow M.A. (1989) Post-depositional stability of long-chain alkenones under contrasting redox conditions. *Nature* **341**, 434-437.

Rashid M.A., (1985) *Geochemistry of marine humic compounds.* Springer-Verlag.

Showers W.J. and Angle D.G. (1986) Stable isotopic characterization of organic carbon accumulation on the Amazon continental shelf. *Cont. Shelf Res.* **6**, 227-244.

Spiker E.C. and Hatcher P.G. (1984) Carbon isotope fractionation of sapropelic organic matter during early diagenesis. *Org. Geochem.* **5**, 283-290.

Sweeney R.E. and Kaplan I.R. (1980) Natural abundances of 15N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chemistry* **9**, 81-94.

Sweeney R.E., Liu K.K. and Kaplan I.R. (1978) Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In *Stable isotopes in earth sciences.* (ed. B.W. Robinson) *D.S.I.R. Bull.* **220**, 9-26.

Thomson J., Colley S., Higgs N.S., Hydes D.J., Wilson T.R.S. and Sorensen J. (1987) Geochemical oxidation fronts in NE Atlantic distal turbidites and their effects in the sedimentary record. In *Geology and Geochemistry of Abyssal Plains* (Eds. P.P.E. Weaver and J. Thomson) *Geol. Spec. Publ. 31*, pp. 167-177.

Weaver P.P.E. and Rothwell R.G. (1987) Sedimentation on the Madeira Abyssal Plain over the last 300,000 years. In *Geology and Geochemistry of Abyssal Plains* (Eds. P.P.E. Weaver and J. Thomson) *Geol. Spec. Publ. 31*, pp. 71-86.

Weaver P.P.E. and Kuijpers A. (1983) Climatic control of turbidite deposition on the Madeira Abyssal Plain. *Nature* **306**, 360-363.

Weiss A. (1969) Organic derivates of clay minerals, zeolites and related minerals. In *Organic Geochemistry* (eds. G. Eglington and M.T.J. Murphy) pp. 737-781. Springer-Verlag.

Wilson T.R.S., Thomson J., Colley S., Hydes D.J., Higgs N.C. and Sorensen J. (1985) Early organic diagenesis; the significance of progressive subsurface oxidation fronts in pelagic sediments. *Geochim. Cosmochim. Acta* **49**, 811-822.

CHAPTER IV

$^{15}N/^{14}N$-RATIOS IN CLAYS AS A SENSITIVE INDICATOR OF SEDIMENTARY ENVIRONMENT

S.O. Scholten, J.H.J. Ebbing* and R. Kreulen
Department of Geochemistry, Institute of Earth Sciences,
University of Utrecht, P.O. Box 80021, 3508 TA Utrecht
*Rijks Geologische Dienst, Richard Holkade 10,
P.O. Box 157, 2000 AD Haarlem

ABSTRACT

The three major nitrogen fractions in clay-rich sediments are organic nitrogen (N_{org}), adsorbed ammonium (exchangeable nitrogen, N_{ex}) and ammonium build in the interlayers of clay minerals (fixed nitrogen, N_{fix}). The $^{15}N/^{14}N$-ratios of these three nitrogen fractions were studied in order to evaluate their potential as an indicator of the sedimentary environment. The samples cover a variety of sedimentary settings from terrestrial to deep-sea.

Although living organic matter is the source of essentially all nitrogen in sediments, only N_{fix} is clearly related with the sedimentary environment. N_{fix} originates from degradation of organic matter, but the exchange rate of ammonium in the clay mineral lattice is very slow. Therefore, the isotopic composition of N_{fix} represents an "integrated signal" which is probably a good approximation of the average ammonium produced by decay of organic matter over a long period. The isotopic composition of N_{org} in the studied samples shows a surprisingly erratic behaviour. This is probably the result of early diagenetic changes whereby a large part of the original organic matter has been decomposed. N_{ex} originates from *in situ* degradation of organic matter in the sedimentary column. Since adsorbed ammonium can easily be replaced, its isotopic composition reflects the last portion of ammonium produced by decomposing organic matter.

The results show that in contrast to the $^{15}N/^{14}N$-ratios of total, organic and exchangeable nitrogen, the isotopic composition of fixed nitrogen in clays can be used as an effective tool to determine the sedimentary environment.

INTRODUCTION

This chapter discusses the isotope behaviour of the three major nitrogen fractions in clay-rich sediments: organic nitrogen, exchangeable nitrogen and fixed nitrogen.

Nitrogen isotopes in recent sediments have been studied to determine the provenance of organic matter (Peters et al., 1978; Sweeney et al., 1978; Sweeney and Kaplan, 1980; Mariotti et al., 1984; Owens and Law, 1989). It was found that marine organic matter has higher δ^{15}N-values than terrestrial organic matter. This difference is inherited from the nitrogen that is consumed by organisms; in the terrestrial environment air is the main nitrogen source, whereas in a marine environment most of the nitrogen is derived from decomposed organic matter (nitrate). Run-off from the continent of suspended and dissolved organic matter and inorganic nitrogen (NO_3^-, NO_2^- and NH_4^+) is the major contributor of nitrogen to the sea. Nitrogen in air has by definition an isotopic value of 0 ‰, whereas the average δ^{15}N of dissolved inorganic nitrogen (NO_3^-, NO_2^- and NH_4^+) in marine environments is 7-10 ‰ (Peters et al., 1978). This difference in nutrient source is reflected in the isotopic composition of organic matter: terrestrial organic nitrogen usually has δ^{15}N-values of 0-5 ‰ whereas marine organic nitrogen has δ^{15}N-values from 7 to 10 ‰. Nitrogen isotope compositions deviating from these ranges have also been documented (e.g. Cline and Kaplan, 1975; Mariotti et al., 1984; Cifuentes et al., 1989), and result from various factors, such as temperature, seasonal variations, depth in the water column, bioactivity and mineralization.

Inorganic nitrogen in sediments occurs mainly as ammonium fixed on the monovalent cation sites of clay mineral lattices (fixed nitrogen, N_{fix}). Ammonium also occurs adsorbed to the surfaces of organic matter and (clay) minerals where it can easily be exchanged with other cations (exchangeable nitrogen, N_{ex}). Also, a substantial amount of ammonium is dissolved in the pore water of the sediments (Rosenfeld, 1979; Boatman and Murray, 1982; DeLange, 1988).

Exchangeable ammonium is mainly derived from decomposing organic matter. Hence, $\delta^{15}N_{ex}$ must be related to the isotopic composition of organic compounds that have been converted to ammonium. The isotopic composition of organic nitrogen, however, is not uniform throughout a sediment; organic matter is a complex mixture and different sorts of organic compounds may have different isotopic compositions. Progressive breakdown of organic matter will therefore lead to the release of ammonium fractions with successively different isotopic compositions. Both the concentration of exchangeable nitrogen and its isotopic composition will be subject to fluctuations (e.g. Rosenfeld, 1979), which will depend on the exchange rate with other cations, redox potential of the sediment and the availability of dissolved ammonium (from decomposed organic matter).

Ammonium is also present in the interlayers of clay minerals, in the monovalent cation position (fixed nitrogen), but the exchange rate of this cation is believed to be several orders of magnitude slower than the exchange rate of adsorbed ammonium (Rosenfeld, 1979; Boatman and Murray, 1982).

As far as we know, there is no record of the relations between the isotopic composition of the three major nitrogen fractions (N_{org}, N_{ex} and N_{fix}). In this paper we will discuss the following questions: What is the relation between organic and inorganic nitrogen fractions in clay-rich sediments? Which factors control the concentration and isotopic composition of the nitrogen fractions? Can nitrogen isotopes of clay-rich sediments serve as indicators of the environment of deposition or as indicators of sediment (clay) provenance? It will be shown that the $^{15}N/^{14}N$-ratio of ammonium in clays is a very useful and sensitive indicator of sedimentary environment.

SAMPLE DESCRIPTION

The samples in this study represent widely different sedimentary environments, ranging from freshwater to deep-sea. Most samples are from cores from the Southern North Sea (Fig. 1), where during the Quaternary terrestrial and marine conditions prevailed alternately. Two other samples from the Southern North Sea (R5 and R7) are of Tertiary age. The deep-sea samples (R12 - R15) are from cores taken in the Atlantic Ocean. The major characteristics of the samples are as follows:

Sample **R1** is a carbonate free (slightly sandy) river-clay belonging to the Kreftenheye Formation; it occurs at 8.00 m below the seabed in core S3-28 and underlies the early-Holocene basal peat. The Kreftenheye Formation is a Weichselian fluviatile deposit which occurs in the western parts of the Netherlands and off the Dutch coast (Doppert et al., 1975).

From core T1-9 a sedimentary sequence typical for the western parts of the Netherlands was sampled (Laban, pers. comm.): **R2** (5.00-6.20 m) brackish-water clay (early-Holocene), **R3** (6.20-6.30 m) basal peat (early-Holocene) and **R4** (6.30-6.80 m) fresh-water clay (late-Pleistocene). For more details of this sequence see Zagwijn (1986).

Sample **R5** (core S7-181, 8.00-9.00 m) is an olive-green-grey silty clay. It is an

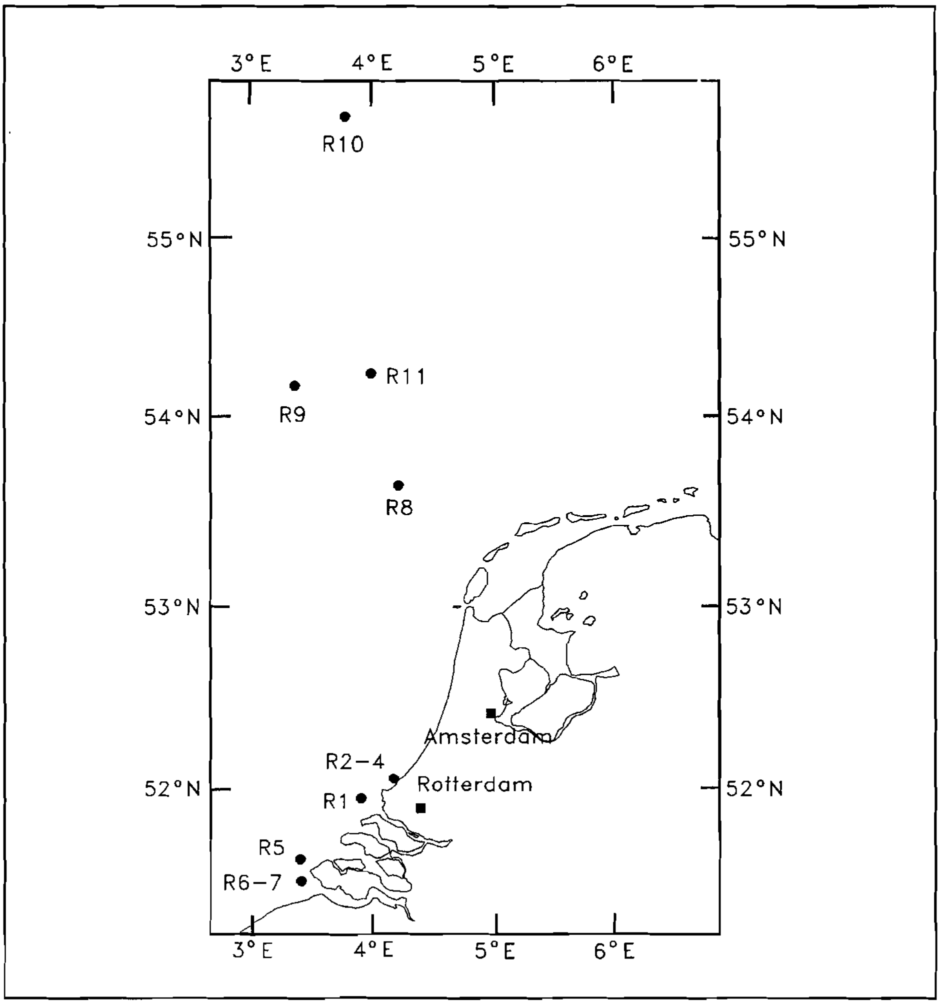


Figure 1. Map of the southern North Sea. The black dots indicate the positions of samples R1 - R11. Sample locations of R12 - R15 are described in the text.

open marine clay with abundant marine fauna (Lombard, 1957; p79). The sediment belongs to the Boom Formation (Rupelian), as can be concluded from the Rabsbank sheet (Ebbing and Laban, 1991) and the work of De Batist (1989).

Sample **R6** (core S11-284) is an olive-grey, vaguely banded clay, laminated with fine sand. It occurs 8.5 m below the seabed. The sediment belongs to the Banjaard formation: outer ebb tidal deposits formed in the coastal area since 1500 BP (Balson et al., 1991).

At 23 m below the seabed, core S11-284 consists of a (locally sandy) olive-green glauconitic clay (sample **R7**). Dinoflagellates indicate a late-Lutetian age and an outer-shelf open marine environment of deposition (Brinkhuis, 1989). This is in good agreement with the findings of Jacobs and Sevens (1988), who showed that the lateral equivalent of these late-Lutetian deposits in the nearby Belgian coastal plain were deposited in an open marine environment.

At 36.60-36.80 m below the seabed in core L7-N1054, a firm greyish-brown glaciolacustrine clay (**R8**) is found which belongs to the Dogger Bank Formation (Laban; pers. comm.). The Dogger Bank Formation has a late-Weichselian age and has been described by Jeffry et al. (1989).

Sample **R9** is a glaciolacustrine silty clay with silt laminae. It belongs to the Cleaver Bank Formation (Laban, pers. comm.) and was collected from core E16-1, 20.13-20.68 m below the seabed. The Cleaver Bank Formation has a Saalian age and has been described by Jeffry et al. (1989).

Sample **R10** (core A9-87) also belongs to the Cleaver Bank Formation and was collected from the same lithology as **R9**, as can been concluded from the Dogger sheet (Jeffry et al., 1991).

Sample **R11** from core E15-5 (3.50-4.00 m) is also a glaciolacustrine clay. The Silverwell sheet (Jeffry et al., 1989) shows that it is possibly a mixture of sediments from the Bolder Bank Formation (Weichselian) and the Cleaver Bank Formation (Saalian) (Laban, pers. comm.).

Core 86PCM13/3 was taken from the Madeira Abyssal Plain (31°26.7'N, 25°18.6'W) at a water depth of 5300 m. Sample **R12** is a red deep-sea clay from this core, sampled 3 m below the seabed (Ebbing et al., 1991).

A carbonate-rich turbiditic clay (**R13**) was sampled 0.90 m below the seabed on the Madeira Abyssal Plain (core 11805#1) at a water depth of 6000 m (25°40.2'N, 30°56.3'W). This sample was described by Scholten and Kreulen (1991). Similar turbidites have been described by Kuijpers et al. (1984) and Weaver and Rothwell (1987).

R14 and **R15** are pelagic olive-gray clays from the Antarctic Weddell Sea (core 87736, 59°40.63S, 51°19.90W), at 4.25 m (**R14**) and 5.25 m (**R15**) below the seabed and at a water depth of 2810 m. The clays were deposited in a cold oceanic environment (Van Enst: unpublished data).

ANALYTICAL METHODS

Clay mineral analysis: The clay mineral composition was determined as follows (Thorez, 1975; Brindley and Brown, 1980): Samples were treated with 30% H_2O_2 to remove organic matter and 2N HCl to remove carbonates. After sieving, the $<2\mu$ fraction was split into two parts which were treated with saturated $MgCl_2$ and KCl solutions respectively. These two fractions were precipitated on glass, dried at room temperature and X-ray diffractograms were made. $CuK\alpha_1$ radiation was used (λ = 1.54050). Hereafter, the KCl-treated sample was heated to 500°C and the $MgCl_2$-treated sample was glycolated; again X-ray diffractograms were made of these fractions. Using these four diffractograms the clay-mineral composition of the sample can be determined semi-quantitatively (Biscaye, 1965). The diffractograms were interpreted following the methods described by Biscaye (1965) and Johns et al. (1954).

Treatment of the samples for *isotopic analysis* was described in detail by Scholten and Kreulen (1991) and is only summarized here. Isotopic compositions of nitrogen are expressed as delta values relative to air.

Total nitrogen was extracted by means of pyrolysis (1250 °C) and subsequent combustion (CuO, 900 °C) of the samples in a sealed quartz tube.

Exchangeable nitrogen (N_{ex}) is released by treating the sample with a 2N KCl solution (Bremner, 1965). The solution is distilled to trap the ammonium in 0.025N H2SO4; the ammonium sulphate is oxidized with LiOBr/LiOH-solution.

Before *fixed nitrogen* (N_{fix}) is extracted, the sample is pretreated with 2N KCl to remove exchangeable nitrogen and with KOBr/KOH-solution to remove organic compounds. The residue is then reacted with 5N HCl/1N HF-solution to release the ammonium that is fixed in the mineral lattice. Further handling of the sample is similar to the treatment for exchangeable nitrogen.

Organic nitrogen (N_{org}) contents are calculated by subtracting the fixed and exchangeable nitrogen from the total nitrogen:

$$X_{org} = X_{tot} - (X_{fix} + X_{ex}) \qquad (1)$$

where X is the concentration of nitrogen.

Similarly, organic nitrogen isotope ratios are calculated by combining mass balance (formula 1) with isotope balance:

$$\delta^{15}N_{org} = \frac{\{X_{tot} \cdot \delta^{15}N_{tot} - (X_{fix} \cdot \delta^{15}N_{fix} + X_{ex} \cdot \delta^{15}N_{ex})\}}{X_{org}} \tag{2}$$

Elemental analyses were made by ICP-OES after treating the samples with a lithium borate-flux. The quality of the analyses was checked regularly by analyses of standard rock samples.

RESULTS AND DISCUSSION

Mineralogy

Mineralogical data on the $<2\mu$ fraction of the samples, as determined from the X-ray diffractograms, are summarized in Table 1. Illite, chlorite, kaolinite and smectite (montmorillonite) are the main compounds; other minerals such as mixed-layers, vermiculites, feldspars, quartz and amphiboles may be present in the $<2\mu$-fraction but no attempt was made to quantify them.

The most abundant clay-mineral in all samples is illite (simplified formula $K_{0.7}Al_2(Si,Al)_4O_{10}(OH)_2$), although smectite and kaolinite may also be present in considerable amounts. Smectites are mainly montmorillonite which has the structural formula $(Al_{2-y}Mg_y^{2+})(S_{4-x}Al_x)O_{10}(OH)_2M^+_{x+y}\cdot nH_2O$ (Güven, 1988), where M^+ represents the interlayer cation.

Müller (1977) used K_2O/Al_2O_3-ratios to express illite concentrations in clay-rich

Table 1. Clay analyses ($<2\mu$ fraction). n.d. = not detected, o = <5%, oo = 5-10%, ooo = 10-25%, oooo = 25-50%, ooooo = >50%.

sample	illite	kaolinite	chlorite	montmorillonite
R1	ooooo	oo	oo	oo
R2	ooooo	oo	oo	oo
R4	ooooo	oo	ooo	ooo
R6	ooooo	ooo	oo	ooo
R7	oooo	ooo	n.d.	oooo
R11	ooooo	oo	oo	o
R12	ooooo	oo	oo	ooo
R13	oooo	oooo	n.d.	oooo
R14	ooooo	o	oooo	o

oceanic sediments. Since illite is the clay mineral with the highest potassium content and is predominant in all studied samples, it is not surprising that K_2O/Al_2O_3-ratios are fairly constant: 0.23 ± 0.03, except for the two deep-sea samples which have lower K_2O/Al_2O_3-ratios of 0.16 and 0.17 (cf. Table 2). Variations can be attributed to the presence of other potassium-bearing minerals such as montmorillonites and feldspars.

Total nitrogen

Total nitrogen in a sediment consists of organic and inorganic (exchangeable and fixed) nitrogen fractions. Organic nitrogen makes up 90% of the total nitrogen content in the fresh-water peat sample (Table 2), but only 43% of the red deep-sea clay. The contribution of exchangeable nitrogen to total nitrogen varies from ≈0% to 15% and fixed nitrogen makes up 4% to 57% of total nitrogen. The isotopic compositions of the three nitrogen fractions behave differently upon transport, sedimentation and early diagenesis. This, together with variations in the source organic matter, results in the observed spread of $\delta^{15}N_{tot}$-values between 1.2 ‰ and 7.2 ‰ (Table 2). The complexity is reflected by the content and the isotopic composition of total nitrogen (Fig. 2) which vary without showing a clear relation to the environment of deposition ($r = 0.20$, $n = 14$). The behaviour of the separate nitrogen fractions will now be discussed in more detail.

Organic nitrogen

The $\delta^{15}N_{org}$-values of the studied samples lie between 0 ‰ and 6 ‰ (Table 2). These values are in the same range as those of previously reported isotopic compositions of organic nitrogen in suspended organic matter and recent sediments (e.g. Peters et al., 1978; Sweeney et al., 1978; Sweeney and Kaplan, 1980; Mariotti et al., 1984), which revealed general trends of increasing $\delta^{15}N$ from fresh water to marine sediments. These studies, however, describe the changes in $\delta^{15}N$ in limited areas, where terrestrial and marine end-members are well defined and where (early) diagenetic changes were minor. It has been shown by Scholten and Kreulen (1991) that early diagenesis in particular may change the original nitrogen isotope systematics beyond recognition.

The samples in the present study do not display a trend (Fig. 3) of increasing isotopic composition of organic nitrogen from a terrestrial to a marine environment. This is not surprising since the sediments were deposited under various conditions, they

Table 2. Concentrations and isotope ratios of the nitrogen fractions (n.d. = not determined). wt%K_2O and wt%Al_2O_3 determin by ICP-OES.

sample	N_{fix} ppm	$\delta^{15}N_{fix}$ ‰	N_{ex} ppm	$\delta^{15}N_{ex}$ ‰	N_{org} wt%	$\delta^{15}N_{org}$ ‰	N_{tot} wt%	$\delta^{15}N_{tot}$ ‰	N_{ex}/N_{tot} %	N_{org}/N_{tot} %	N_{fix}/N_{tot} %	Al_2O_3 wt%	K_2O wt%	K_2O/Al_2O_3	N_{fix}/Al_2O_3 $*10^3$	N_{fix}/K_2O $*10^4$
R1	353	2.3	54	2.7	0.085	5.2	0.125	4.3	4.3	67.7	27.9	10.27	2.02	0.20	3.4	175
R2	182	3.0	69	1.2	0.158	1.3	0.184	1.5	3.8	85.9	10.4	7.18	1.64	0.23	2.5	111
R3	308	1.0	517	0.9	0.760	1.2	0.843	1.2	6.1	90.2	3.7	6.45	1.55	0.24	4.8	199
R4	465	2.1	193	3.2	0.103	1.0	0.169	1.6	11.4	60.8	27.8	12.30	2.65	0.22	3.8	175
R5	254	3.7	38	3.1	0.051	3.2	0.080	3.4	4.7	62.9	32.6	16.47	3.27	0.20	1.5	78
R6	181	8.9	117	19.4	0.094	4.6	0.123	6.6	9.5	75.9	14.6	7.15	1.54	0.22	2.5	118
R7	107	3.7	43	3.3	0.022	4.7	0.037	4.2	11.6	58.8	29.9	10.08	3.39	0.34	1.1	32
R8	338	4.5	18	7.7	0.047	0.3	0.083	2.2	2.2	56.8	41.2	17.30	3.83	0.22	2.0	88
R9	232	4.2	54	5.6	0.040	3.1	0.069	3.7	7.8	57.5	35.1	10.61	2.74	0.26	2.2	85
R10	387	4.4	45	6.9	0.038	2.2	0.081	3.5	5.5	46.6	48.1	15.59	3.45	0.22	2.5	112
R11	260	4.3	19	7.3	0.033	2.8	0.061	3.6	3.1	53.9	43.0	13.01	3.42	0.26	2.0	76
R12	170	4.6	<5	n.d.	0.013	0.9	0.030	3.5	0.0	43.3	56.7	12.54	3.01	0.24	1.4	56
R13	115	5.4	9	n.d.	0.038	2.3	0.048	3.0	1.8	78.4	20.0	9.50	1.65	0.17	1.2	70
R14	219	6.6	107	16.2	0.040	5.2	0.073	7.2	14.7	55.1	30.2	13.75	2.22	0.16	1.6	99
R15	207	6.8	134	21.5	0.059	4.4	0.103	6.7	13.0	57.2	29.8	12.63	2.95	0.23	1.6	70

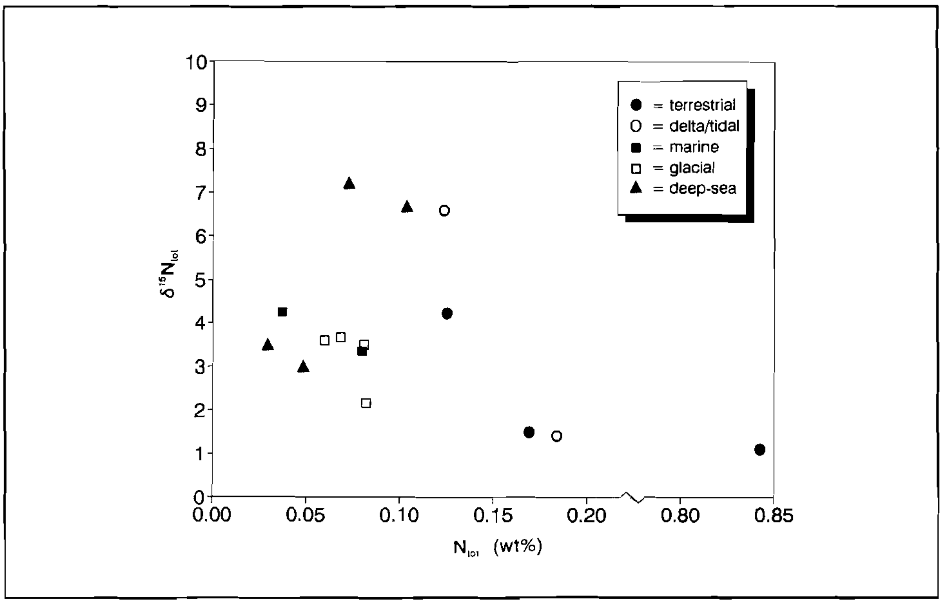


Figure 2. Plot of the isotopic composition ($\delta^{15}N_{tot}$ in ‰) versus the content (wt%) of total nitrogen. The triangles indicate samples from the Atlantic Ocean.

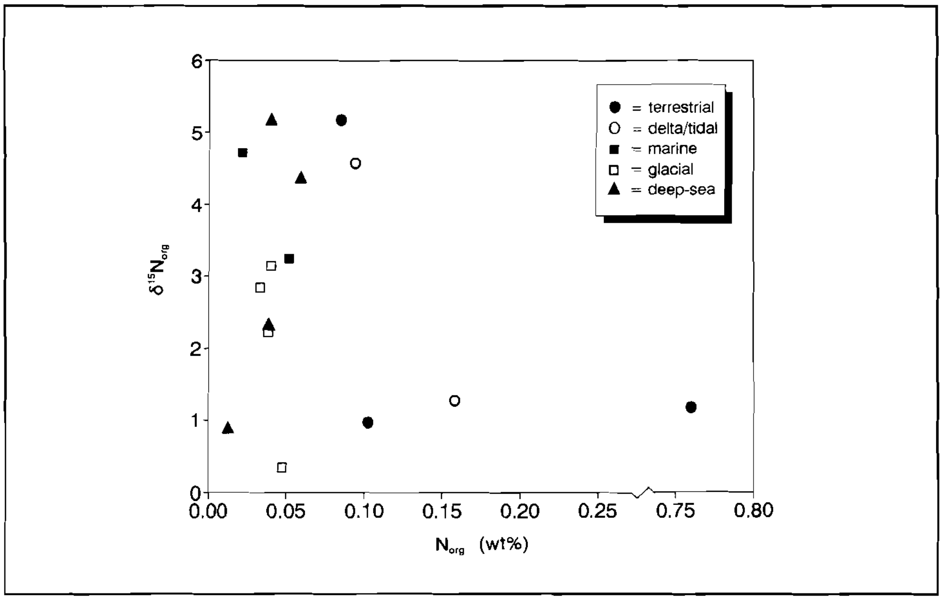


Figure 3. Relation between the content (wt%) and the isotopic composition ($\delta^{15}N_{org}$) of organic nitrogen.

have different ages and different sources of organic matter, and they were subject to different degrees of diagenesis. The organic matter content and the isotopic composition of organic nitrogen in sediments depend on complex factors such as environment of deposition (hydrology, abundance and provenance of nutrients, bioproductivity, climate), water depth and redox potential of the sediment. Fluctuations in the content and $\delta^{15}N$ of organic matter in the water column with changing season and water depth have been reported (Minagawa and Wada, 1984; Altabet and Deuser, 1985; Altabet, 1988; Goering et al., 1990). This implies that the organic matter that eventually settles in sediments may have a very heterogeneous isotopic composition.

After deposition, organic matter is subject to early diagenetic changes. Microbial activity is the major cause of the alteration in the isotopic composition of organic matter during early diagenesis (Macko and Estep, 1984). Through oxidation, the organic matter contents may decrease considerably and $\delta^{15}N_{org}$ changes due to differences in $\delta^{15}N$ of the oxidized compounds and the residue (Scholten and Kreulen, 1991). It was reported that hydrolysable nitrogen in soils may have $\delta^{15}N$-values which are more than 20 ‰ higher than non-hydrolysable nitrogen (Cheng et al., 1964). Similarly, Macko et al. (1987) reported variable isotopic compositions of nitrogen in aminoacids isolated from blue-green algae, with differences of up to 13 ‰. Thus, the $\delta^{15}N$ of organic matter can be subject to large alterations after deposition of the sediment, depending on the amount, composition, re-metabolization and preservation of the organic compounds.

The fact that the sediments described in this study have different sources of organic matter and have been subject to different degrees of early diagenesis, means that $\delta^{15}N$-values of organic matter cannot be regarded as useful indicators of the environment of deposition.

Exchangeable nitrogen

Exchangeable nitrogen shows larger variations both in contents and in isotope values than the two other nitrogen fractions: Contents range from <5 ppm to 517 ppm and $\delta^{15}N_{ex}$-values lie between 0.9 ‰ and 19.4 ‰ (Table 2).

Exchangeable nitrogen is essentially ammonium (NH_4^+) that is derived from decomposed organic matter and then adsorbed on various solid phases in the sediments. Ammonium is adsorbed in particular on the charged surfaces of clay minerals (Boatman and Murray, 1982), but also on organic particles (Rosenfeld, 1979). Several factors control the exchange of ammonium in sediments: The large monovalent cations, such as NH_4^+, K^+, Rb^+ and Cs^+ are held more tightly than other cations such as Ca^{2+}, Mg^{2+} and Sr^{2+}. This selective sorption is thought to result from the low hydration energy of the large cations (Sawhney, 1972 and refs. therein). The selective sorption is strongest on the interlayer sites of the clay mineral lattice where the cation can be held strongly or even "fixed" (N_{fix}). The selective sorption of large monovalent cations is also important at the frayed edges (sites) of clay minerals. In weathered clay minerals, these frayed edge sites can contribute a large proportion of the exchangeable cations. Weaver (1989) suggested mineral selectivity with cation sorption; in particular illite may show anomalously high exchangeable potassium contents. It is clear that comparison and interpretation of data on exchangeable ammonium in samples from such diverse sedimentary settings are complicated by a variety of factors such as sorption by organic matter, selective sorption, sorption sites on clay minerals and mineral selectivity.

In Fig. 4 exchangeable nitrogen contents are plotted versus Al_2O_3, K_2O/Al_2O_3-ratio and wt%N_{org} respectively. There seems to be a good correlation between N_{ex} and N_{org} contents ($r = 0.88$, $n = 15$), but this relation depends heavily on one organic-rich peat sample; If this sample is omitted the relation is much poorer ($r = 0.29$, $n = 14$). Exchangeable nitrogen does not seem to be correlated with Al_2O_3 (≈clay) content or with K_2O/Al_2O_3 (illite) either.

It is more likely that the concentration of exchangeable nitrogen in the studied samples depends primarily on the oxidation state of the pore waters. Under oxidizing conditions, ammonium derived from decomposed organic matter will readily be oxidized to nitrate (nitrification) and the exchangeable ammonium content will decrease. Only in organic-rich sediments that maintained reducing conditions can a high content of exchangeable nitrogen contents be expected. The red deep-sea clay sample (86PCM13/3) contains little organic nitrogen (0.013 wt%N_{org}) and no measurable amount of exchangeable nitrogen. However, the presence of fixed nitrogen in this sample (170 ppm) indicates that ammonium must have been formed during the degradation of organic matter, even though the present oxidizing conditions of the sediment inhibit the presence of *in situ* exchangeable ammonium.

Just as in the case of $\delta^{15}N_{org}$-values, the isotopic composition of exchangeable nitrogen does not show any relation with the environment of deposition (Table 2). Exchangeable nitrogen is fairly mobile, and therefore is probably derived from "currently decomposing" organic matter. As a consequence $\delta^{15}N_{ex}$ may vary considerably over time when the isotopic composition of organic matter is not homogeneous. Scholten and Kreulen (1991) have found that the isotopic composition of the small fraction of

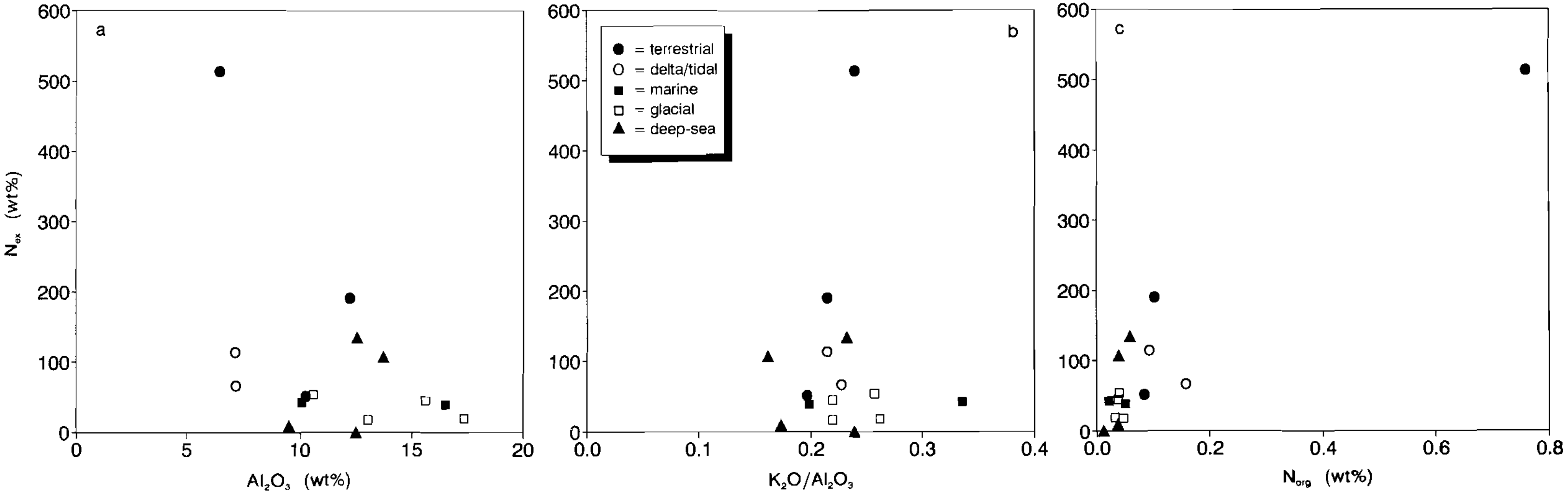


Figure 4. Plot of the exchangeable nitrogen content (wt%) versus (a) Al_2O_3 (wt%) as an indication of the clay content, (b) K_2O/Al_2O_3 (weight-ratios) as an indication of the illite content and (c) N_{org} (wt%).

exchangeable nitrogen that remained in the oxidation front of an organic-rich turbidite differed by -6.3 ‰ from the exchangeable nitrogen in the unoxidized layers of the same turbidite. This indicates that when the sediment is oxidized there will be a release of ammonium with deviating $\delta^{15}N$-values which will be partly adsorbed by minerals and organic matter.

The extremely high $\delta^{15}N_{ex}$-values found in some samples (e.g. R6 with $\delta^{15}N_{ex} = 19.4$ ‰) must be derived from decomposed organic compounds with very high $\delta^{15}N$-values. Cheng et al. (1964) and Macko et al. (1987) reported large variations in the $\delta^{15}N$ of organic nitrogen compounds of living organic matter; This suggests that isotopic inhomogeneity may also be common in sediments. It is therefore not surprising that in sediments a wide spread in $\delta^{15}N$-values is found not only in the residual organic matter but also in the exchangeable nitrogen. $\delta^{15}N_{ex}$ then depends on the $\delta^{15}N$ of the released fraction of decomposing organic matter.

Mechanism of nitrogen fixation

The ammonium "fixed" at the sites of large monovalent cations in the lattice of clay minerals is held much more strongly than the exchangeable ammonium as discussed earlier. Although fixed ammonium can be displaced from its lattice position and substituted by other cations, this replacement will take place only at relatively slow rates and under favourable conditions (Bolt et al., 1963; Sawhney, 1972; Comans, 1990). This is due to the position of fixed cations in the mineral lattice: When a rock weathers, clay minerals will form, in which the interlayer positions between the charged surfaces of the crystals are occupied by cations (Weaver, 1989). If large monovalent cations with low hydration energy, such as K^+ and NH_4^+, are included in the interlayer, the space between the layers can decrease upon dehydration (Sawhney, 1972 and refs. therein). As a result of this interlayer collapse the monovalent cations will be *fixed* in the mineral lattice and can only be released if the interlayer expands so that hydrated cations (in particular Ca^{2+} and Mg^{2+}) can replace the monovalent cations. Conversely, hydrous cations in expanded interlayers of existing clay minerals can be replaced by a process of selective sorption of large monovalent cations and subsequent fixation through interlayer collapse (Sawhney, 1972).

Ammonium (NH_4^+) has an ionic radius of 1.43 Å, which is nearly the same as the ionic radius of potassium ($r_{K^+} = 1.33$ Å) and, as outlined above, can be fixed in the interlayer position during formation of the clay mineral or through exchange with cations. Exchange of fixed cations at their highly specific interlayer positions takes place only at very slow rates through a solid- or film-diffusion process (Mortland and Ellis, 1959; Bolt et al., 1963) and becomes increasingly more difficult from the (frayed) edges of the minerals towards the centre (Sawhney, 1972).

Variations in fixed nitrogen contents

The amount of fixed nitrogen relative to clay-content (Al_2O_3) may be a primary effect, in which case it depends on the availability of both potassium and ammonium upon formation of the clay minerals or it may be a secondary effect, in which case it depends on the availability of potassium and ammonium and their exchange-rates after formation. In Fig. 5 N_{fix}/Al_2O_3 is plotted versus K_2O/Al_2O_3; it can be seen clearly that the ammonium content is not proportional to the potassium concentration, but depends heavily on the environment in which the clay is deposited: N_{fix}/Al_2O_3 decreases from $5 \cdot 10^{-3}$ (wt%/wt%) in a terrestrial environment to $1 \cdot 10^{-3}$ (wt%/wt%) in deep-sea clays. Iffixed nitrogen contents in clays depended only on the availability of NH_4^+ and K^+ in

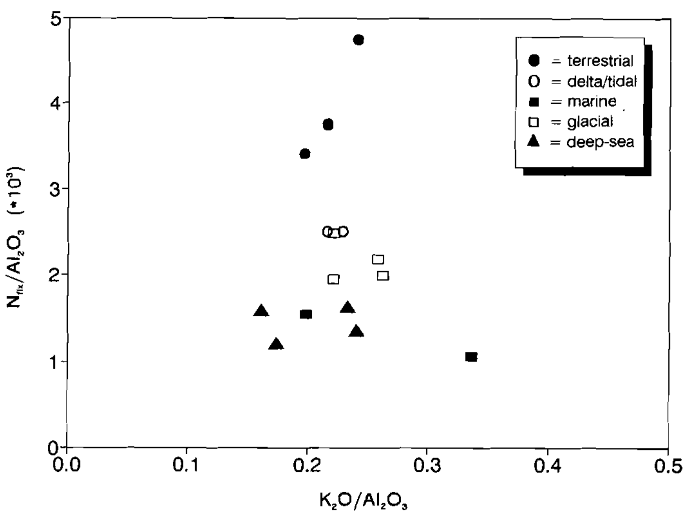


Figure 5. Plot of the N_{fix}/Al_2O_3-ratio (wt%/wt%) versus the K_2O/Al_2O_3-ratio (wt%/wt%). Samples from the terrestrial environment are clearly enriched in fixed nitrogen compared to samples from marine sediments.

the environment of sedimentation, then we would expect N_{fix}/Al_2O_3 to decrease considerably more because from terrestrial to marine environment potassium increases by as much as two orders of magnitude. Potassium concentrations in the river Rhine are 6.0 mg/l (e.g. Van der Weijden and Middelburg, 1989), whereas in the North Sea and the Atlantic Ocean the concentrations are about 400 ppm. Ammonium is available only in very small amounts under oxidizing marine conditions, whereas in terrestrial waters ammonium can be present in fairly large amounts as a result of the reducing conditions created by degradation of organic matter. Thus, in view of the typical NH_4^+ and K^+ distributions in the aquatic environments, one would expect a very wide range (much wider than observed) of N_{fix}/Al_2O_3 with very small ammonium concentrations in marine sediments if the clay minerals had actually been formed in the environment of sedimentation, or if complete exchange between potassium and ammonium had occurred during the transportation of the clay minerals.

Most marine clay minerals, in particular illite, are not formed authigenically. Savin and Epstein (1970) concluded from the isotopic compositions of oxygen and hydrogen that marine sediments contain mainly detrital clays derived from the continent. The terrestrial origin of clay minerals in Atlantic sediments has also been confirmed by radiogenic isotope measurements done by Dasch (1969), Hurley et al. (1963) and Lawrence (1979). Therefore, the relatively small decrease in N_{fix}/Al_2O_3-ratios from terrestrial to marine environment may result from the preservation of NH_4^+ in the interlayer position during and after transportation of the clay minerals. This implies that the ammonium in marine clays originates from decomposed terrestrial organic matter. Alternatively, this small decrease may result from exchange of potassium and ammonium with NH_4^+ produced after deposition in the marine sediment during the degradation of organic matter (as a result of decomposition of organic matter, the NH_4^+-contents in pore-waters of marine sediments increase rapidly below the sediment-water interface). As will be discussed below, the isotopic composition of fixed nitrogen indicates that the latter explanation is the most likely reason for the relatively high NH_4^+-contents in marine clays.

$\delta^{15}N_{fix}$ as environment indicator

The isotopic composition of fixed nitrogen shows a remarkable change with sedimentary environment (Fig. 6). Continental clays have $\delta^{15}N_{fix}$-values between 1.0 ‰ and 3.0 ‰. $\delta^{15}N_{fix}$ shifts to values higher than 3.0 ‰ in clays from the North Sea, whereas glacial

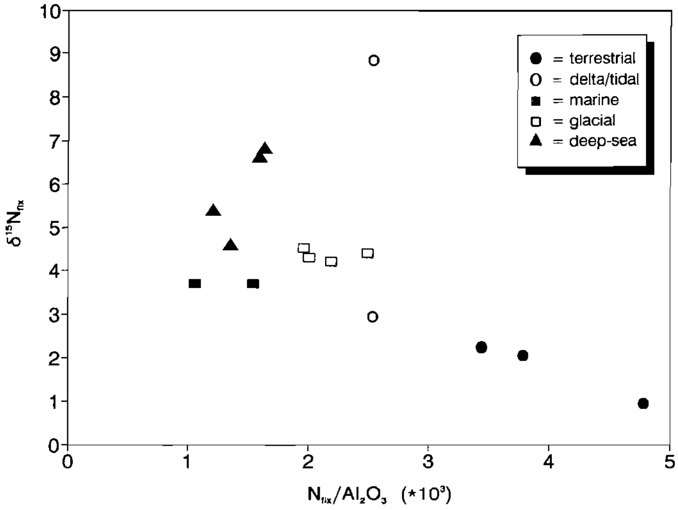


Figure 6. Relation between the N_{fix}/Al_2O_3-ratio (wt%/wt%) and the $\delta^{15}N_{fix}$-values (‰). Note the decreased scatter in $\delta^{15}N$-values of fixed nitrogen compared to total nitrogen (Fig. 2).

sediments from the North Sea Basin show consistent $\delta^{15}N_{fix}$-values between 4.2 ‰ and 4.5 ‰. Atlantic Ocean clays have the highest $\delta^{15}N_{fix}$-values, up to 6.8 ‰.

The observed increase in $\delta^{15}N_{fix}$ in a marine environment indicates that isotope exchange must have occurred with ammonium derived from decomposed organic matter (NH_4^+ dissolved in the pore water of the sediment and exchangeable NH_4^+ sorbed to the mineral surface and frayed edges). Thus, fixed nitrogen reflects the isotopic composition of organic matter decomposed after burial of the sediment. Although the isotopic composition of the degraded organic compounds may be heterogeneous and consequently $\delta^{15}N_{ex}$ varied considerably over time, the average isotopic composition of the bulk of the decomposed organic matter is probably related to the isotope signature of the organic matter that was originally deposited. Especially in those cases where much of the organic matter has been decomposed and only a small fraction is preserved, the isotopic composition of the residual organic matter will no longer be representative for the original sediment. Then the decomposed organic matter will represent a better measure of the original nitrogen isotopic composition of the sediment. We believe that the $\delta^{15}N_{fix}$-value gives a fair approximation of the average isotopic composition of the ammonium releasedupon the decomposition of organic matter in the sediment. As a result of the slow exchange rates, fixed nitrogen gives a well preserved and integrated signal over a long period of the isotopic composition of the decomposed organic matter in the sediment.

On the basis of the results shown in Fig. 6, we propose that the isotopic composition of fixed nitrogen might be a valuable tool for determining the original sedimentary environment. The strength of the method is illustrated by the red deep-sea clay sample **R12**. This sample contains only a minor fraction of organic nitrogen (0.013 wt%N_{org}) and no exchangeable nitrogen. However, the fixed nitrogen content (170 ppm) and the $\delta^{15}N_{fix}$-value (4.6 ‰) of this sample resemble those of other deep-sea clays with much higher organic and exchangeable nitrogen contents. In cases where organic matter has almost or completely disappeared, the $\delta^{15}N_{fix}$-value is still a reliable indicator of the environmental setting of a sediment.

CONCLUSIONS

Total nitrogen is the sum of three major nitrogen fractions which occur in widely varying proportions in the studied clay-rich sediments. The three nitrogen fractions have related but different histories and, accordingly, the isotopic composition of total nitrogen is **not** a reliable indicator for determining the environment of deposition of clay-rich sediments.

The nitrogen isotopic composition of organic matter in a sediment depends on the source and on alteration processes which occur after deposition. Once deposited, selective decomposition of isotopically inhomogeneous organic matter may alter the $\delta^{15}N_{org}$-value of the residue beyond recognition. This conceals the trend of increasing $\delta^{15}N_{org}$-values from a terrestrial to a marine environment which can be found in recent organic matter that has not yet been subject to early diagenetic changes. For this reason, the isotopic composition of organic nitrogen is not a reliable indicator of the source of organic matter.

Exchangeable nitrogen is adsorbed as ammonium on charged surfaces and frayed edges of clay minerals and on organic matter. The ammonium is derived from the decomposition of organic matter. N_{ex} contents depend strongly on the oxidation state of the sediment pore water: under oxidizing conditions dissolved ammonium is converted into nitrate and the N_{ex} contents become very low. The isotopic composition varies considerably (1 ‰ < $\delta^{15}N_{ex}$ < 21 ‰) and since exchangeable ammonium can easily be replaced, we propose that the varying $\delta^{15}N_{ex}$-values reflect the isotopic composition of ammonium derived from currently decomposed organic matter. The large range of $\delta^{15}N_{ex}$-values can be accounted for by the isotopic inhomogeneity of the decomposed organic compounds.

Fixed nitrogen concentrations and especially their isotope values are related to the environment of deposition. From a terrestrial to a marine environment the N_{fix} contents decrease relative to the clay content. Most fixed NH_4^+ in clays must have been incorporated after the deposition of the sediment and is derived from decomposed organic matter. The very consistent contents and $\delta^{15}N$-values of fixed nitrogen can only be explained if it is assumed that exchange of fixed nitrogen with potassium or isotopically deviating ammonium takes place at a slow rate, sufficiently slow to average the sometimes large isotopic variations of the available ammonium (exchangeable and dissolved ammonium). $\delta^{15}N_{fix}$ therefore gives an "integrated signal" of the ammonium produced by degradation of organic matter.

This makes the isotopic composition of fixed nitrogen a very promising tool for determining the environmental setting of sediments that have already undergone early diagenesis. More data are needed to confirm the general applicability of this new isotope tracer.

Acknowledgements

We are grateful to J.A.N. Meesterburrie for technical and analytical assistance. We thank the Director of the Rijks Geologische Dienst (RGD) for permission to use core samples and data of ICP-analyses. R.D. Schuiling carefully read the manuscript and suggested many improvements. S.M. McNab is thanked for linguistic and stylistic advice. The mass spectrometer was partly financed by the Netherlands Organization for the Advancement of Pure Research (NWO).

References

Altabet M.A. (1988) Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean. *Deep-Sea Res.* 35, 535-554.

Altabet M.A. and Deuser W.G. (1985) Seasonal variation in the flux of particulate matter to the deep ocean. *Nature* 315, 218-219.

Balson P.S., Laban C., SchÜttenhelm R.T.E., Paepe R. and Baeteman C. (1991). Ostend: Sheet 51°N 02°E. B.G.S., B.G.D. and R.G.D. 1:250.000 series: Seabed Sediment and Holocene.

Biscaye P.E. (1965) Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacant seas and oceans. *Geol. Soc. Am. Bull.* **76**, 803-832.

Boatman C.D. and Murray J.W. (1982) Modeling exchangeable NH_4^+ adsorption in marine sediments: Process and controls of adsorption. *Limnol. Oceanogr.* **27**, 99-110.

Bolt G.H., Sumner M.E. and Kamphorst A. (1963) A study of the equilibria between three categories of potassium in an illitic soil. *Soil Sci. Soc. Am. Proc.* **27**, 294-299.

Bremner J.M. (1965) Inorganic forms of nitrogen. In *Methods of soil analysis, Part 2. Agronomy 9* (ed. C.A. Black), pp. 1179-1237. Americ. Soc. Agron., Madison, WI.

Brindley G.W. and Brown, G. (1980) Crystal structure of clay minerals and their X-ray identification. Min. Soc. London. pp. 495.

Brinkhuis H. (1989). Dinoflagellates research on a North Sea boring S11-284. LPP Foundation int. rep., letter.

Cheng H.H., Bremner J.M. and Edwards A.P. (1964) Variations of nitrogen-15 abundance in soils. *Science* **146**, 1574-1575.

Cifuentes L.A., Fogel M.A., Pennock J.R. and Sharp, J.H. (1989) Biogeochemical factors that influence the stable nitrogen isotope ratio of dissolved ammonium in the Delaware Estuary. *Geochim. Cosmochim. Acta* **53**, 2713-2721.

Cline J.D. and Kaplan I.R. (1975) Isotopic fractionation of dissolved nitrate during denitrification in the Eastern Tropical North Pacific. *Mar. Chem.* **3**, 271-299.

Comans R.N.J. (1990) Sorption of cadmium and cesium at mineral/water interfaces. Ph.D. thesis, Univ. of Utrecht.

Dasch E.J. (1969) Strontium isotopes in weathering profiles, deep sea sediments and sedimentary rocks. *Geochim. Cosmochim. Acta* **33**, 1521-1552.

De Batist M. (1989) Seismostratigrafie en structuur van het Paleogeen in de zuidelijke Noordzee. Ph.D. thesis, Univ. of Ghent.

DeLange G.J. (1988) Geochemical and early diagenetic aspects of interbedded pelagic/turbiditic sediments in two N. Atlantic Abyssal Plains. Ph.D. thesis, Univ. of Utrecht.

Doppert J.W.C., Ruegg G.H.J., VanStaalduinen C.J., Zagwijn W.H. and Zandstra J.G. (1975) Formaties van het Kwartair en Boven-Tertiar in Nederland. In *Toelichting bij geologische overzichtskaarten van Nederland.* (Eds. W.H. Zagwijn and C.J. VanStaalduinen) Rijks Geologische Dienst, Haarlem.

Ebbing J.H.J. and Laban C. (1991) Rabsbank: Sheet 51°20N 3°0E. Rijks Geologische Dienst 1:100.000 series, Haarlem (in press).

Ebbing J.H.J., Van der Borg K., De Jong A.F.M. and Nederlof H.P. (1991) Continuous surface dwelling of manganese nodules on a hill in the Madeira Abbyssal Plain during abrupt sedimentation changes. *Mar. Geol.* (in press).

Goering J., Alexander V. and Haubenstock N. (1990) Seasonal variability of stable carbon and nitrogen isotope ratios of organisms in a North Pacific bay. *Estuar. Coast. Shelf Sci.* **30**, 239-260.

Güven N. (1988) Smectites. In *Hydrous phyllosilicates.* (ed. S.W. Bailey) *Rev. Miner.* **19**, 497-559.

Hurley P.M., Heezen B.C., Pinson W.H. and Fairbairn H.W. (1963) K-Ar age values in pelagic sediments of the North Atlantic. *Geochim. Cosmochim. Acta* **27**, 393-399.

Jacobs P. and Sevens E. (1988) Lithostratigrafie van de Eo-Oligocene overgangslagen in Noordwest Belgie. *Prof. Paper Ministerie van Economische Zaken van België* **235**.

Jeffry D.H., Frantsen P., Laban C. and SchÜttenhelm R.T.E. (1989) Silver Well: Sheet 54°N 02°E. B.G.S. and R.G.D. 1:250.000 series. Quaternary Geology.

Jeffry D.H., Laban C., Mesdag C.S. and SchÜttenhelm R.T.E. (1991) Dogger: Sheet 55°N 02°E. B.G.S. and R.G.D. 1:250.000 series. Quaternary Geology.

Johns W.D., Grim R.E. and Bradley W.F. (1954) Quantitative estimations of clay minerals by diffraction methods. *J. Sed. Pet.* **24**, 242-251.

Kuijpers A., Rispens F.B. and Burger A.W. (1984) Late Quaternary sedimentation and sedimentary processes on the Madeira Abyssal Plain, eastern North Atlantic. *Meded. Rijksgeol. Dienst* **38**, 91-118.

Lawrence J.R. (1979) O^{18}/O^{16} of the silicate fraction of recent sediments used as a provenance indicator in the South Atlantic. *Mar. Geol.* **33**, 1-7.

Lombard A. (1957) Geologie de la Belgique, une introduction. Les Naturalistes Belges.

Macko S.A. and Estep M.L.F. (1984) Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter. *Org. Geochem.* **6**, 787-790.

Macko S.A., Estep M.L.F., Hare P.E. and Hoering T.C. (1987) Isotopic fractionation of nitrogen and carbon in the synthesis of aminoacids by microorganisms. *Chem. Geol. (Isot. Geosci. Sect.)* **65**, 79-92.

Mariotti A., Lancelot C. and Billen G. (1984) Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. *Geochim. Cosmochim. Acta* **48**, 549-555.

Minagawa M. and Wada E. (1984) Stepwise enrichment of ^{15}N along food chains: Further evidence and the relation between δ^{15}N and animal age. *Geochim. Cosmochim. Acta* **48**, 1135-1140.

Mortland M.M. and Ellis B.G. (1959) Release of fixed potassium as a diffusion controlled process. *Soil Sc. Soc. Am. Proc.* **23**, 503-508.

Müller P.J. (1977) C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* **44**, 765-776.

Owens N.J.P. and Law C.S. (1989) Natural variations in ^{15}N content of riverine and estuarine sediments. *Estuar. Coast. Shelf Sci.* **28**, 407-416.

Peters K.E., Sweeney R.E. and Kaplan I.R. (1978) Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr.* **23**, 598-604.

Rosenfeld J.K. (1979) Ammonium adsorption in nearshore anoxic sediments. *Limnol. Oceanogr.* **24**, 356-364.

Savin S.M. and Epstein S. (1970) The oxygen and hydrogen isotope geochemistry of ocean sediments and shales. *Geochim. Cosmochim. Acta* **34**, 43-63.

Sawhney B.L. (1972) Selective sorption and fixation of cations by clay minerals: a review. *Clays Clay Miner.* **20**, 93-100.

Scholten S.O. and Kreulen R. (1991) Early diagenetic changes in nitrogen and carbon isotopes in marine sediments. *Geochim. Cosmochim. Acta* submitted.

Sweeney R.E., and Kaplan I.R. (1980) Natural abundances of 15N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chemistry* **9**, 81-94.

Sweeney R.E., Liu K.K. and Kaplan I.R. (1978) Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In *Stable isotopes in earth sciences.* (ed. B.W. Robinson) *D.S.I.R. Bull.* **220**, 9-26.

Thorez J. (1975) Phyllosillicates and clay minerals. (a laboratory handbook for their X-ray diffraction analysis). Ed. Letolle. Dison. Belgique. pp. 581.

Van der Weijden C.H. and Middelburg J.J. (1989) Hydrogeochemistry of the river Rhine: Long term and seasonal variability, elemental budgets, base levels and pollution. *Wat. Res.* **10**, 1247-1266.

Weaver C.E. (1989) Clays, Muds, and Shales. Developments in sedimentology 44.

Weaver P.P.E. and Rothwell R.G. (1987) Sedimentation on the Madeira Abyssal Plain over the last 300,000 years. In *Geology and Geochemistry of Abyssal Plains* (Eds. P.P.E. Weaver and J. Thomson) *Geol. Spec. Publ. 31*, pp. 71-86.

Zagwijn W.H. (1986) Nederland in het Holoceen. In *Geologie van Nederland* **1**, Rijks Geologische Dienst, Haarlem.

CHAPTER V

APPLICATION OF $\delta^{15}N$ AS A PALAEO-ENVIRONMENT INDICATOR IN QUATERNARY SEDIMENTS IN THE SOUTHERN NORTH SEA

S.O. Scholten, L.P. Sha* and R. Kreulen
Department of Geochemistry, Institute of Earth Sciences,
University of Utrecht, P.O. Box 80021, 3508 TA Utrecht
*Rijks Geologische Dienst, Richard Holkade 10,
P.O. Box 157, 2000 AD Haarlem

ABSTRACT

Ammonium can replace potassium in the mineral lattice of clay minerals. The nitrogen isotopic composition ($\delta^{15}N_{fix}$) of thisammonium is used to determine the environment of deposition of Quaternary sediments from the southern North Sea. The sediments were deposited under alternating marine and terrestrial sedimentary conditions. Absence of fossils and disturbance of the sedimentary structures upon sampling often complicate the interpretation of the environmental settings by traditional methods. On the basis of the $\delta^{15}N_{fix}$-values of the clay minerals, it is possible to make a clear distinction between terrestrial, deltaic and marine environments.

The results agree well with environmental interpretations based on sedimentological and palaeontological observations.

INTRODUCTION

The nitrogen isotopic composition of biomass depends on the environment in which it is formed. In particular, there are often large differences between the $^{15}N/^{14}N$-ratios of marine and terrestrial organic matter: Whereas the atmosphere ($\delta^{15}N = 0$ ‰) is the major nitrogen source for land plants, marine organic matter derives its nitrogen mainly from dissolved nitrogen compounds (NO_3^-, NO_2^- and NH_4^+) which have on average higher isotopic compositions (+7 to +10‰). As a consequence, $\delta^{15}N$ of organic matter increases gradually from terrestrial to marine environment (e.g. Peters et al., 1978; Sweeney et al., 1978; Sweeney and Kaplan, 1980; Owens and Law, 1989). Despite the clear relation of $\delta^{15}N$ of living organic matter with the environment, only a few sedimentary settings have reported where this "regular" trend exists; most of the organic matter that is deposited in sediments is recycled (through processes such as biodegradation and mineralization), which leads to a significant loss of organic matter and a change in the $\delta^{15}N_{org}$-value (Scholten and Kreulen, 1991).

Recently, Scholten et al. (1991) found that the $^{15}N/^{14}N$-ratio of ammonium in clays (fixed nitrogen, N_{fix}) is a much better indicator of the sedimentary environment than the $^{15}N/^{14}N$-ratio of organic nitrogen or total nitrogen. Although the reason for this is only partly understood, the major factors controlling the isotopic composition of fixed nitrogen are the NH_4^+ which is released upon decomposition of organic nitrogen compounds and the very slow exchange between NH_4^+ and K^+ which are fixed in the interlayer position of the clay minerals. Since most of the organic matter is decomposed during early diagenesis (Emerson and Hedges, 1988), the average isotopic composition of the dissolved NH_4^+ will probably be similar to the $\delta^{15}N$ of the organic matter that was originally deposited (i.e. closed system behaviour). Dissolved and adsorbed ammonium, in turn, determine the isotopic composition of the fixed nitrogen through replacement of cations by ammonium in the interlayers of the clay minerals. This replacement is highly selective for large monovalent cations (NH_4^+ and K^+) and occurs at a very slow rate (Bolt et al., 1963; Sawhney, 1972). The most likely explanation for the preservation of the environment signature by fixed nitrogen is that ammonium is built into the interlayers fairly soon after the deposition of the clay minerals. Once the vacant interlayer sites are occupied by NH_4^+ and K^+, they will not readily be replaced by other cations (e.g. Ca^{2+} and Mg^{2+}). Hence, the $\delta^{15}N_{fix}$-value of a sediment is not subject to transient fluctuations and is believed to reflect the isotopic composition of the organic matter that was decomposed during early diagenesis.

The potential of using $^{15}N/^{14}N$-ratios of ammonium in clays as an indicator of the sedimentary environment has been demonstrated for sediments from the Northwest European continent, the North Sea, and the Atlantic Ocean (Scholten et al., 1991). In the present study, this new geochemical tool is applied to Quaternary sediments collected from two boreholes in the southern North Sea. This research is part of a major project in which the geological surveys of several European countries are participating. The aims of this project are to obtain an understanding of the Pleistocene development of the southern North Sea basin and to reconstruct its palaeo-environmental and palaeo-climatic conditions. The Quaternary succession of glacial and interglacial intervals caused changes in the sea level and large scale regressions and transgressions of the shallow sea.

In this paper, the interpretations obtained from $\delta^{15}N_{fix}$-values of clays are compared with the available lithological and palaeontological data. It will be demonstrated that the $\delta^{15}N_{fix}$-values do indeed reflect the changes in the environmental setting of these Quaternary sediments. Therefore $\delta^{15}N_{fix}$ can provide important evidence for the environmental interpretation of *cored* soft sediments where sedimentary structures are not well preserved and there are very few fossils.

SEDIMENTOLOGICAL CHARACTERISTICS

Boreholes BH89/2(A) and BH89/3 were drilled in 1989 at water-depths of about 40 m as part of the research project 'Quaternary Geology of the southern North Sea basin' sponsored by the European Community (Fig. 1). Cores were collected usually every one to five metres with wireline drilling equipment. The cores were occasionally disturbed, and total recovery averages 23%. Several undisturbed clay intervals were subsampled for analysis of the fixed nitrogen isotopic composition. Both boreholes cover a large part of the Quaternary successions in the southern North Sea. The sedimentary sequences of these two boreholes have been reconstructed on the basis of core descriptions and gamma logs. Initially, the palaeo-environmental interpretation was based solely on sedimentological data and on the information obtained from palaeontological analyses. Schematic diagrams of the sedimentary settings of BH89/2(A) and a part of BH89/3 are shown in Figs. 2 and 3.

BH89/2(A)

The Holocene sediments (unit A) were deposited during the last transgression and consist of sandy mud (Fig. 2).

The upper and middle Pleistocene sequences (units B-I) are characterized by alternations of regressive glacial deposits and transgressive shallow marine deposits which correspond to the glacial-interglacial eustatic sea-level changes (Long et al. 1988). The glacial sediments comprise poorly sorted tills (units G and I). All other units were deposited in shallow marine or near-shore environments. The sediments of units G-I include frequently chalk and occasionally abraded shell fragments. Unit E occasionally contains layers of gyttja which were deposited in lacustrine environments.

The early Pleistocene sequence between 109-220 m (units J-N) comprises fluvial, distributary channel, coastal plain, fluvial and prodelta/shallow-marine facies. These sediments are associated with the progradation of the early Pleistocene deltas in the southern North Sea (cf. Laban et al., 1984). The early Pleistocene sediments are generally not calcareous. Layers of clay and silt (unit K) intercalated with sandy sediments are relatively organic-rich. The sediments at the base of this core are characterized by massive clay (unit N) which are gradually overlain by fine sand with clay lamination (unit M) (Sha et al., 1991).

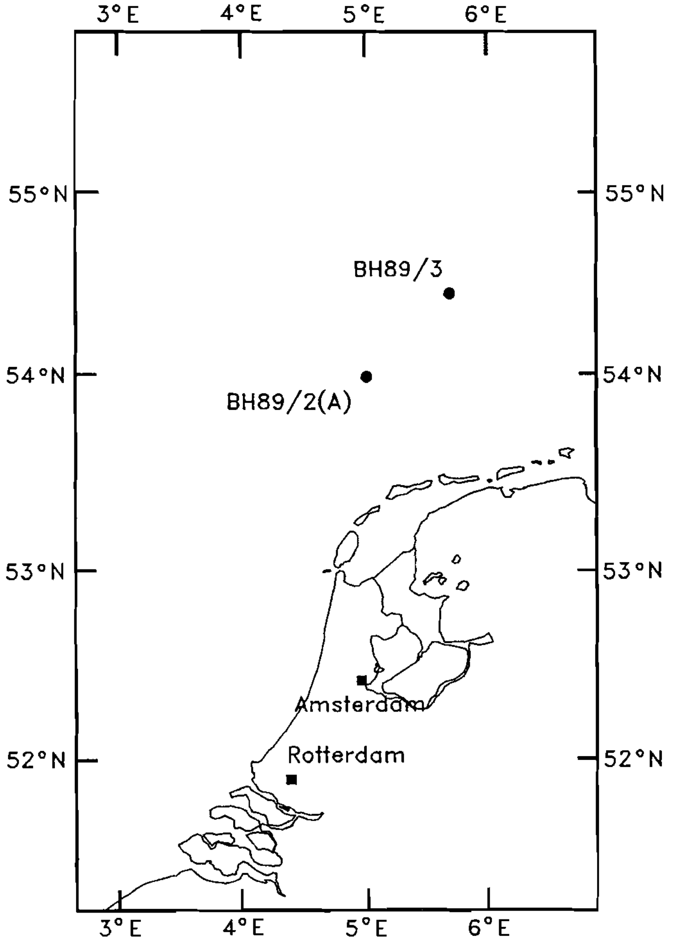


Figure 1. Locations of boreholes BH89/2(A) (54'00.01 N, 5'00.04 E) and BH89/3 (54'26.83 N, 5'47.24 E) in the Southern North Sea, off the Dutch coast line. The water-sediment interface at both locations lies at 40 m below sea-level.

BH89/3

The lower part of this borehole was sampled for δ^{15}N-analyses since sedimentological interpretation indicated that it contains sediments which were deposited in a terrestrial environment (Fig. 3). Sediments in this part of the borehole (114-274 m, units v-z) are not calcareous and are mostly of early Pleistocene age. The whole section between 114-274 m consists of several fining-upward sandy sequences separated by fine-grained sediments with interlaminated clay and sand (Schwarz and Streif, 1991). The lower boundary of the individual sandy sequences always seems to be erosional.

A mottled clay horizon occurs at the base of unit w, indicating possibly subareal exposure. In general, these units were deposited in a fluvial and coastal plain environment (Sha, 1991b). However, further environmental differentiation between these units is impossible on the base of the available sedimentological data. The limited palaeontological data may provide some indication of marine influence at certain intervals which will be discussed below together with the interpretation of the $\delta^{15}N_{fix}$-values.

MINERALOGY AND CHEMISTRY

The mineralogy of a few samples was determined by means of X-ray diffractograms of the $<2\mu$ mineral fraction (Table 1). The major clay mineral in all samples is illite ($(K_{0.7}Al_2(Si,Al)_4O_{10}(OH)_2)$), with minor amounts of smectite (montmorillonite), kaolinite and chlorite. Similar clay compositions in Quaternary sediments in the North Sea have been described by Favejee (1960) and Jørgensen et al. (1982) among others.

The concentrations of fixed nitrogen in the two cores range from <25 ppm in the gyttja layer (unit E) to 345 ppm (Figs. 2b and 3b). In Fig. 2c, fixed nitrogen contents

Table 1. Clay analyses ($<2\mu$ fraction). Interpretation of the X-ray diffractograms has been discussed in Chapter IV. o = <5%, oo = 5-10%, ooo = 10-25%, oooo = 25-50%, ooooo = >50%.

sample	depth (m)	illite	kaolinite	chlorite	montmorillonite
D_2	27.75	ooooo	ooo	oo	oo
I_4	104.95	ooooo	ooo	oo	ooo
K_3	149.65	ooooo	ooo	oo	o
M_1	209.00	ooooo	o	oo	oo
x_2	199.42	ooooo	ooo	oo	oo

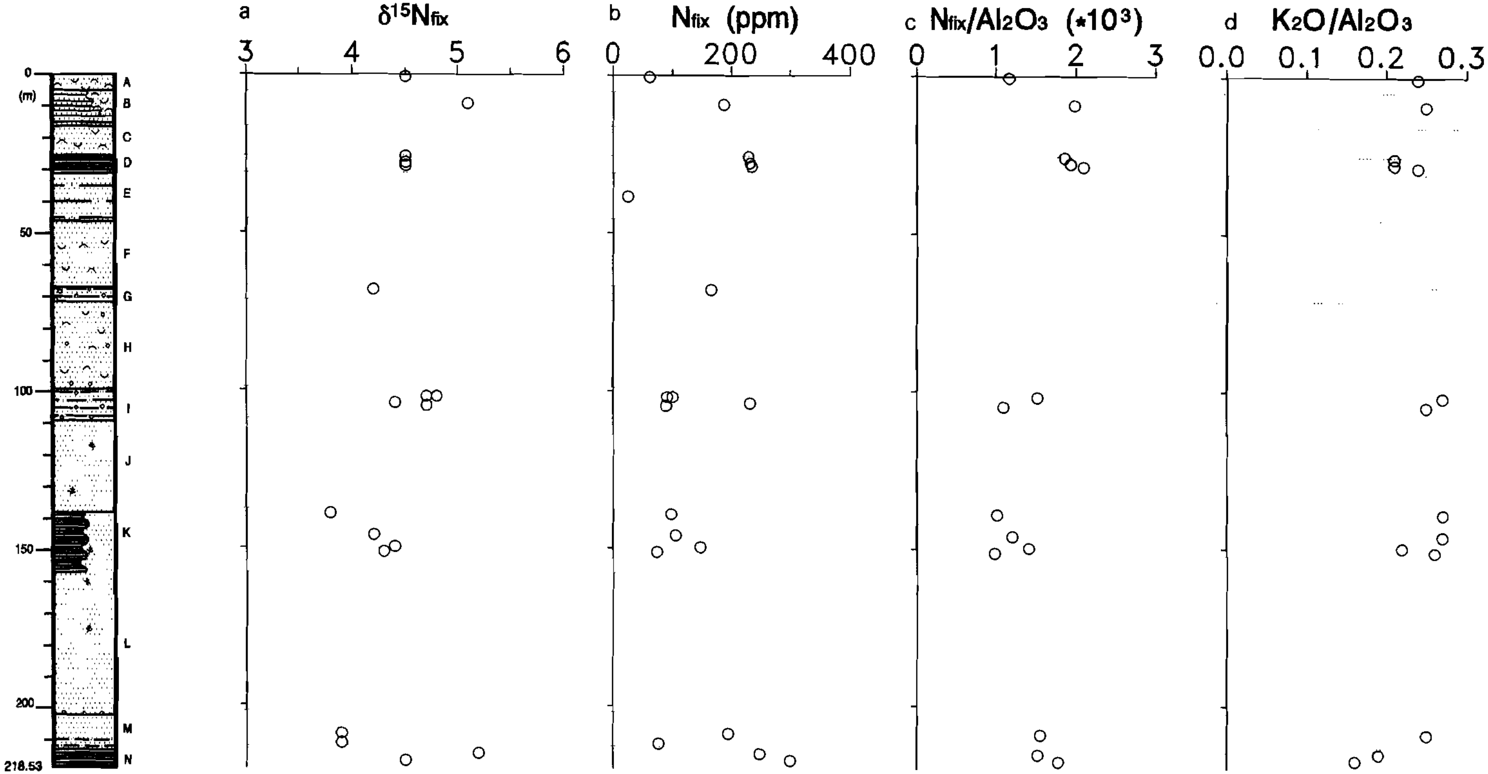


Figure 2. Lithological column of core BH89/2(A). See Fig. 3 for legend. The boundaries of the units are marked by dotted line (a) isotopic composition of fixed nitrogen ($\delta^{15}N_{fix}$ in ‰). (b) fixed nitrogen contents. (c) N_{fix}/Al_2O_3-ratios. (d) K_2O/Al_2O_3-ratios. The content and isotopic composition of fixed nitrogen were determined according to Scholten and Kreulen (1991); Al_2O_3 and K_2O contents were measured at IRI, Delft, by means of instrumental neutron activation analysis (INAA).

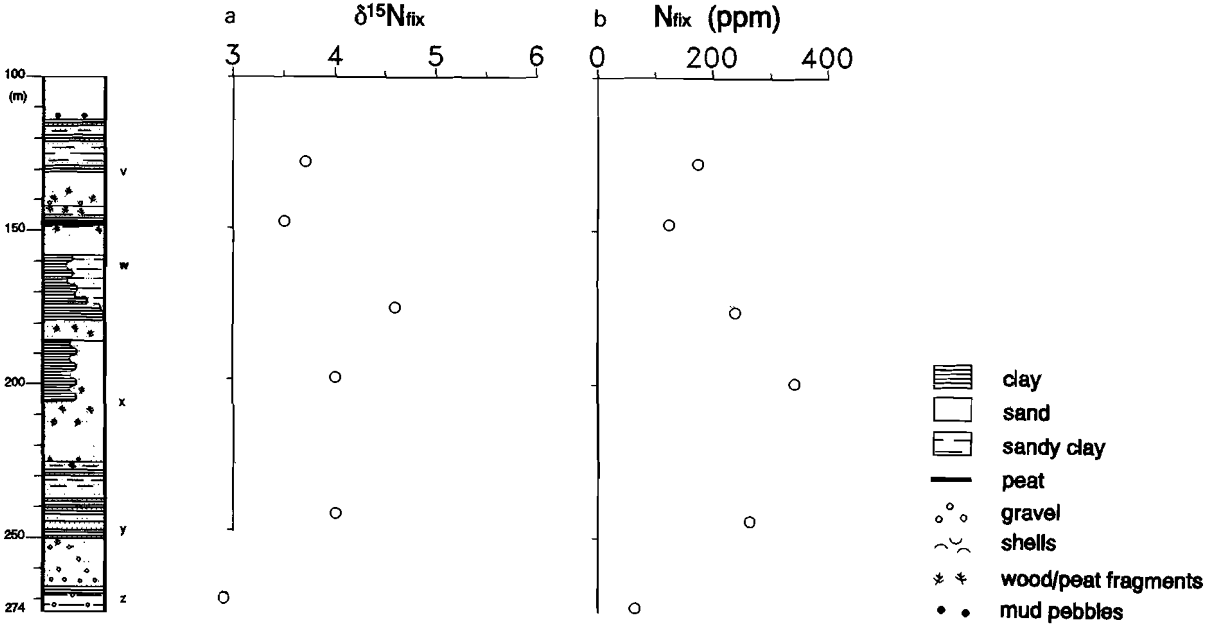


Figure 3. Lithological column of core BH89/3. (a) isotopic composition of fixed nitrogen ($\delta^{15}N_{fix}$ in ‰). (b) fixed nitrogen contents.

are shown relative to Al_2O_3, which is used as a measure of the clay content. The N_{fix}/Al_2O_3-ratios are all between $1 \cdot 10^{-3}$ and $2.3 \cdot 10^{-3}$ (weight ratios). Hence, it can be concluded that the observed large spread in N_{fix}-content of the samples depends mainly on their clay content. Similarly, the K_2O/Al_2O_3-ratios lie within a limited range, namely from 0.19 to 0.31 (weight ratios) (Fig. 2d). Since NH_4^+ and K^+ have almost identical radii, they occupy the same positions in the interlayers of clay minerals, particularly in illite and montmorillonite. Variations in N_{fix} relative to K_2O in the clay minerals probably depend on the availability of ammonium in the porewaters which, in turn, depends on the decomposition rate of organic matter (the redox conditions of the sediment).

ENVIRONMENTAL CONTROL ON THE $^{15}N/^{14}N$-RATIO OF FIXED NITROGEN

The isotopic composition of fixed nitrogen in the sediment cores varies between 2.9 ‰ and 5.2 ‰ (Figs. 2a and 3a). As was shown by Scholten et al. (1991), $\delta^{15}N_{fix}$ increases from terrestrial to marine environment through replacement of monovalent cations in the interlayers of clay minerals, particularly illite. Decomposition of organic nitrogen compounds yields dissolved and adsorbed NH_4^+ with variable $\delta^{15}N$-values, but the slow replacement of fixed ammonium over a long time interval gives an average value for the isotopic composition of the ammonium (Scholten et al., 1991). Thus, upon early diagenesis the environmental signal originally present in the organic nitrogen isotopes is transferred to the fixed nitrogen isotopes.

The $\delta^{15}N_{fix}$-values higher than 4 ‰ (Fig. 2a) indicate that the fine-grained sediments in core BH89/2(A) are predominantly *marine*. The most recent sediment (unit A) was deposited under present day marine conditions and has a $\delta^{15}N_{fix}$-value of 4.5 ‰. Three lagoonal sediment samples (unit D) also have $\delta^{15}N_{fix}$-values of 4.5 ‰. This similarity must reflect similar isotopic compositions of the precursor organic matter in these sediments. The fixed nitrogen isotopic composition in units G and I, deposited during glacial intervals, is $\geq$ 4.2 ‰. These isotope values suggest that the ammonium in clays from the glacial intervals had a predominantly marine origin.

The only samples of core BH89/2(A) in which $\delta^{15}N_{fix}$-values of less than 4 ‰ have been found are from the *deltaic* sediments in units K and M. As expected, the transitions from deltaic to marine environment show an increase in $\delta^{15}N_{fix}$-values, unit N showing fully marine conditions of deposition (4.5 - 5.2 ‰); these results agree well with the sedimentological interpretation of this interval.

In core BH89/3, the low $\delta^{15}N_{fix}$-values of units v and w (3.7 ‰ and 3.5 ‰ respectively) show that these sediments were deposited under *terrestrial* conditions. This environmental interpretation is in accordance with the absence of marine fossils and the occurrence of a peat layer at 148 m (Fig. 3). Increasing marine influence causes a temporal shift of $\delta^{15}N_{fix}$ to 4.5 ‰ in the interlaminated clays and silts of unit x. The $\delta^{15}N_{fix}$-values of units x and y (4.0 ‰) are in between terrestrial and marine conditions. Indeed minor amounts of both fresh water and especially marine diatoms were found in unit x (pers. com. H. de Wolf), and sediments of unit y contain relatively abundant dinoflagellate cysts (pers. com. J. de Jong). Clays in unit z have a characteristic low isotopic composition of fixed nitrogen (2.9 ‰), indicating a fluvial environment.

DISCUSSION

The interpretation of the environment of deposition based on the nitrogen isotopic composition of clays is generally consistent with sedimentological and palaeontological evidence. The variations in $\delta^{15}N_{fix}$-values reflect major changes in environmental conditions during the Quaternary, and point to a complex sedimentary history. Some types of sediments, in particular, the glacial deposits, and the lagoonal and deltaic deposits need further discussion.

Glacial deposits

The $\delta^{15}N_{fix}$-values of the glacial deposits (BH89/2(A), units G and I) suggest marine rather than terrestrial conditions and are similar to those of the adjoining inter-glacial units. Possible explications for this similarity in $\delta^{15}N_{fix}$-values are:

(a) Different nitrogen isotopic composition of terrestrial organic matter. Variations in $\delta^{15}N$-values of organic matter depend on changes in the isotopic composition of the nutrients which are consumed by the plants. The main nitrogen source of land plants is the atmosphere. Molecular nitrogen is converted to organic nitrogen compounds by bacteria living symbiotically in plants such as legumes and lichens (Berner and Berner, 1987). Little isotope fractionation occurs during this process of biological fixation of nitrogen by plants (Sweeney et al., 1978), and this is reflected by the near-atmospheric isotopic composition of terrestrial organic nitrogen. Stuermer et al. (1978), for instance, reported isotopic compositions of organic nitrogen of 1 ‰ in saline lacustrine environments, which are the result of the uptake of atmospheric nitrogen by the abundantly present blue-green algae. Since the atmosphere is a very large nitrogen reservoir, it is unlikely that the isotopic composition of atmospheric nitrogen changed significantly during the Quaternary. Therefore, we do not believe that the high $\delta^{15}N_{fix}$-values of the glacial sediments result from changes in the isotopic composition of terrestrial organic nitrogen.

(b) It is more likely that the fixed ammonium present in the clays of the glacial sediments was derived from decomposing *marine* organic matter. The glacial sediments (Core BH89/2(A) units G and I) were deposited as a till and consist of gravelly and sandy clay and are erosionally overlain by marine sediments. The clay in the tills was probably derived from the reworked marine deposits. It is also possible that the till was deposited at the tide-water glacial front that was intermittently under marine influence. We suggest that the glacial clays do indeed reflect the isotopic composition of marine organic matter.

Lagoonal and deltaic deposits

Lagoons and deltas are deposited in the transition zones between terrestrial and marine environments, and they are expected to have $\delta^{15}N_{fix}$-values that lie somewhere between the terrestrial and marine endmembers. This will only be true if the isotopic compositions of fixed nitrogen in these intermediate environments is determined by mixing of the two components. This, however, is not always the case; *in situ* formed organic matter may predominate and determine the ultimate $\delta^{15}N_{fix}$-values of the sediments (Owens, 1985). Particularly in restricted environments such as lagoons, the specific biota that live under the prevailing conditions may have deviating isotopic compositions which will subsequently be reflected by the $\delta^{15}N_{fix}$ of the sediment. Owens (1985) reported $\delta^{15}N$-values of up to 14.7 ‰ for particulate material in an estuarine environment and concludes that this high isotope value is caused by microbial mineralization of organic nitrogen, which in turn leads to isotope enrichment of the refractory nitrogen. Similarly, Mariotti et al. (1984) and Cifuentes et al. (1989), among others, report large variations in $\delta^{15}N$ of dissolved inorganic nitrogen compounds (NH_4^+ and NO_3^-) in estuarine environments as a result of seasonal variations in bioproductivity (e.g. blooming and reservoir effects).

In spite of such reported deviations from "normal" isotopic compositions of organic nitrogen, the isotope values of the deltaic sediments in core BH89/2(A) are between the terrestrial and marine isotope endmembers, and the lagoonal sediments of unit D show normal marine $\delta^{15}N_{fix}$-values. Factors such as seasonal variations and transient specific microbial activity were probably levelled out before fixed nitrogen was incorporated into the clays.

The diversity in sedimentary conditions during the Pleistocene in the shallow southern North Sea complicates the correlation of the units in the two cores. Large lateral variations may occur on the scale of a few kilometres. The $\delta^{15}N_{fix}$-values can only be used to correlate contemporary sediments if their environments of deposition were similar. In both cores the $\delta^{15}N_{fix}$-profile with depth indicates that alternating marine and terrestrial conditions predominated in these sediments. In general, the sediments of core BH89/3 have lower $\delta^{15}N_{fix}$-values than the sediments of core BH89/2(A). This is consistent with the fact that the early Pleistocene delta prograded westward. Detailed research on the lithostratigraphical correlation between the units of the cores is in progress (Sha, 1991a). We know that unit K (core BH89/2(A)) and unit v (core BH89/3) possibly belong to the same depositional cycle, and the isotope values in these units show that they were both deposited in deltaic environments.

CONCLUSIONS

It has been demonstrated that the isotopic composition of fixed nitrogen is a good tool for obtaining information on the environment of deposition of sediments. The $\delta^{15}N_{fix}$-values are significantly lower in terrestrial sediments than in marine sediments, whereas intermediate isotopic compositions are found in sediments from transitional (deltaic) environments. If NH_4^+ originating from other sedimentary sequences is introduced into the sediment through processes such as reworking of the sediment or diffusion, this may eventually alter the environmental signal of the fixed nitrogen isotopes. However, the slow rates at which fixed nitrogen is exchanged make changes induced by "contamination" rare, and in general the isotopic composition of ammonium in clays is a reliable indicator for the sedimentary environment. A combination of $\delta^{15}N_{fix}$-values and sedimentary and palaeontological markers can considerably improve the interpretation of the environmental settings of cored sediments.

Acknowledgements

We thank the director and the Department of Marine Geology of the Dutch Geological Survey (RGD) for kindly permitting us to use the core samples (BH89/2A). We thank

C. Schwarz of the Niedersächsisches Landesamt für Bodenforschung (Germany) for providing the samples of core BH89/3. G. Frapporti and B. van Os are thanked for assistance with the computer and S.M. McNab for linguistic advice. R.D. Schuiling, E.C. Kosters, H.G.M. Eggenkamp and J.J. Middelburg made many helpful comments which improved the manuscript. This research is part of the southern North Sea Quaternary Geology Project and is sponsered by the Commision of the European Communities Science Programme (contract no. SCI* 0128-C EDB). The mass spectrometer was partly financed by the Netherlands Organization for the Advancement of Pure Research (NWO).

References

Berner E.K. and Berner R.A. (1987) The global water cycle. Prentice-Hall, New Jersey. pp. 397.

Bolt G.H., Sumyner M.E. and Kamphorst A. (1963) A study of the equilibria between three categories of potassium in an illitic soil. *Soil Sci. Soc. Am. Proc.* **27**, 294-299.

Cifuentes L.A., Fogel M.A., Pennock J.R. and Sharp, J.H. (1989) Biogeochemical factors that influence the stable nitrogen isotope ratio of dissolved ammonium in the Delaware Estuary. *Geochim. Cosmochim. Acta* **53**, 2713-2721.

Emerson S. and Hedges J.I. (1988) Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* **3**, 621-634.

Favejee J.CH.L. (1960) On the origin of the mud deposits in the Ems-estuary. *Verh. Kon. Geol. Mijnbouwk. Gen.* **19**, 147-151.

Jørgensen P., Erlenkeuser H., Lange H., Nagy J., Rumohr J. and Werner F. (1981) Sedimentological and stratigraphical studies of two cores from the Skagerrak. *Spec. Publs. int. Ass. Sediment.* **5**, 397-414.

Laban C., Cameron T.D.J. and Schüttenhelm R.T.E. (1984) Geologie van het Kwartair in de zuidelijke Bocht van de Noordzee. *Meded. Wrkgr. Tert. Kwart. Geol.* **21**, 139-154.

Long D., Laban C., Streif H., Cameron T.D.J. and Schüttenhelm R.T.E., (1988) The sedimentary record of climatic variation in the southern North Sea. *Phil. Trans. R. Soc. Lond.* **B 318**, 523-537.

Mariotti A., Lancelot C. and Billen G. (1984) Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. *Geochim. Cosmochim. Acta* **48**, 549-555.

Owens N.J.P. (1985) Variations in the natural abundance of ^{15}N in estuarine suspended particulate matter: A specific indicator of biological processing. *Estuar. Coastal Shelf Sc.* **20**, 505-510.

Owens N.J.P. and Law C.S. (1989) Natural variations in ^{15}N content of riverine and estuarine sediments. *Estuar. Coast. Shelf Sci.* **28**, 407-416.

Peters K.E., Sweeney R.E. and Kaplan I.R. (1978) Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr.* **23**, 598-604.

Sawhney B.L. (1972) Selective sorption and fixation of cations by clay minerals: a review. *Clays Clay Miner.* **20**, 93-100.

Scholten S.O. and Kreulen R. (1991) Early diagenetic changes in nitrogen and carbon isotopes in marine sediments. *Geochim. Cosmochim. Acta*, submitted.

Scholten S.O., Ebbing J.H.J. and Kreulen R. (1991) $^{15}N/^{14}N$-ratios in clays as a sensitive indicator of sedimentary environment. *Geochim. Cosmochim. Acta*, submitted.

Schwarz C. and Streif H. (1991) Sedimentological results and their interpretation from Boreholes 89/3, 89/4 and 89/9, German North Sea Sector. In *Quaternary sedimentary sequences in the southern North Sea Basin.* (ed. L.P. Sha) Report of the Commission of the European Communities (SCI* 0128-C EDB), 44-74.

Sha L.P. (1991a) Correlation of depositional cycles (in the Quaternary sediments of the southern North Sea). In *Quaternary sedimentary sequences in the southern North Sea Basin.* (ed. L.P. Sha) Report of the Commission of the European Communities (SCI* 0128-C EDB), 97-103.

Sha L.P. (1991b) Depositional system and paleogeography (during the Quaternary in the southern North Sea). In *Quaternary sedimentary sequences in the southern North Sea Basin.* (ed. L.P. Sha) Report of the Commission of the European Communities (SCI* 0128-C EDB), 106-108.

Sha L.P., Laban C. and Schüttenhelm R.T.E. (1991) Depositional sequences of Quaternary deposits in Borehole 89/2(A), Dutch North Sea Sector. In *Quaternary sedimentary sequences in the southern North Sea Basin.* (ed. L.P. Sha) Report of the Commission of the European Communities (SCI* 0128-C EDB), 3-22.

Stuermer D.H., Peters K.E. and Kaplan I.R. (1978) Source indicators of humic substances and protokerogen: stable isotope ratios, elemental compositions and electron-spin resonance spectra. *Geochim. Cosmochim. Acta* **42**, 989-997.

Sweeney R.E., Liu K.K. and Kaplan I.R. (1978) Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In *Stable isotopes in earth sciences.* (ed. B.W. Robinson) *D.S.I.R. Bull.* **220**, 9-26.

Sweeney R.E. and Kaplan I.R. (1980) Natural abundances of 15N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chemistry* **9**, 81-94.

Zöllmer V. (1991) Clay mineral composition of Quaternary sediments in the southern North Sea. In *Quaternary sedimentary sequences in the southern North Sea Basin.* (ed. L.P. Sha) Report of the Commission of the European Communities (SCI* 0128-C EDB), 78-92.

CHAPTER VI

VARIATIONS IN $^{15}N/^{14}N$ AND $^{13}C/^{12}C$-RATIOS DURING MATURATION OF KEROGEN-RICH SHALES AND RELATED OILS

S.O. Scholten, J.A.N. Meesterburrie and R. Kreulen
Department of Geochemistry, Institute of Earth Sciences,
University of Utrecht, P.O. Box 80021, 3508 TA Utrecht

ABSTRACT

Concentrations and isotope ratios of nitrogen and carbon were determined in samples from the Posidonien Schiefer, the Kimmeridge shales and corresponding North Sea oils. Both organic nitrogen and ammonium in clays were determined in order to obtain more information about the behaviour of nitrogen during the maturation of shales. The following general systematics have been found:

(1) *Organic nitrogen and carbon* contents decrease with maturation of the shales. The organic nitrogen isotope ratios are fairly constant in the Posidonien Schiefer, except in shales from the advanced maturation stage when most organic matter has been lost. The organic carbon isotope ratios of the shales increase gradually with maturation. The Kimmeridge shales, on the other hand, show variations in $^{13}C/^{12}C$- and $^{15}N/^{14}N$-ratios of organic matter for all degrees of maturation. This must be due to the lateral inhomogeneity of these shales which show both marine and terrestrial signatures.

(2) *Ammonium in clays.* At early maturation stages (Rm $\leq 0.6\%$) the isotopic composition of ammonium in clay minerals from both the Posidonien Schiefer and the Kimmeridge shales shows large variations. However, during maturation the $^{15}N/^{14}N$-ratios in the clays increase to values that lie close to those of the organic matter. It is assumed that the ammonium in the clays is derived from thermally degraded organic matter and that in particular the transition of smectite to illite (I/S) enhances the incorporation of NH_4^+. Most likely, the NH_4^+ derived from decomposing organic matter (oil formation) has a fairly constant nitrogen isotopic composition. This is consistent with the homogeneous nitrogen isotopic composition of the North Sea oils.

(3) The *total nitrogen* contents vary independently of the degree of maturation. This is probably due to variations in the original sediments and to the contradictory effects of increasing ammonium in clays and decreasing organic nitrogen content during maturation.

In conclusion, the ammonium content of clay minerals can be used to determine the degree of maturation of a shale, whereas the isotopic composition of ammonium in clays gives information about the original organic matter that has been degraded.

INTRODUCTION

The Posidonien Schiefer and in particular the Kimmeridge shales are the major source rocks for oil in northwest Europe. The oil-generating potential of shales depends largely on the initial content and composition of the organic matter (e.g. Tissot and Welte, 1984 and refs. therein) and on the changes that occur after deposition of the sediment. Nitrogen is an important element in living organic matter (Delwiche, 1970) and its contribution to biological processes has been the subject of numerous studies. Much less is known, however, about the fate of sedimentary nitrogen upon diagenesis. In the present study we consider the behaviour of nitrogen during the maturation of sediments. Since nitrogen occurs in organic compounds as well as in clays, we separated these nitrogen fractions and studied them both.

Shortly after sedimentation, the composition of the organic matter is altered substantially. Organic carbon and organic nitrogen contents in sediments generally decrease with increasing depth of burial. Only a small fraction of the initially precipitated organic matter is preserved for burial into the sediment, the remainder is recycled. Waples and Sloan (1980) conclude that the gradual loss of organic carbon and nitrogen in deep-sea sediments results from early-diagenetic transformations and that microbial activity is a major factor in this process. They found a significant decrease in the C/N-ratio, namely from 10 in the uppermost sediments to 5 at a burial depth of about 200 metres, which is an indication for selective decomposition of the organic compounds. Müller (1977) suggests that this decrease in C/N-ratio during early diagenesis is related to sorption on clay minerals, which protects organic nitrogen compounds against bacterial attack. During maturation of protokerogen, when the organic matter is buried below the depth of oxygen penetration, and microbial activity has slowed down, C/N-ratios increase again (Waples, 1977; Peters et al., 1981). The C/N-ratio in kerogen also depends on its precursor organic matter. Especially in organic matter of terrestrial origin, the C/N-ratio can be very high, i.e. 30 or more. Marine and waxy (terrestrial) organic matter have much lower C/N-ratios, usually between 8 and 15 (e.g. Meybeck, 1982; Boudou et al., 1984; Rashid, 1985 and refs. therein).

During maturation of kerogen, the carbon and nitrogen contents are subject to changes as a result of physical and chemical processes. The isotopic composition of oils, however, is generally correlated with their source kerogen (Stahl, 1977), and the overall isotopic composition of the kerogen does not alter significantly during the process of maturation (Macko and Quick, 1986). The δ^{13}C-values of oils and kerogens usually range between -31 ‰ and -25 ‰ (e.g. Stahl, 1977; Macko and Quick, 1986) and the δ^{15}N-values range between +1 ‰ and +17 ‰ (e.g. Drechsler and Stiehl, 1977; Hirner et al., 1984; Macko and Quick, 1986; this study).

Nitrogen in sediments is mainly present in the organic matter (kerogen), but can also be incorporated in minerals (in particular illite and montmorillonite) as fixed NH_4^+ or, in minor amounts, be adsorbed as NH_4^+ by clay-minerals. In this study we describe the changes in content and isotopic composition that occur both in the organic and in the fixed nitrogen (clay) fractions, during the maturation of two north-west European shales: the Kimmeridge shales and the Posidonien Schiefer. In addition, the results of isotope measurements on samples of North Sea oils (originating from the Kimmeridge shales) are discussed. This study addresses the following questions:

- Do nitrogen isotopes fractionate during thermal breakdown of organic matter?
- Can the nitrogen isotopic composition be used for oil-source rock correlation?
- Can nitrogen fixed in clay minerals be used as an indicator of the degree of maturation?
- Is the δ^{15}N-value of ammonium in clays related to the organic nitrogen?

GEOLOGICAL SETTINGS

During the Jurassic, shaly carbonates with finely laminated, organic-rich interlayers were deposited in NW Europe. The wide areal distribution of these organic-rich shales made them an important source rock for oil.

The **Posidonien Schiefer** in Germany are of Lower Jurassic (Lower Toarcian) age. These organic-rich shales were deposited in anoxic bottom waters of a shallow transgressive marine basin (e.g. Demaison and Moore, 1980; Jenkyns and Clayton, 1986; Hallam, 1987; Robert, 1988). Stratigraphic equivalents of the Posidonien Schiefer, often with equal source rock potentials, can also be found elsewhere in Europe under different names, e.g. in France (Schistes Carton) and in England (Jet Rock) (Hallam, 1987 and refs. therein).

Tectonic uplift during the Late Cretaceous in the north-west of Germany resulted in the formation of the *Bramsche Massif*, and was accompanied by magma intrusion

Table 1. Posidonien Schiefer: Concentrations and isotope ratios of organic carbon and the nitrogen fractions. wt%K_2O and wt%Al_2O_3 determined by ICP-OES.

sample	Rm %	N_{tot} wt%	$\delta^{15}N_{tot}$ ‰	N_{fix} wt%	$\delta^{15}N_{fix}$ ‰	N_{org} wt%	$\delta^{15}N_{org}$ ‰	C_{org} wt%	$\delta^{13}C_{org}$ ‰	C_{org}/N_{org}	Al_2O_3 wt%	K_2O wt%	K_2O/Al_2O_3	N_{fix}/Al_2O_3 $*10^3$
P2	≤0.6	0.307	2.5	0.022	-0.2	0.285	2.7	10.89	-29.1	44.6	9.05	0.88	0.10	2.4
P3	≥0.9	0.176	0.8	0.072	1.7	0.104	0.2	6.01	-27.3	67.4	20.36	2.73	0.13	3.5
P4	0.6<Rm<0.9	0.307	2.6	0.074	1.4	0.233	3.0	9.54	-28.9	47.8	12.18	1.83	0.15	6.1
P6	≤0.6	0.173	3.0	0.015	2.3	0.158	3.1	8.37	-29.2	61.8	4.71	1.37	0.29	3.2
P7	≤0.6	0.247	2.4	0.033	0.3	0.214	2.7	8.46	-29.4	46.1	12.10	1.26	0.10	2.7
P8	0.6<Rm<0.9	0.239	3.2	0.064	2.8	0.175	3.3	5.41	-28.6	36.1	10.60	1.51	0.14	6.0
P9	≤0.6	0.339	2.7	0.045	-0.6	0.294	3.2	10.77	-29.9	42.7	16.15	2.18	0.13	2.8
P10	≤0.6	0.470	2.9	0.042	0.7	0.428	3.1	16.2	-29.3	44.2	15.78	2.62	0.17	2.7
P11	≤0.6	0.265	3.0	0.032	1.5	0.233	3.2	9.2	-29.4	46.1	10.63	2.06	0.19	3.0
P13	≥0.9	0.252	4.0	0.128	3.1	0.124	4.9	6.52	-28.6	61.3	12.71	1.71	0.13	10.1
P14	0.6<Rm<0.9	0.232	3.0	0.050	2.7	0.182	3.1	7.31	-29.2	46.9	13.69	1.97	0.14	3.7

Table 2. Kimmeridge shales: Concentrations and isotope ratios of organic carbon and the nitrogen fractions. wt%K_2O and wt%Al_2O_3 determined by ICP-OES.

sample	Rm %	N_{tot} wt%	$\delta^{15}N_{tot}$ $^{o}/_{oo}$	N_{fix} wt%	$\delta^{15}N_{fix}$ $^{o}/_{oo}$	N_{org} wt%	$\delta^{15}N_{org}$ $^{o}/_{oo}$	C_{org} wt%	$\delta^{13}C_{org}$ $^{o}/_{oo}$	C_{org}/N_{org}	Al_2O_3 wt%	K_2O wt%	K_2O/Al_2O_3	N_{fix}/Al_2O_3 $*10^3$
K1	≤ 0.6	0.274	0.5	0.016	-1.0	0.258	0.6	8.2	-26.5	37.1	12.44	1.42	0.11	1.3
K2	$0.6 < Rm < 0.9$	0.150	1.4	0.026	0.5	0.123	1.6	5.2	-26.5	49.2	11.43	2.92	0.26	2.3
K3	$0.6 < Rm < 0.9$	0.233	2.1	0.063	-0.2	0.170	3.0	7.7	-27.9	52.8	13.97	3.09	0.22	4.5
K4	≥ 0.9	0.268	2.4	0.100	1.2	0.168	3.1	6.6	-29.1	45.8	15.08	2.68	0.18	6.6
K5	≥ 0.9	0.421	0.2	0.126	-0.2	0.295	0.4	7.6	-26.7	30.1	11.72	2.10	0.18	10.8
S2	≤ 0.6	0.503	1.1	0.034	-4.2	0.469	1.5	13.0	-25.3	32.4	15.33	2.32	0.15	2.3
S3	$0.6 < Rm < 0.9$	0.220	1.6	0.045	-1.5	0.174	2.4	5.9	-28.6	39.5	10.54	2.54	0.24	4.3
S4	≥ 0.9	0.402	1.8	0.129	-0.4	0.273	2.8	8.4	-26.2	35.9	11.66	2.13	0.18	11.1

which locally caused strong thermal alteration of the sedimentary sequences (Bartenstein et al., 1971; Stadler and Teichmüller, 1971; Teichmüller et al., 1979; Robert, 1988). Different degrees of maturation of the Posidonien Schiefer can therefore be found within a small area. We studied 11 samples from this geological setting (Table 1). Samples were selected from each major stage of oil formation: immature shales ($Rm \leq 0.6\%$) which expelled mainly light hydrocarbons, mature oil-generating shales ($0.6\% < Rm < 0.9\%$) and advanced mature shales ($Rm \geq 0.9\%$).

The Upper Jurassic **Kimmeridge shales** are the major source rocks of North Sea oils (e.g. Oudin, 1976; Barnard and Cooper, 1981; Cornford et al., 1983; Brooks et al., 1987; Peters et al., 1989). They consist of organic-rich laminated shales which were generally deposited under low energetic marine conditions with high algae productivity (Gallois, 1976; Tyson et al., 1979). The presence of waxy sapropelic components, in particular along the margins of the North Sea grabens, and the presence of high wax crudes in the Dutch onshore fields, are indications of a major contribution from land-derived organic matter (Barnard and Cooper, 1981; Bodenhausen and Ott, 1981). Kimmeridge shales with different degrees of maturation were studied (Table 2).

Also included in this study are nitrogen and carbon isotope analyses of **North Sea oils**. The selected oil samples are known to be derived from the Kimmeridge shales and to have been trapped in the adjoining reservoir rocks. The oils correspond to different stages of maturation; this is reflected by their API-gravity and sulphur content (Table 3).

Table 3. Carbon and nitrogen isotope ratios of samples from North Sea oils. Gravities (API) and sulphur contents of the oils are also indicated.

sample	API	S	$\delta^{13}C$	$\delta^{15}N$
		wt%	‰	‰
2181	31.9	0.7	-29.1	2.1
2407	36.8	0.1	-29.0	2.0
2713	36.3	0.8	-28.9	1.4
2724	39.0	1.0	-28.5	1.6
2729	39.0	0.4	-28.6	1.5
2760	34.6	0.8	-28.9	1.5
2985	36.8	0.7	-29.0	0.9
3056	45.6	0.0	-29.0	1.8
3078	26.3	1.2	-29.1	1.2

ANALYTICAL PROCEDURES

The analytical procedures used for extracting nitrogen from the samples have been discussed extensively by Scholten and Kreulen (1991). An outline of the methods is presented here. All fractions were measured at least in duplicate to ensure the reliability of the presented results.

The *total nitrogen* content is determined by pyrolysis (1250°C) and subsequent combustion (CuO, 900°C) of circa 0.1 g of oil or powdered shale sample in a sealed evacuated quartz tube. The released gases are treated with Ag-wool (450°C) to convert nitrogen oxides to N_2 and with CuO (900°C) to oxidize any possible carbon monoxide. After cryogenic separation of the nitrogen gas, the yield is measured manometrically and the isotopic composition is measured. Precision of $wt\%N_{tot}$ is better than 5% (95% confidence level) and the standard deviation of the $\delta^{15}N_{tot}$-value is less than 0.2 ‰.

Fixed nitrogen: The sample is pretreated with 2N KCl to remove adsorbed (exchangeable) nitrogen and with KOBr/KOH-solution to remove organic compounds. Subsequently, the residue is reacted with 5N HCl/1N HF-solution to break down the mineral lattices and release fixed NH_4^+. The solution is distilled and ammonium is trapped in 0.025N H_2SO_4. Hereafter, the ammonium sulphate is oxidized with LiOBr/LiOH-solution to release N_2-gas. Precision of the $wt\%N_{fix}$ is better than 2% and the standard deviation of the $\delta^{15}N_{fix}$-values is better than 0.1 ‰.

Organic nitrogen contents are calculated by subtraction of fixed nitrogen from total nitrogen:

$$X_{org} = X_{tot} - X_{fix} \qquad (1)$$

where X is the concentration of nitrogen. Exchangeable nitrogen is omitted from the calculation since its contribution to total nitrogen is too small to play a significant role; exchangeable nitrogen contents relative to total nitrogen contents of three Kimmeridge shale samples with different degrees of maturation (Rm = 0.60%, 0.72% and 1.00%) were 0.95%, 2.2% and 1.5% respectively.

Organic nitrogen isotope ratios are calculated by combining mass balance (formula 1) with isotope balance:

$$\delta^{15}N_{org} = \frac{X_{tot} \cdot \delta^{15}N_{tot} - X_{fix} \cdot \delta^{15}N_{fix}}{X_{org}} \qquad (2)$$

Precision of the calculated organic nitrogen content is better than 6% and the standard deviation of $\delta^{15}N_{org}$ is less than 0.3 ‰.

Before the determination of *organic carbon* the sample is treated with 6N HCl (Jasper and Gagosian, 1990) to remove carbonates. Hereafter, the dried residue is combusted (0.2 atm O_2, CuO, 900°C) in a closed circulation system and the released CO_2-gas is cryogenically separated from the other gases; CO_2 yield is determined manometrically. Precision of the yield measurements is better than 5% and standard deviation of the $\delta^{13}C$-values is less than 0.1 ‰.

Elemental analyses were made by ICP-OES after treating the samples with a lithium borate-flux. The quality of the analyses was checked regularly by analysing standard rock samples. The data on mean vitrinite reflectance equivalent (Rm), sulphur content and API gravities were obtained from Koninklijke/Shell Laboratories (KSEPL).

RESULTS

The **organic nitrogen and carbon** contents of the Posidonien Schiefer are quite variable: 0.10 wt% < N_{org} < 0.43 wt% and 5.4 wt% < C_{org} < 11 wt% (Table 1). A good correlation can be observed between organic nitrogen and carbon contents (r = 0.95,

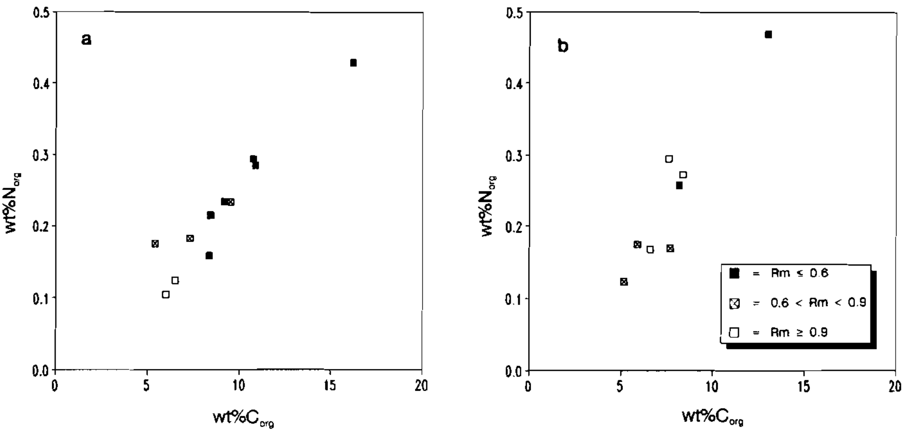


Figure 1. Relation between organic carbon content (wt%C_{org}) and organic nitrogen content (wt%N_{org}) at different degrees of maturation in (a) the Posidonien Schiefer (r = 0.95, n = 11) and (b) the Kimmeridge shales (r = 0.94, n = 8).

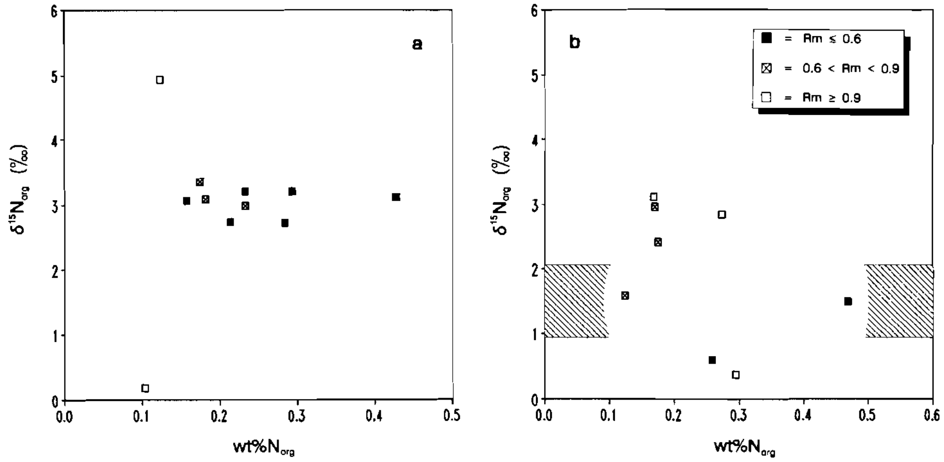


Figure 2. Plot of the isotopic composition of organic nitrogen ($\delta^{15}N_{org}$) versus the content (wt%N_{org}) in: (a) the Posidonien Schiefer. Note that the $\delta^{15}N_{org}$-values are not consistent any more in the samples with Rm ≥ 0.9%. (b) the Kimmeridge shales. The shaded area indicates the range of δ^{15}N-values of the North Sea oils (1.6 ±0.4‰, n = 9).

n = 11) and both constituents decrease proportionally with increasing maturation (Fig. 1). The organic nitrogen and carbon contents of samples from the Kimmeridge shales are also closely correlated (r = 0.94, n = 8).

In the Posidonien Schiefer samples with Rm < 0.9% the isotopic composition of organic nitrogen is remarkably constant: 2.7 ‰ $\leq \delta^{15}N_{org} \leq$ 3.3 ‰ (Fig. 2a). The $\delta^{13}C_{org}$-values of the Posidonien Schiefer increase with decreasing carbon content and range from -29.9 ‰ in an immature shale sample to -27.3 ‰ in a shale of advanced maturity (cf. Table 1 and Fig. 3a). The Kimmeridge shales have isotopic compositions of organic nitrogen and carbon that are not related to the degree of maturation. The $\delta^{15}N_{org}$-values lie between 0.6 ‰ and 3.1 ‰ (Fig. 2b). The immature shale samples (Rm ≤ 0.6%) seem to have slightly lower $\delta^{15}N_{org}$-values (1.1 ± 0.6 ‰) than the samples with higher maturity. Similar variations, but not related to the degree of maturation, are found for the isotopic composition of organic carbon: the δ^{13}C-values range from -25.3 ‰ to -29.1 ‰ (Fig. 3b).

There is a clear relationship between increasing degree of diagenesis and increasing **fixed nitrogen** content of the Posidonien Schiefer. In Fig. 4a, N_{fix}/Al_2O_3 is plotted versus K_2O/Al_2O_3. Aluminium reflects the clay content and the K_2O/Al_2O_3-ratio

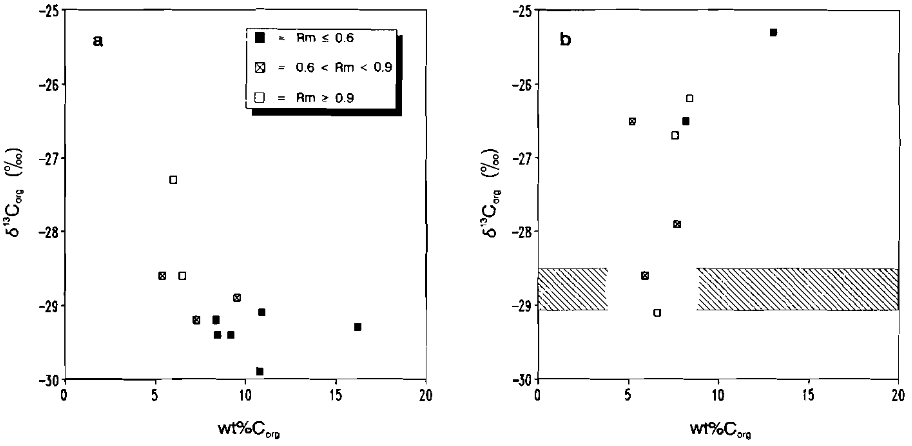


Figure 3. Plot of the isotopic composition of organic carbon ($\delta^{13}C_{org}$) versus the content (wt%C_{org}). Contrary to the Posidonien Schiefer (a), there is no relationship of $\delta^{13}C_{org}$ with the degree of maturation in the Kimmeridge shales (b). The shaded area indicates the range of δ^{13}C-values of the North Sea oils (-28.9 ±0.2‰, n = 9).

therefore reflects the proportion of potassium-bearing clays, in particular illite and smectite (Müller, 1977), although the presence of other potassium and aluminum minerals may interfere with this simple approach. The N_{fix}/Al_2O_3-ratios are remarkably constant (average $2.8 \cdot 10^{-3}$ weight ratios) during the early stage of maturation ($Rm \leq 0.6\%$). However, with $Rm > 0.6\%$, an increase in the N_{fix}/Al_2O_3-ratio is found (up to $1.0 \cdot 10^{-2}$). The Kimmeridge shales show a similar clear relationship between the fixed nitrogen content of clays and the degree of maturation (Fig. 4b).

In Fig. 5, the isotopic composition of fixed nitrogen is plotted as a function of the fixed nitrogen content of clays (N_{fix}/Al_2O_3). The $\delta^{15}N_{fix}$-values of the immature Posidonien Schiefer samples vary considerably (average 0.7 ±1.1‰, n = 6). During maturation, both the fixed nitrogen content and the isotopic composition increase (average 2.3 ±0.7‰, n = 5). A similar relation between $\delta^{15}N_{fix}$-values and maturity can be found in the Kimmeridge shales; the two samples representing the initial stages of maturation have considerably deviating $\delta^{15}N_{fix}$-values (-1.0 ‰ and -4.2 ‰) compared to the advanced mature shales (0.2 ±0.9‰).

The opposite behaviour of fixed nitrogen and organic nitrogen upon maturation explains why the content and isotopic composition of **total nitrogen** are not related to

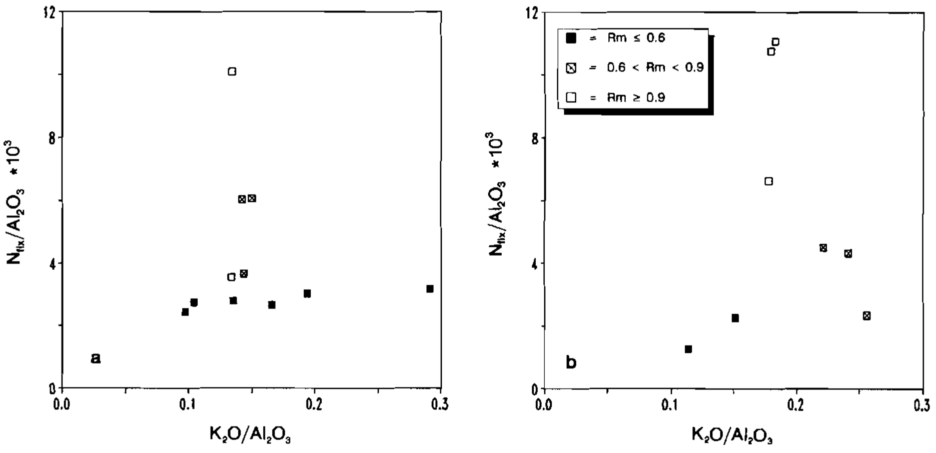


Figure 4. Plot of the N_{fix}/Al_2O_3-ratio (wt%/wt%) versus the K_2O/Al_2O_3-ratio (wt%/wt%) at different degrees of maturation in (a) the Posidonien Schiefer and (b) the Kimmeridge shales. Note the increasing fixed nitrogen contents with increasing maturation.

the vitrinite reflectance (Fig. 6). Though not all organic nitrogen that disappears upon maturation is preserved as fixed ammonium in the clay mineral lattice, the contribution of fixed nitrogen to total nitrogen increases from 7.2 % to 50.8 % and from 6.9% to 37.3% in the Posidonien Schiefer and the Kimmeridge shales respectively. The systematics of the nitrogen fractions upon maturation (both in the distribution of nitrogen contents and in the isotopic compositions) make total nitrogen a rather useless indicator of diagenetic processes. Conclusions based on total nitrogen data might therefore lead to a misunderstanding of the geological processes involved.

The $\delta^{13}C_{oil}$-values and in particular the $\delta^{15}N_{oil}$-values of the studied North Sea oils are in accordance with the carbon and nitrogen isotopic composition of the Kimmeridge shales which are the source rocks of these oils (cf. Table 3 and Figs. 2b and 3b). There is no relationship between the $\delta^{13}C_{oil}$-values, the $\delta^{15}N_{oil}$-values, the gravity (API) and the sulphur content.

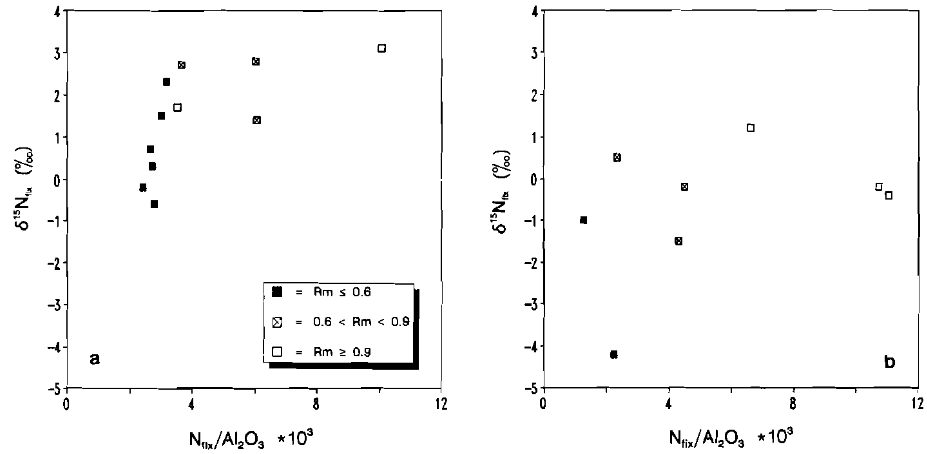


Figure 5. Relation between the N_{fix}/Al_2O_3-ratio (wt%/wt%) and the $\delta^{15}N_{fix}$-values (‰). The immature shales show more variation in $\delta^{15}N_{fix}$-values than the mature shales. For explanation see text.

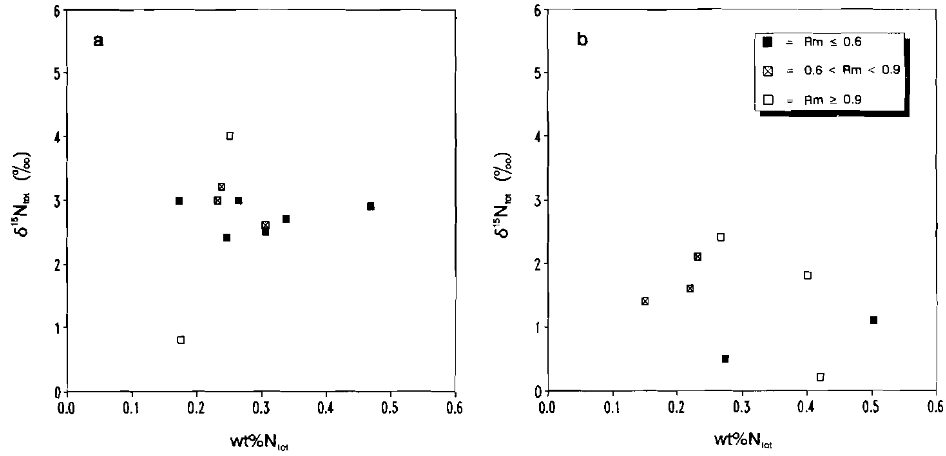


Figure 6. Plot of the total nitrogen isotopic composition ($\delta^{15}N_{tot}$) versus the nitrogen content (wt%N_{tot}) in (a) the Posidonien Schiefer and (b) the Kimmeridge shales.

DISCUSSION

Organic nitrogen and carbon in shales

The C/N-ratios of organic matter in the Posidonien Schiefer and Kimmeridge shales range from 30 to 67 (molar ratios) but they are not related to the degree of maturation (cf. Table 1 and 2). The immature samples of the Posidonien Schiefer already display a wide spread of C/N-ratios from 42 to 62 (molar ratios) which indicates that the organic matter in these shales is of inhomogeneous composition. It is therefore difficult to verify whether preferential breakdown of organic carbon or nitrogen compounds took place during maturation: evidence for such preferential breakdown may be masked by variations in C/N-ratios of the precursor organic matter.

The increase in $\delta^{13}C$ of the Posidonien Schiefer is probably the result of the expulsion of isotopically lighter hydrocarbons from the kerogen during maturation of the shales (Tissot en Welte, 1984 and refs. therein). However, such a trend cannot be observed in the Kimmeridge shales. This is probably due to the heterogeneity of the precursor organic matter resulting from the lateral facies changes in the Kimmeridge shales (Macko and Quick, 1986). Over distances of only a few kilometres, the organic matter in the Kimmeridge shales may vary from marine to terrestrial sapropel (Barnard and Cooper, 1981). These large lateral differences in the composition of the organic matter make it particularly difficult to recognize a relationship between the degree of maturation and the organic carbon isotopic composition of the shales.

The differences in the carbon isotope systematics of the Posidonien Schiefer and the Kimmeridge shales are partly reflected by the isotopic compositions of organic nitrogen: the Posidonien Schiefer show very consistent $\delta^{15}N_{org}$-values which do not change until the advanced maturity stages (Rm $\geq 0.9\%$) when only a small fraction of the original organic nitrogen is left. Probably, the Posidonien Schiefer were deposited under uniform (marine) conditions, which resulted in initial homogeneity of $\delta^{15}N_{org}$ and $\delta^{13}C_{org}$. The dissimilarity in the behaviour of organic nitrogen and carbon isotopic compositions upon maturation is an indication of selective decomposition of the organic compounds. There is no systematic relation between the breakdown of the nitrogen-bearing organic compounds and the breakdown of the carbon compounds.

In contrast to the Posidonien Schiefer, the $\delta^{15}N_{org}$-values in the Kimmeridge shales vary substantially in samples from all maturation stages. Similar to the carbon isotopic compositions in the Kimmeridge shales, these variations in $\delta^{15}N_{org}$ are assumed to reflect differences in the precursor organic matter, which are related to lateral variations in the sedimentary environment. As a consequence, any changes in the nitrogen isotopic composition resulting from fractionation during thermal breakdown of the organic matter will be masked.

Isotopic composition of North Sea oils

Whereas the Kimmeridge shales show a wide range of δ^{13}C-values (Fig. 3b) related to variations in sedimentary environment, the oil samples have fairly uniform carbon isotopic compositions. An explanation for the narrow range of the $\delta^{13}C_{oil}$-values is that oils originating from different precursor organic matter were mixed, averaging out the initial isotope variations of the source rocks. Another explanation for the uniform carbon isotope values is that all the oils described in this study may have been derived from organic matter that was deposited under similar environmental conditions.

The difference between δ^{13}C of the oils and the average $\delta^{13}C_{org}$ of the shales is fairly small (1.8 ‰). This difference may be related to the preferential release of lighter hydrocarbons upon maturation of organic matter, leading to a slightly lower δ^{13}C in the oil than in the shale. This is in accordance with the general observation that isotope fractionation of organic carbon occurs in particular during the initial stages of maturation, when isotopically light hydrocarbons are released from the kerogen (e.g. Silverman, 1967; Sackett, 1968 and 1978; Schoell, 1980 and 1984). During the oil generating stage, the isotopic composition of organic carbon remains fairly constant and therefore no relationship is found between $\delta^{13}C_{oil}$ and gravities (API) of the oil samples.

The North Sea oils have δ^{15}N-values similar to those of the Kimmeridge shales from which they are derived. This suggests that no significant nitrogen isotope fractionation occurs during maturation. This conclusion is in good agreement with the findings of Macko and Quick (1986) who reported a high correlation between nitrogen in asphaltenes and nitrogen in kerogens from Kimmeridge shales. Nitrogen in asphaltenes extracted from the shales had δ^{15}N-values which never deviated by more than 0.5 ‰ from nitrogen in the remaining kerogen, and the authors concluded that probably no nitrogen isotope fractionation occurred during maturation of the shales. The findings of these authors coincide with our observation that there is little variation in the nitrogen isotopic composition of the oil, which comprises the bulk of the organic nitrogen that is released during maturation. This explains why $\delta^{15}N_{oil}$-values are not related to the gravity or sulphur content, and why $\delta^{15}N_{org}$ of the shales does not change with maturation. The consistent $\delta^{15}N_{org}$-values are in contrast with the situation under early diagenetic conditions where the nitrogen isotopic composition of organic matter can be change drastically as a result of bacterial activity (Scholten and Kreulen, 1991).

From the narrow ranges in $\delta^{15}N$- and $\delta^{13}C$-values we conclude either that these oils are derived from similar precursor organic matter (specific sedimentary environment), or that different oils have been mixed thoroughly in the reservoir rocks to isotopically homogeneous composites.

Fixed ammonium in clays

Fixed nitrogen contents of clays (N_{fix}/Al_2O_3) seem to depend solely on the degree of maturation. In both the Posidonien and the Kimmeridge shales, the N_{fix}/Al_2O_3-ratios increase from $\approx 2 \cdot 10^{-3}$ in immature shales ($Rm \leq 0.6\%$) to higher than $10 \cdot 10^{-3}$ in advanced mature shales ($Rm \geq 0.9\%$). An increase in fixed nitrogen contents upon maturation has also been described by among others Cooper and Evans (1983) and Williams et al. (1989). This behaviour contrasts with that of organic nitrogen where the original input of organic matter in the sediments is an important variable. The observed increase in fixed nitrogen must be related to processes that occur during the maturation. Two important processes that may operate together are: **(a)** The increasing release of NH_4^+ derived from breakdown of organic matter during the maturation of the shales, followed by replacement of K^+ in the clay mineral lattices by NH_4^+, and **(b)** extensive recrystallization of clays in this particular maturation interval. Upon burial of sediments, the mixed-layers of illite and smectite (I/S) become more ordered, concurrent with a decrease in smectite layers and an increase in illite (Weaver, 1960). The smectites are transformed initially to irregular I/S and with increasing maturation to regular I/S and illite by a process of dehydration, isomorphic substitution of Si^{4+} by Al^{3+} and uptake of K^+ in the interlayers (Foscolos et al., 1976; Powell et al., 1978; Weaver, 1989). Concurrent with the uptake of potassium, NH_4^+ can be fixed in the interlayer of the newly formed I/S (Williams et al., 1989).

It is difficult to relate the transition from smectite to I/S directly to the vitrinite reflectance since the maturation of organic matter (Rm, spore colour) depends mainly on the maximum thermal heating of the sediment, whereas the illite crystallinity and I/S-transition in buried sediments are believed to be primarily time controlled (Hillier and Clayton, 1989 and refs. therein). Nevertheless, the major I/S-transitions are generally found in the maturation interval where oil generation is highest (e.g. Burst, 1969; Powell et al., 1978; Hillier and Clayton, 1989; Weaver, 1989; Williams et al., 1989). This would explain the rapid increase in the fixed nitrogen contents of the Posidonien Schiefer and Kimmeridge shales at Rm > 0.6% (Figs. 4a and 4b) since changes in the mineral composition (I/S-transition) facilitate the incorporation of NH_4^+ in the mineral lattice of the clays.

The isotopic composition of fixed nitrogen is a strong indication that the ammonium in clays was derived from thermally degraded organic matter: The immature shales (Rm ≤ 0.6%) have $\delta^{15}N_{fix}$-values which are considerably lower than the $\delta^{15}N_{org}$-values. However, upon maturation the isotopic compositions of fixed nitrogen in both the Posidonien Schiefer and the Kimmeridge shales increase to values comparable to those of the organic matter. Earlier, we mentioned the similarity between the nitrogen isotopic compositions of the Kimmeridge shales and oils argues against significant fractionation of organic nitrogen during the major stage of oil generation. Although the isotopic composition of the residual organic nitrogen in advanced mature shales varies considerably, it seems safe to asssume that most of the organic matter that was broken down during maturation had an isotopic composition similar to the initial (Rm ≤ 0.6%) $\delta^{15}N_{org}$-values which lie around 3.0 ‰ for the Posidonien Schiefer and in the range of 1.9 ± 1.1 ‰ (n = 8) for the Kimmeridge shales. This indicates that the increase in the $\delta^{15}N_{fix}$-values upon maturation can be fully explained by uptake of decomposed organic nitrogen (NH_4^+) into the clay mineral lattice. Therefore, in advanced mature shales, $\delta^{15}N_{fix}$ is probably a good indicator of the isotopic composition that organic matter had before its thermal decomposition. This signal is probably well preserved since NH_4^+, once it is fixed in the mineral lattice, remains strongly bound under diagenetic conditions (Williams et al., 1989).

Summarizing, it can be concluded that the increase in the fixed nitrogen content of clays seems to be a good indicator of the maturity of shales, whereas the nitrogen isotopic composition of clays in mature shales can be used as an indicator of the origin of the degraded organic matter.

CONCLUSIONS

The results of this study clearly demonstrate the importance of separating the organic and inorganic nitrogen fractions in a shale. Due to the opposite behaviour of these two nitrogen fractions during maturation, total-nitrogen data are of little use for interpretations of the sedimentary and maturation history.

From the results on the Posidonien Schiefer we conclude that the organic nitrogen contents in shales decrease during maturation. However, the isotopic composition of organic nitrogen remains constant in these shales which were all deposited in a shallow marine environment. Only in the advanced stages of maturation when most organic matter has been degraded does the isotopic composition of the residuary organic matter vary considerably. The isotopic composition of organic nitrogen in the Kimmeridge shales varies as a result of the sedimentary input of alternating marine and terrestrial organic matter. The North Sea oils, derived from Kimmeridge source rocks, have δ^{15}N-values which indicate that no significant isotope fractionation occurs during oil formation.

The fixed nitrogen contents of clay minerals in the shales increase upon maturation. Ammonium is released upon thermal degradation of the organic matter and is incorporated into the lattices of newly formed clay-minerals (I/S-transition). The increase in fixed nitrogen content of clays seems to be a good indicator of the maturity of shales, while the nitrogen isotopic composition of clays is a useful indicator of the origin of the degraded organic matter.

Acknowledgements

We thank A. van Leeuwen Tolboom for analytical assistance and S.M. McNab for linguistic advice. R.D. Schuiling read the manuscript carefully and suggested many improvements. We are grateful to Koninklijke/Shell Laboratories (KSEPL) in Rijswijk, the Netherlands, for providing the samples.

References

Barnard P.C. and Cooper B.S. (1981) Oils and source rocks of the North Sea area. In *Petroleum geology of the continental shelf of North-West Europe* (Eds. L.V. Illing and G.D. Hobson). pp. 169-175. Heyden & Son Ltd. London.

Bartenstein H., Teichmüller M. and Teichmüller R. (1971) Die Umwandlung der organichen Substanz in Dach des Bramscher Massivs. *Fortschr. Geol. Rheinld. u. Westf.* **18**, 501-538.

Bodenhausen J.W.A. and Ott W.F. (1981) Habitat of the Rijswijk Oil Province, onshore, The Netherlands. In *Petroleum geology of the continental shelf of North-West Europe* (Eds. L.V. Illing and G.D. Hobson). pp. 301-309. Heyden & Son Ltd. London.

Boudou J.P., Durand B. and Oudin J.L. (1984) Diagenetic trends of a Tertiary low-rank coal series. *Geochim Cosmochim. Acta* **48**, 2005-2010.

Brooks J., Cornford C. and Archer R. (1987) The role of hydrocarbon source rocks in petroleum exploration. In *Marine petroleum source rocks* (Eds. J. Brooks and A.J. Fleet) *Geol. Soc. Spec. Publ.* **26**, 1-14.

Burst J.F. (1969) Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration. *Am. Assoc. Petr. Geol. Bull.* **53**, 73-93.

Cooper J.E. and Evans W.S. (1983) Ammonium-nitrogen in Green River formation oil shale. *Science* **219**, 492-493.

Cornford C., Morrow, J., Turrington A., Miles J.A. and Brooks J. (1983) Some geological controls on oil composition in the North Sea. In *Petroleum geochemistry and exploration of Europe.* (Ed. J. Brooks) *Geol. Soc. Spec. Publ.* **12**, 175-194.

Demaison G.J. and Moore G.T. (1980) Anoxic environments and oil source bed genesis. *Bull. Am. Ass. Petrol. Geol.* **64**, 1179-1209.

Delwiche C.C. (1970): The nitrogen cycle. *Scientific American* **223**, 136-147.

Drechsler M. and Stiehl G. (1977) Stickstoffisotopenvariationen in organischen Sedimenten: I. Untersuchungen an humösen Kohlen. *Chem. Erde* **36**, 126-138.

Foscolos A.E., Powell T.G. and Gunther P.R. (1986) The use of clay minerals and inorganic and organic geochemical indicators for evaluating the degree of diagenesis and oil generating potential of shales. *Geochim. Cosmochim. Acta* **40**, 953-966.

Gallois R.W. (1976) Coccolith blooms in the Kimmeridge Clay and origin of North Sea Oil. *Nature* **259**, 473-475.

Hallam A. (1987) Mesozoic marine organic-rich shales. In *Marine Petroleum Source Rocks* (Eds. J. Brooks and A.J. Fleet). *Geol. Soc. Spec. Publ.* **26**, 251-261.

Hillier S. and Clayton T. (1989) Illite/smectite diagenesis in Devonian lacustrine mudrocks from Northern Scotland and its relationship to organic maturity indicators. *Clay Miner.* **24**, 181-196.

Hirner A.V., Graf W., Treibs R., Melzer A.N. and Hahn-Weinheimer P. (1984) Stable sulfur and nitrogen isotopic composition of crude oil fractions from Southern Germany. *Geochim. Cosmochim. Acta* **48**, 2179-2186.

Jasper J.P. and Gagosian R.B. (1990) The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta* **54**, 1117-1132.

Jenkyns H.C. and Clayton C.J. (1986) Black shales and carbon isotopes in pelagic sediments from the Tethyan lower Jurassic. *Sedimentology* **33**, 87-106.

Macko S.A. and Quick R.S. (1986) A geochemical study of oil migration at source rock reservoir contacts: Stable isotopes. In *Advances in Organic Geochemistry 1985* (Eds. D. Leythaeuser and J. Rullkötter) *Org. Geochem.* **10**, 199-205. Pergamon Press, Oxford.

Meybeck M. (1982) Carbon, nitrogen and phosphorus transport by world rivers. *Am. J. Sci.* **282**, 401-450.

Müller P.J. (1977) C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* **44**, 765-776.

Oudin J.L. (1976) Etude Géochimique du bassin de la Mer du Nord. *Bull. Centre Rech. Pau - SNPA* **10**, 339-358.

Peters K.E., Rohrback B.G. and Kaplan I.R. (1981) Geochemistry of artificially heated humic and sapropelic sediments I: Protokerogen. *Am. Assoc. Pet. Geol. Bull.* **65**, 688-706.

Peters K.E., Moldowan J.M., Driscole A.R. and Demaison G.J. (1989) Origin of Beatrice Oil by co-sourcing from Devonian and Middle-Jurassic source rocks, Inner Moray Firth, United Kingdom. *Am. Assoc. Pet. Geol. Bull.* **73**, 454-471.

Powell T.G., Foscolos A.E., Gunther P.R. and Snowdon L.R. (1978) Diagenesis of organic matter and fine clay minerals: a comparative study. *Geochim. Cosmochim. Acta* **42**, 1181-1197.

Rashid M.A. (1985) Geochemistry of marine humic compounds. Springer Verlag, New York, 300p.

Robert P. (1988) Organic metamorphism and geothermal history. Reidel Publ. Company, Dordrecht, 311p.

Sackett W.M. (1968) Carbon isotope composition of natural methane occurrences. *Am. Assoc. Petr. Geol. Bull.* **52**, 853-857.

Sackett W.M. (1978) Carbon and hydrogen isotope effects during the thermocatalytic production of hydrocarbons in laboratory simulation experiments. *Geochim. Cosmochim. Acta* **42**, 571-580.

Schoell M. (1980) The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* **44**, 649-661.

Schoell M. (1984) Recent advances in petroleum isotope geochemistry. In Advances in Organic Geochemistry 1983 (Eds. P.A. Schenck, J.W. De Leeuw and G.W.M. Lijmbach) *Org. Geochem.* **6** 645-663. Pergamon Press, Oxford.

Scholten S.O. and Kreulen R. (1991) Early diagenetic changes in nitrogen and carbon isotopes of marine sediments. *Geochim. Cosmochim. Acta* (submitted).

Silverman S.R. (1967) Carbon isotopic evidence for the role of lipids in petroleum formation. *J. Am. Oil Chem. Soc.* **44**, 691-695.

Stadler G. and Teichmüller R. (1971) Zusammenfassender Überblick über die Entwicklung des Bramscher Massivs und des Niedersächsischen Tektogens. *Fortschr. Geol. Rheinld. u. Westf.* **18**, 547-564.

Stahl W.J. (1977) Carbon and nitrogen isotopes in hydrocarbon research and exploration. *Chem. Geol.* **20**, 121-149.

Teichmüller M., Teichmüller R. and Weber K. (1979) Inkohlung und Illit-Kristallinität vergleichende Untersuchungen im Mesozoikum und Paläozoikum von Westfalen. *Fortschr. Geol. Rheinld. u. Westf.* **27**, 201-276.

Tissot B.P. and Welte D.H. (1984) Petroleum formation and occurrence. 2nd ed. Springer Verlag, Berlin, 699p.

Tyson R.V., Wilson R.C.L. and Downie C. (1979) A stratified water column environmental model for the type Kimmeridge Clay. *Nature* **277**, 377-380.

Waples D.W. (1977) C/N ratios in source rock studies. *Colo. Sch. Mines Miner. Ind. Bull.* **20**, 1-7.

Waples D.W. and Sloan J.R. (1980) Carbon and nitrogen diagenesis in deep sea sediments. *Geochim. Cosmochim Acta* **44**, 1463-1470.

Weaver C.E. (1960) Possible use of clay minerals in search for oil. *Am. Assoc. Petr. Geol. Bull.* **44**, 1505-1518.

Weaver C.E. (1989) Clays, muds, and shales. *Developments in Sedimentology* **44**. Elsevier Sci. Publ. B.V., Amsterdam, 819p.

Williams L.B., Ferrell R.E., Chinn A.W. and Sassen R. (1989) Fixed-ammonium in clays associated with crude oils. *Appl. Geochem.* **4**, 605-616.

SAMENVATTING

In de vaste bestanddelen van een sediment kan stikstof in drie vormen (fracties) voorkomen: als bouwstof van organische verbindingen (organisch stikstof), als ammonium dat geadsorbeerd is zowel aan de anorganische als aan de organische deeltjes waaruit een sediment is opgebouwd (uitwisselbaar stikstof) en als ammonium dat is opgenomen in het rooster van kleimineralen (gefixeerd stikstof). Dit proefschrift doet verslag van de studie naar de onderlinge verdeling en isotopensamenstellingen van deze drie stikstoffracties in sedimenten en de veranderingen die optreden bij diagenese en maturatieprocessen (olie-vorming).

Tijdens de biologische stikstofcyclus kan de isotopenverdeling van organisch stikstof (uitgedrukt als $\delta^{15}N_{org}$) worden veranderd (fractionering). Onder andere wordt gevonden dat de gemiddelde $\delta^{15}N_{org}$-waarde van recent organisch materiaal systematisch toeneemt van terrestrisch naar marien milieu. Dit milieusignaal gaat echter verloren nadat het organisch materiaal in een sediment is afgezet. De oorzaak hiervan wordt gevonden in de aanwezigheid van bacteriën die organisch materiaal afbreken, onder andere om in hun energiebehoefte te voorzien.

De bacteriële afbraak van organisch materiaal in turbidieten van de Madeira Abyssale Vlakte blijkt beduidend sterker te zijn onder oxyderende dan onder suboxysche omstandigheden. Tijdens deze oxydatie verandert de $\delta^{15}N_{org}$-waarde doordat bepaalde organische verbindingen, die ieder op zich verschillende isotopensamenstellingen kunnen hebben, selectief worden afgebroken. Ten gevolge van deze selectieve afbraak van organische verbindingen kan de $\delta^{15}N$-waarde van uitwisselbaar stikstof sterk variëren.

Gefixeerd stikstof ($\delta^{15}N_{fix}$) daarentegen heeft een zeer constante isotopensamenstelling die nauwelijks beïnvloed wordt door bacteriële oxydatie. Het gefixeerde ammonium, afkomstig van afgebroken organisch materiaal, is waarschijnlijk in een vroeg stadium na afzetting van het sediment en onder voornamelijk reducerende omstandigheden in de kleimineralen ingebouwd. Isotopen metingen op diverse niet-recente, kleirijke monsters tonen aan dat de $\delta^{15}N_{fix}$-waarden systematisch afhankelijk zijn van het afzettingsmilieu. Deze systematiek is vergelijkbaar met de veranderingen in isotopensamenstellingen van stikstof in recent organisch materiaal. Door de afbraak van labiele organische verbindingen in het sediment wordt ammonium gevormd dat opgenomen kan worden door de kleien. Deze labiele stikstofverbindingen hebben in het algemeen een gemiddelde isotopensamenstelling die kenmerkend is voor het afzettingsmilieusignaal.

Ammonium dat eenmaal gefixeerd is in het mineraalrooster, wordt niet meer gemakkelijk onder vroeg diagenetische omstandigheden vervangen. Hierdoor kan de $\delta^{15}N_{fix}$-bepaling worden toegepast om de paleomilieus te onderscheiden van niet-recente sedimenten. Dit is gedaan op monsters van Kwartaire sedimenten afkomstig van twee boorkernen uit de Noordzee. Veranderingen in de $\delta^{15}N_{fix}$-waarden van de kleirijke sedimenten in deze kernen blijken zonder uitzonderingen overeen te komen met paleontologische en sedimentaire veranderingen die op afwisselende afzettingsmilieus (terrestrisch, deltaïsch, marien en glaciaal) duiden. Daar waar fossielen en sedimentaire structuren ontbreken kan de $\delta^{15}N_{fix}$-waarde gebruikt worden om het afzettingsmilieu te interpreteren.

Veranderingen die tijdens de vroege diagenese in de isotopensamenstelling van de stikstoffracties optreden zijn dus het gevolg van bacteriële activiteit. Met toenemende diepte echter worden de omzettingen in organisch materiaal voornamelijk veroorzaakt door de temperatuurstijging (maturatie). Hoewel het organisch stikstof gehalte afneemt tijdens de maturatie, veranderen de gemiddelde $\delta^{15}N$-waarden van het residuaire organisch materiaal pas in het laatste stadium van de maturatie. Kleimineralen daarentegen rekristalliseren tijdens de maturatie of zetten om naar andere (klei)mineralen. Bij de omzetting van smectiet naar illiet neemt het gehalte aan gefixeerd ammonium, afkomstig van afgebroken organisch materiaal, sterk toe. Hierdoor wordt de $\delta^{15}N_{fix}$-waarde van sedimenten tijdens de maturatie gelijk aan de isotopensamenstelling van het afgebroken organisch materiaal. De $\delta^{15}N_{fix}$-waarde in een sterk omgezet sediment kan dan een indicatie zijn voor de $\delta^{15}N_{org}$-waarde die het sediment voor de maturatie had.

CURRICULUM VITAE

Sven Olaf Scholten werd geboren op 18 juli 1964 te Hilversum. In 1982 behaalde hij het diploma Gymnasium (ongedeeld) aan het Gemeentelijk Gymnasium te Hilversum. In september van dat jaar begon hij met de studie Geologie aan de Rijksuniversiteit te Utrecht. In februari 1984 werd het propaedeutisch examen afgelegd en in januari 1987 het doctoraal examen (cum laude) met als hoofdvak Endogene Geochemie en bijvak Isotopen Geologie. Vanaf februari 1987 was hij werkzaam bij de afdeling Chemische Geologie van het Instituut voor Aardwetenschappen te Utrecht, eerst als assistent in opleiding en vanaf februari 1991 als toegevoegd onderzoeker. Thans is de auteur werkzaam als geoloog bij de Shell Internationale Petroleum Maatschappij, te 's-Gravenhage.


LAWRENCE VRIEND