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Ammonium as a biomarker in Precambrian metasediments

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Abstract

The following article assesses the potential of ammonium as a biomarker in Precambrian metasediments. A modern marine environment is considered to highlight the processes that contribute to the isotopic composition of organic nitrogen, notably the roles played by nitrogen-fixing organisms (cyanobacteria) and denitrifying bacteria. The carbon and nitrogen biogeochemical cycles are compared and contrasted. Unlike carbon, the major nitrogen isotope variations may be controlled by local environmental conditions, such as season of the year and water depth. However, such local environmental factors may have been superimposed on more gradual changes related to the long-term chemical evolution of the exterior environments of the Earth. The great potential of nitrogen as a biomarker is that the breakdown product of organic nitrogen (ammonium) behaves like a trace element, and is stable in high temperature crustal processes. Thus, ammonium may survive as a biomarker when all other evidence for former life has been destroyed, and ammonium studies may be able to identify sedimentary (pelitic) components in high-grade Precambrian terrains. Previous results from Precambrian rocks are reviewed, to highlight that very little work has been completed to date, and that only very general conclusions can be drawn. Much work needs to done in order to understand the basic biogeochemistry and geochemistry of crustal nitrogen, and it is suggested that the best way to proceed is by numerous detailed case studies. The interpretation of isotope ratios in ancient sediments usually assumes uniformitarianism, and the justification of this approach is considered briefly. Overall, this article highlights the under-developed potential of Precambrian ammonium biogeochemistry, and suggests area for future research. Not only does the development of the subject have implications for the search for former life on Mars, but it may also open up new areas of Precambrian research. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nitrogen cycle; Nitrogen isotopes; Biogeochemistry; Sediments; Continental crust

1. Introduction

Although palaeontologists and isotope geochemists have been searching for traces of ancient life for many years (e.g. Schopf, 1983; Schidlowski, 1988; Schopf and Klein, 1992; Mojzsis et al., 1996), there has been renewed interest following the discovery of organic matter and other possible traces of former life in meteorites that are believed to have originated on Mars (Wright et al., 1989; McKay et al., 1996). Whilst the interpretation of the observed features is open to question, few doubt the possibility of there having

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been former life on Mars, and several space missions are planned, either to perform experiments in situ or to return samples to Earth.

In the absence of obvious fossils, the success of such missions depends upon the recognition of life from other biomarkers, notably chemical 'fossils' and isotope ratios. Prior to the return of any material from Mars, much work will need to be completed on biomarkers in terrestrial samples, and Precambrian sediments and metasediments are obvious candidates for study. Indeed, there has already been much success with carbon isotope ratios which indicate that life on Earth is probably older than the oldest rocks (e.g. Schidlowski, 1988; Mojzsis et al., 1996).

Compared with carbon, little work has been completed on nitrogen, although there are many opportunities for study. The great advantage of nitrogen is that the breakdown product of organic matter (NH_4^+) has a high thermal stability, and can survive metamorphism, being found in granites and other crustal melts (e.g. Hall, 1999). Thus, NH_4^+ may be present as a biomarker when all other evidence of former life has been destroyed. Furthermore, NH_4^+ can be detected by infrared spectroscopy, and may be used to select Precambrian metasediments, which can be then be examined for other geochemical biomarkers. Not only would the development of Precambrian ammonium biogeochemistry help in the recognition of the former presence of life in ancient rocks, but it may also open up new areas of Precambrian research.

This article reviews all aspects of NH_4^+ biogeochemistry, with the primary objective of assessing the potential of NH_4^+ as a biomarker in Precambrian metasedimentary rocks. A detailed account of the production of NH_4^+ in modern sediments is given to highlight the minimum sequence of events that may have been required for the production of NH_4^+ in Precambrian rocks. Emphasis is placed on the enzymes involved, because their action controls the isotope composition of nitrogen, and their present day complexity needs to be taken into consideration when studying ancient sediments. The interpretation of ancient biomarkers usually assumes uniformitarianism, where present day processes are considered to be the same as those that have acted in the past, and the justification of this approach is considered briefly. Areas of uncertainty and possibilities for future research are highlighted throughout.

2. Modern environments

The interpretation of biomarkers in Precambrian sediments/metasediments is heavily reliant on an understanding of biomarkers in more recent samples. Present day processes can be studied directly in modern environments, and the preservation of palaeo-environmental data can be assessed by studying geologically recent samples (e.g. <20 Ma). For nitrogen, this concerns the nature and isotope composition of organic matter in sediments, and the preservation of information when the organic nitrogen is converted to NH_4^+ during diagenesis and metamorphism. One can then go back in time and study older samples, to see whether there are any marked changes in the $\delta^{15}N$ values of the sedimentary record, due to such major events such as the change from anoxic to oxic conditions on the Earth (Beaumont and Robert, 1999), or the 'arrival' of life on the continents.

2.1. General

Fig. 1 (Boyd, 2001, modified from Sweeney et al., 1978) shows the cycling of nitrogen in a modern shallow shelf sea. A detailed description is provided by Boyd (2001), however a brief summary is given below.

The principal inputs of nitrogen to the marine basin are by rain, rivers, and lightning strikes and by the direct fixation of atmospheric nitrogen by cyanobacteria. These inputs are largely balanced by denitrification, a bacterial process that converts dissolved nitrate back to nitrogen gas and nitrous oxide, with only 12% (Jaffe, 1992) of the nitrogen being lost from the basins by the sedimentation of organic matter.

Although this article is only concerned with NH_4^+ in ancient metasediments, all of the inorganic species shown in Fig. 1 need to be taken into consideration. This is because NH_4^+ in metasediments will have been derived from organic matter, and the cycling of all of the other inorganic species will control the isotope composition of the organic matter. For example, dissolved NH_4^+ and NO_3^- both play important roles in the biogeochemical nitrogen cycle, and a consideration of their sources at the present time suggests that Precambrian oceans would have been different from today. However, it is unclear whether these differences would have been registered in the sedimentary record.

2.2. *'Seawater' ammonium*

NH_4^+ in ancient sediments will have been produced predominantly by the in situ decomposition of organic matter. However, Fig. 1 shows the presence of NH_4^+ in seawater, which cannot be ignored.

Before discussing seawater NH_4^+, it is worth considering the relationship that exists between NH_3 and NH_4^+, because it is NH_3 that is the initial product of biochemical reactions. However NH_3 may be rapidly protonated to NH_4^+, because the two species exist in a pH dependent equilibrium,

$$\mathrm{pH} = 9.25 + \log\left\{\frac{[\mathrm{NH_3}]}{[\mathrm{NH_4^+}]}\right\} \tag{1}$$

At pH 9.25, the two species will be in equal proportions and NH_3 only becomes dominant in alkaline environments. For pH 8 and lower (seawater, cells), NH_4^+ is the dominant chemical species.

The direct production of NH_4^+ in seawater occurs during the degradation of organic matter. The initial stage of this degradation is termed *mineralisation*, which essentially means the release of organically bound nutrients. For nitrogen, it is taken to mean the release of the amine group of amino acids, through transamination (e.g. alanine),

$$\text{Alanine} + \text{2-oxoglutarate} \xrightarrow{\text{amino-transferase}} \text{pyruvate} + \text{glutamate} \tag{2}$$

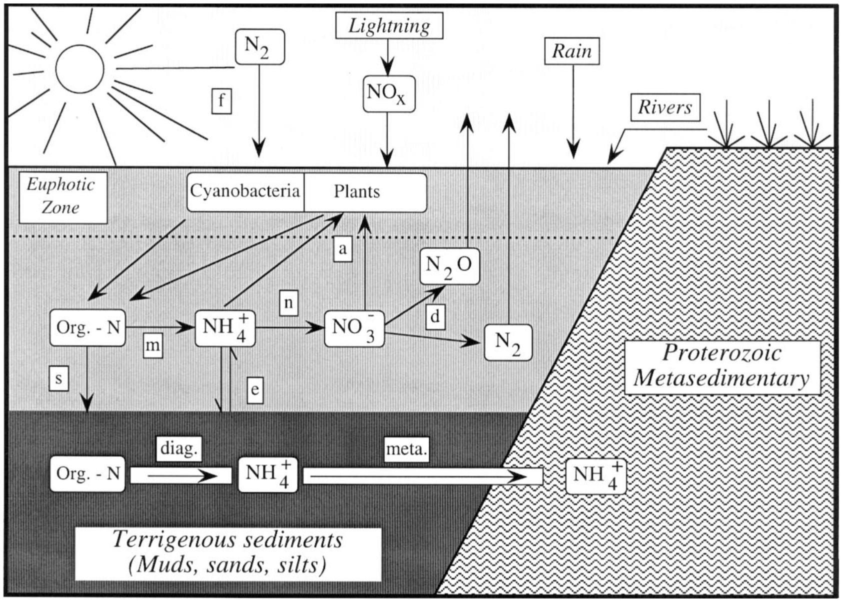

Fig. 1. The cycling of nitrogen in a shallow shelf sea, showing how organic nitrogen could have become incorporated into Precambrian rocks. Exchange between sea-water NH_4^+ and sediments is probably negligible, however NH_4^+ can exchange readily with basalts, during hydrothermal activity at ocean ridges. Most NH_4^+ in sediments has been produced by the in situ degradation of organic matter. Symbols, s, sedimentation; m, mineralisation; e, exchange; n, nitrification; a, assimilation; d, denitrification; f, fixation, diag., diagenesis; meta., metamorphism.

Followed by deamination

$$\text{Glutamate} + \text{NAD}^+ + H_2O \xrightarrow{\text{GDH}} \text{2-oxoglutarate} + \text{NADH} + NH_4^+ \quad (3)$$

where GDH is the enzyme glutamate dehydrogenase and NAD in the co-enzyme nicotinamide-adenine dinucleotide. Most animals excrete the waste nitrogen as urea or uric acid, whereas some marine organisms excrete NH_4^+.

In addition to in situ production, much NH_4^+ may be produced from NH_3 derived from continental ecosystems (Jaffe, 1992; Boyd, 2001). Perhaps the most important source of the NH_3 is through the volatilisation of animal wastes, and may account for about 20% of the total biologically active nitrogen that is being transported to the oceans at the present time (Jaffe, 1992). It is unknown whether atmospheric NH_3 was important in the Precambrian, and much depends on when life first arrived on the continental areas (Boyd, 2001).

Fig. 1 shows that seawater NH_4^+ may *exchange* with sediments. In detail, this means that NH_4^+ will exchange with K^+ present within the clay minerals of sediments. For significant exchange to occur, requires a high concentration of NH_4^+, and the circulation of a large quantity of seawater through the sediments. For most situations, the latter will not apply, and the sediments will remain essentially 'closed' to seawater NH_4^+. Indeed, seawater will be expelled from sediments during compaction. However, massive circulation of seawater may occur during hydrothermal activity at ocean ridges, where igneous rocks (basalts) may be affected. For example, a fresh crystalline basalt will contain little or no NH_4^+, however Hall (1989) found that spilitised basalts could contain nearly 200 ppm NH_4^+. The subduction of such material is one way in which biologically fixed nitrogen may be recycled into the deep mantle.

Ancient hydrothermally altered rocks, although not preserving fine-scale information, may provide general palaeo-oceanographic information concerning the concentration of seawater NH_4^+, and the nitrogen isotope composition of ancient oceans.

2.3. 'Seawater' nitrate

Although NH_4^+ is produced by mineralisation, it is nitrate that is the principal inorganic form of nitrogen in the oceanic reservoir (Sweeney et al., 1978; Letolle, 1980; Jaffe, 1992). Nitrate is produced from NH_4^+ in two sequential reactions,

$$NH_4^+ + \tfrac{3}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (4)$$

$$NO_2^- + \tfrac{1}{2}O_2 \rightarrow NO_3^- \quad (5)$$

Bacteria of the genus *Nitrosomonas* are responsible for the first step, whereas *Nitrobacter* perform the second.

In addition to the direct formation within the oceans, nitrates can also be washed in from the land (leachates from continental ecosystems), or fall as 'acid rain' during thunderstorms. Again there are considerations here for the Precambrian (Boyd, 2001), because continental ecosystems (soils) may be fairly recent, and the production of NO_x during thunderstorms requires atmospheric O_2, which may only have become important during the Proterozoic (e.g. Kasting, 1993; Holland, 1994).

Nitrate is an important source of inorganic nitrogen for phytoplankton (Fig. 1). Nitrate is not assimilated directly, but is first converted to NH_4^+ by reductases, and the NH_4^+ is then incorporated into amino acids involving one of several enzymes (e.g. Pelmont, 1993).

$$NO_3^- \xrightarrow{\text{nitrate reductase}} NO_2^- \quad (6)$$

$$NO_2^- \xrightarrow{\text{nitrite reductase}} NH_4^+ \quad (7)$$

$$NH_4^+ \xrightarrow{\text{glutamine synthetase}} \text{amino acids} \quad (8)$$

2.4. The isotope composition of organic nitrogen

Information regarding the nitrogen biogeochemical cycle in the Precambrian will be preserved as elemental ratios (e.g. C/N), nitrogen concentrations, and the $\delta^{15}N$ values of organic matter and its derivatives, notably sedimentary NH_4^+.

The isotopic composition of the organic matter will be controlled initially by the source of the inorganic nitrogen. At the present time, the two most important considerations are biological ni-

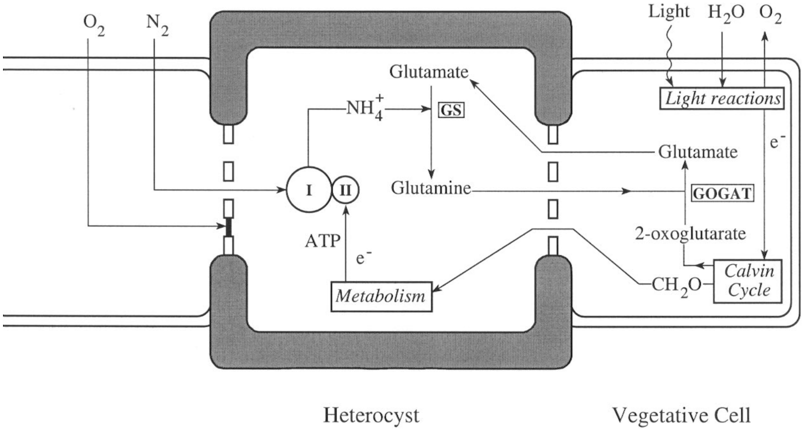

Fig. 2. Nitrogen fixation in cyanobacteria (Blondeau, 1980; Pelmont, 1993). I, dinitrogenase, II, dinitrogenase reductase, GS, glutamine synthetase, GOGAT, glutamine-2-oxoglutarate-amino-transferase.

trogen fixation and the isotopic composition of dissolved nitrate assimilated by phytoplankton. However, local environmental effects will be superimposed on these controls, and such effects will be considered later.

2.5. Direct fixation of atmospheric nitrogen

When dissolved inorganic forms of nitrogen cannot meet the requirements of the biota in the euphotic zone, certain organisms undergo physiological changes that enable them to fix nitrogen directly from the atmosphere. In cyanobacteria, this is characterised by the differentiation of heterocysts (Fig. 2), and the synthesis of the nitrogenase enzyme complex, which is common to all nitrogen fixing organisms (e.g. Sprent, 1987; Sprent and Sprent, 1990).

The nitrogenase enzyme complex (Fig. 2) consists of two separate components, component I (dinitrogenase), which is an Fe-Mo-bearing protein, and component II, (dinitrogenase reductase), which is an Fe-bearing protein. Both are deactivated by oxygen, so the heterocyst is impermeable to molecular oxygen, but permeable to nitrogen.

Photosynthesis in the vegetative cells produces carbohydrates that can be used in the heterocysts. Carbohydrate metabolism provides adenosine triphosphate (ATP), and a pool of electrons, that are necessary for the reduction of N_2 to NH_4^+. NH_4^+ can then combine with glutamate (from the vegetative cell) to form glutamine, and the reaction is catalysed by glutamine synthetase (GS). Glutamine is exported from the heterocyst, where it combines with 2-oxoglutarate to form glutamate, and the reaction is catalysed by glutamine-2-oxoglutarate-amino-transferase (GOGAT). For each mole of glutamine ‘consumed’, two moles of glutamate are produced. Glutamate can either be exported to the heterocysts for the synthesis of more glutamine, or can be used to produce the amino acids necessary for the functioning of the cyanobacterium.

Only minimal fractionation of the nitrogen isotopes is associated with nitrogen fixation, although it may lead to slightly negative $\delta^{15}N$ values (e.g. Macko et al., 1987). For example, Rau et al. (1987) reported negative $\delta^{15}N$ values from Cretaceous sedimentary sequences. The authors suggested that a scarcity of dissolved nitrate resulted in phytoplankton assemblages being dominated by nitrogen-fixing organisms.

2.6. Denitrification and the isotopic composition of ‘seawater’ nitrate

2.6.1. General

During its passage through the water column, organic matter is oxidised by microorganisms, which leads to a depletion in the oxygen content of the sea-water. A depth is reached (the oxygen minimum) where there may be insufficient oxygen for the continued degradation of organic matter. In anoxic environments, heterotrophic bacteria such as *Pseudomonas dentrificans* can utilise NO_3^- as the terminal electron acceptor, with N_2 and N_2O being the gaseous nitrogen products.

$$5C_6H_{12}O_6 + 24NO_3^- + 24H^+ \rightarrow 30CO_2 + 42H_2O + 12N_2 \quad (9)$$

$$C_6H_{12}O_6 + 6NO_3^- + 6H^+ \rightarrow 6CO_2 + 9H_2O + 3N_2O \quad (10)$$

The importance of denitrification is reflected in the nitrogen isotopic composition of dissolved marine NO_3^-. This is because there is a marked kinetic isotope effect associated with denitrification. Denitrifying bacteria preferentially use $^{14}NO_3^-$, and the gaseous products (N_2, N_2O) are depleted in ^{15}N, and the residual dissolved NO_3^- becomes enriched in ^{15}N. Sweeney et al. (1978) quote a mean $\delta^{15}N$ value of +6 to +7‰ for dissolved oceanic nitrate, clearly distinct from atmospheric N_2 (0‰, by definition; e.g. Mariotti, 1983).

The magnitude of the instantaneous fractionation factor (α) is in dispute, although values of around 1.030 are commonly quoted (e.g. Hopkins et al., 1998). Part of the problem arises because controlled laboratory experiments (e.g. Mariotti et al., 1981) can give different results from natural systems (e.g. Cline and Kaplan, 1975).

Residual NO_3^- (enriched in ^{15}N) can be reduced to NH_4^+ (by the enzymes nitrate and nitrite reductase), and assimilated by organisms. Therefore, marine phytoplankton (which do not fix N_2) have mean $\delta^{15}N$ values close to +7‰ (Sweeney et al., 1978; Beaumont and Robert, 1999, and references therein). Because phytoplankton are a major source of the organic matter in sediments, the latter tend to have positive bulk $\delta^{15}N$ values. Peters et al. (1978), in a survey of recent (surface and near surface) sediments, found $\delta^{15}N$ values between +2.4 and +9.9‰, with a mode in the distribution between +6 and +7‰, again similar to the values of dissolved nitrate (Fig. 3).

2.6.2. *Comparisons with the carbon biogeochemical cycle*

At this point, it is worth comparing and contrasting the biogeochemical nitrogen cycle with that of carbon. This is useful because it highlights why nitrogen isotope ratios in the sedimentary record are probably less variable than carbon isotope ratios, and the discussion also introduces why the major nitrogen isotope variations are controlled mainly by local environmental conditions.

The ultimate source of carbon in sediments is CO_2 from the mantle, which has a $\delta^{13}C$ value close to −5‰ (e.g. Javoy et al., 1986; Mattey, 1986). There is a marked fractionation of the carbon isotopes associated with photosynthesis (e.g. Schidlowski et al., 1983) that results in sedimentary organic matter having a mean $\delta^{13}C$ value close to −25‰. The extraction of 'light' carbon (20% of total sedimentary carbon; Hayes et al., 1983), necessarily created a 'residue' enriched in ^{13}C, which has been precipitated as sedimentary carbonate (80% of total) with a mean $\delta^{13}C$ value close to 0‰. Both the 'light' and 'heavy' components are preserved in sediments, and the near constant partitioning of isotopes between carbonate and organic matter since 3800 Ma ago has been used as strong evidence for the antiquity of life (e.g. Schidlowski, 1988; Mojzsis et al., 1996).

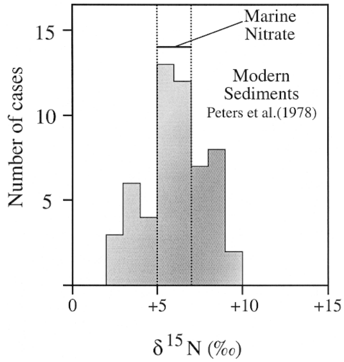

Fig. 3. The nitrogen isotope composition of modern sediments.

Variations around the mean $\delta^{13}C$ values of organic carbon and carbonate are usually interpreted in terms of global processes. For example, increased burial of organic carbon in the Carboniferous is believed to have resulted in a significant increase in the oxygen content of the atmosphere (21% → > 30% O_2) which may have caused gigantism amongst insects (e.g. Berner and Canfield, 1989; Berner et al., 2000). In general terms, the sedimentary record of carbon can be used to study large-scale effects. This may not be the case with nitrogen isotopes.

In many ways, the fractionation of the nitrogen isotopes that accompanies denitrification is similar to the fractionation of the carbon isotopes that accompanies photosynthesis. There is an initial pool of an oxidised inorganic species (NO_3^-) that is equivalent to the CO_2 and HCO_3^- of the carbon cycle. Denitrification results in gaseous reduced products (N_2, N_2O) that are markedly depleted in the heavy isotope, similar to the ^{13}C depleted nature of organic matter produced during photosynthesis. The loss of these ^{15}N-depleted gaseous species from the oceans necessarily enriches the oxidised inorganic pool (NO_3^-) in the heavy isotope, which is again similar to the carbon cycle. ^{15}N enriched NO_3^- is reduced to NH_4^+(nitrate and nitrite reductase) and assimilated by organisms, and the organic matter can subsequently accumulate in sediments.

Despite the similarities, there are important differences between the carbon and nitrogen biogeochemical cycles. In the case of carbon, both the reduced product (organic matter) and the oxidised residue (carbonates) are preserved in sediments, and the difference in the isotope composition between the two is a direct record of photosynthesis. For nitrogen, the reduced products are gaseous (N_2, N_2O), and are lost to the atmosphere, so the characteristic isotope fractionation associated with denitrification is not preserved in sediments. Indeed, the $\delta^{15}N$ value of organic matter produced during nitrate assimilation preserves information similar to $\delta^{13}C$ values of carbonates, and because the latter only show small variations, one may expect that the $\delta^{15}N$ values of organic matter will only exhibit small variations in the sedimentary record. However, nitrate is actively cycled, which can lead to marked variations in $\delta^{15}N$ on the local scale.

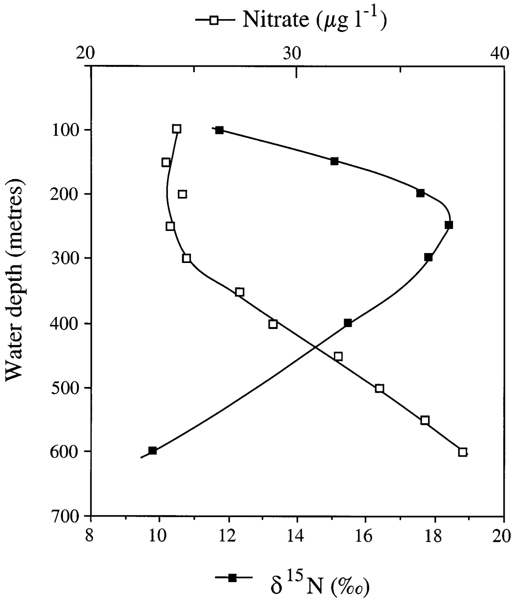

Fig. 4. The covariation of dissolved nitrate and $\delta^{15}N$ associated with denitrification in the oxygen minimum (Cline and Kaplan, 1975).

2.6.3. Variations in $\delta^{15}N$ on the local scale

Denitrification involves the degradation of organic matter, and the isotope composition of dissolved nitrate depends initially upon the flux of such material. Under steady state conditions, there can be a stratification of the $\delta^{15}N$ value of dissolved nitrate. Fig. 4 shows the results of Cline and Kaplan (1975), where extreme $\delta^{15}N$ values occur in the zones of active denitrification. Clearly, such stratification could never be 'global' and could be disrupted locally by upwelling. Similarly, stratification may not occur in shallow shelf seas (< 100 m deep), although it is unknown whether shallow water and deep water settings give different nitrogen isotope records.

The results of Muzuka et al. (1991) stress the importance of local conditions (Fig. 5). Their samples were collected as part of the ocean drilling project (ODP, site 725) and the sediments were of Pleistocene–Holocene age. The marked variations in $\delta^{15}N$ over a short range of sediment depth are due to local conditions such as fluctuations in the oxygen minimum. Overall, the ^{15}N enriched nature of the sediments at site 725 suggest extensive denitrification, hence oxygen-poor conditions.

As well as oceanographic considerations, the season of the year can also influence the $\delta^{15}N$ values of dissolved inorganic species and sedimentary organic matter. This has been demonstrated by Mariotti et al. (1984) for samples collected in the North Sea. The $\delta^{15}N$ values ranged from +4 to +11.5‰ (mean value +8‰), with the lower values being found in early spring and the highest values being found in summer. Similarly, Ostrom et al. (1998) measured the $\delta^{15}N$ value of nitrate from one soil over a period of 9 months. They found low to negative values (−4 to +2‰) in the colder months (April, December), but very positive values (+8 to +10‰) in the warmer months (August, September). The cyclicity was simply due to there being several biological processes involved, with one becoming dominant when the temperatures increased.

Because such local controls would have been present throughout Earth history, the nitrogen isotope records of ancient sediments may reveal novel data concerning environmental conditions in the Precambrian. However, such local fluctuations in Precambrian rocks may not be directly comparable with present day environments, because the chemical composition of the exterior environments of the Earth (atmosphere/oceans) would have been very different to the present day (e.g. Kasting, 1993; Holland, 1994), and the mean $\delta^{15}N$ values may provide some general information concerning the oxidation state of ancient marine basins (Beaumont and Robert, 1999). However, it is probable that short-range variability in $\delta^{15}N$ also occurs in Precambrian rocks, which would provide additional information concerning the earliest biogeochemical nitrogen cycle.

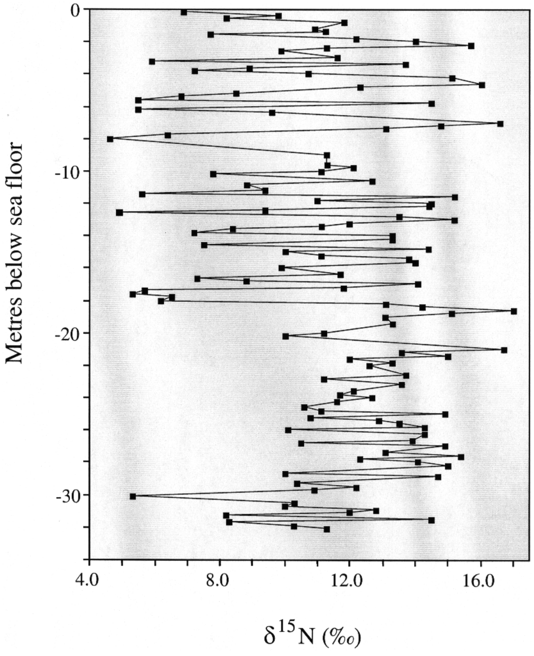

Fig. 5. Large scale fluctuations in $\delta^{15}N$ caused by local environmental conditions (Muzuka et al., 1991).

3. The formation of sedimentary NH_4^+ from organic matter

The above discussion outlined the origin of nitrogen isotope variations in sedimentary organic matter, and now one needs to consider the preservation of information during the burial of sediments. Boyd (2001) provides a summary of the chemical and isotope changes that accompany diagenesis and metamorphism, and only a brief account is provided here.

During diagenesis, biological and thermal degradation of organic matter both result in the formation of significant quantities of NH_4^+ that can be fixed by clay minerals in the sediment (Williams et al., 1992; Hall, 1999). Although some nitrogen may be expelled along with pore waters during compaction, concentrations of nitrogen in 'post-diagenetic' sediments can be as high as 1000 ppm (Waples and Sloan, 1980). The conversion of organic nitrogen to NH_4^+ may not affect the $\delta^{15}N$ values significantly (Williams et al., 1995), hence the isotope ratio of ammoniacal nitrogen may preserve evidence regarding the sum total of all of the processes shown in Fig. 1.

Where the rocks have only been mildly altered, then NH_4^+ may co-exist with other biomarkers related to the carbon and sulphur cycles (for

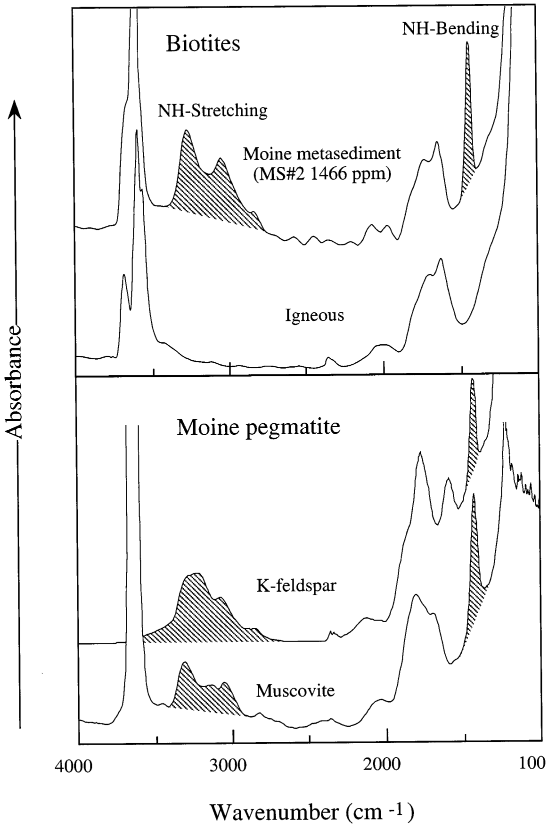

Fig. 6. The infra-red absorption spectra of ammonium-bearing minerals. The shaded areas show the absorptions due to the ammonium ion.

example). However, it is during metamorphism that the true potential of NH_4^+ as a biomarker becomes apparent. NH_4^+ has a high thermal stability, and an ionic radius similar to K^+. Thus, during metamorphism, NH_4^+ readily enters into the crystal lattices of common minerals such as micas and feldspars (Honma and Itihara, 1981), where its presence can be easily detected by infrared spectroscopy (Vedder, 1965; Shigorova, 1982; Boyd, 1997). Indeed, NH_4^+ is so stable that it can survive high grade metamorphism and be found in granites and other crustal melts (Hall, 1999), and it may be the most stable biomarker that has yet been identified.

Fig. 6 shows the infrared absorption spectra of a biotite from the Moine metasediments of Scotland (Neoproterozoic; Friend et al., 1997) compared with a spectra obtained from an igneous biotite (Boyd, 1997). The absorptions due to NH_4^+ are strong and free from interferences. Also shown are the spectra obtained from muscovite and potassium feldspar from a pegmatite vein from the same sequence. The latter highlight the thermal stability of NH_4^+ during partial melting.

Although there may be little alteration of the nitrogen isotopes during diagenesis, the $\delta^{15}N$ values change markedly during metamorphism into amphibolite facies (Haendel et al., 1986; Bebout and Fogel, 1992; Bebout et al., 1999). The fractionation of the nitrogen isotopes is due to the break-down of NH_4^+, and its subsequent loss as N_2 (Kreulen and Schuiling, 1982; Duit et al., 1986). Attempts are being made to characterise metamorphic rocks in order understand fully the mechanisms of isotope fractionation (e.g. Sadofsky and Bebout, 2000), which may allow ancient sediments to be corrected for the effects of metamorphism (Boyd and Philippot, 1998).

Fig. 7 shows the data of Haendel et al. (1986). The greenschist facies samples have $\delta^{15}N$ values that are indistinguishable from modern marine sediments, however, the breakdown of ammonium in amphibolite facies lowered the nitrogen concentrations, and the $\delta^{15}N$ values of the residual ammonium are notably higher. Also shown in Fig. 7 are metasediments from the Moine Succes-

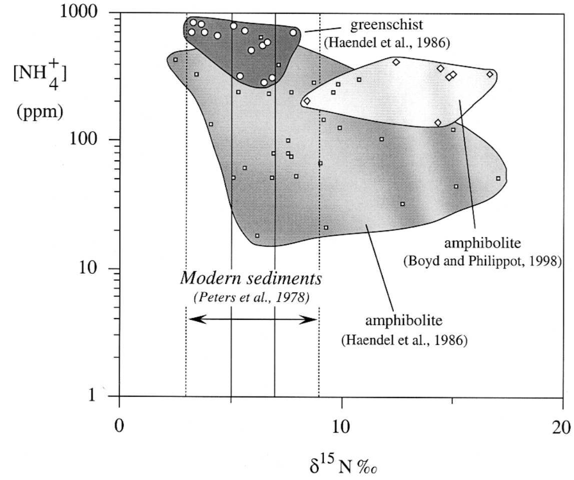

Fig. 7. The content and isotope composition of ammoniacal nitrogen in metasedimentary rocks.

sion (Boyd and Philippot, 1998). Because the rocks have been metamorphosed in amphibolite facies, one can be sure that the $\delta^{15}N$ values were altered during metamorphism. However, due to uncertainties regarding the extent of nitrogen isotope fractionation during metamorphism, all one can say at the present time is that their original values lay somewhere to the upper left of their current position on the diagram. Thus, the nitrogen isotope compositions of the organic matter in the Moine sedimentary basin were probably similar to modern sediments.

4. The Precambrian

Up to present, very little work has been completed on the Precambrian. Beaumont and Robert (1999) studied the organic matter trapped within ancient cherts. The samples had been powdered and dissolved in strong acids (HF/HCl) so any NH_4^+ would have been removed to leave the acid-resistant kerogen. For most of the Precambrian, the authors obtained positive $\delta^{15}N$ values, similar to today, however a number of the earliest Archean samples gave negative ^{15}N values. The results were consistent with anoxia in the earliest Archean (e.g. Kasting, 1993; Holland, 1994), and a different nitrogen cycle that produced organic matter with negative $\delta^{15}N$ values.

Isotope studies of NH_4^+ have been restricted to the Neoproterozoic (Haendel et al., 1986; Boyd and Philippot, 1998) and the positive $\delta^{15}N$ values are again consistent with active denitrification (Fig. 7). However, this may not be surprising because nitrogen is cycled rapidly on a geological time scale. Indeed, the cycling is so fast that the inputs of fixed nitrogen to the marine basin (Fig. 1) would totally deplete atmospheric nitrogen in about 35–100 Ma, if nitrogen was not lost from the marine basins by denitrification (Sweeney et al., 1978; Jaffe 1992; Boyd, 2001). Furthermore, it is generally accepted that the exterior regions of the Earth were oxidising by the Neoproterozoic (e.g. Kasting, 1993; Holland, 1994), hence it is almost certain that the predominant inorganic nitrogen-bearing species in the oceans would have been NO_3^-. Thus, it is likely that the basic biogeochemical processes in Neoproterozoic oceans were the same as those observed today. However, there is a severe lack of data from older rocks.

Despite the lack of isotope data, high NH_4^+ contents have been reported in older Proterozoic rocks (Itihara and Suwa, 1985), and also the 3.8 Ga Isua metasediments (Honma, 1996). Clearly, isotope measurements would be desirable for these rocks, however it is important to distinguish between 'primary ammonium', that has been formed by the in situ decomposition of ancient organic matter, and 'secondary ammonium', that has been introduced by later fluids. This will be especially true for very old metasediments.

5. Primary and secondary ammonium

Ammonium is highly soluble, and studies of granites have revealed that it can be readily introduced by hydrothermal fluids (Hall, 1999). This can result in NH_4^+ being introduced into igneous rocks that are not directly related to sediments. It has already been noted that seawater NH_4^+ can be introduced into basalts at ocean ridges (Hall, 1989), and Hall and Stamatakis (1992) also report very high NH_4^+ concentrations in zeolitized tuffs from Greece (up to 600 ppm). Such anomalies are relatively easy to identify, because one is finding biological fragments in igneous rocks. However, it cannot be ruled out that metasedimentary rocks have also been affected by fluids, which may be far more difficult to identify.

An advantage of NH_4^+ over carbon and sulphur is that it behaves like a trace element in crustal processes, and there are strong links to mineralogy and petrology. Organic matter collects in low energy marine environments, which are dominated by clay minerals. Conversely, in high-energy environments, the sediments may be dominated by quartz/feldspar sands, with any organic matter being washed away by currents. Following diagenesis, metamorphism, and the conversion of organic matter to NH_4^+, this may lead to garnet-muscovite-biotite-schists, in which the biotites have high NH_4^+ contents, and psammitic bands in which the biotites have low NH_4^+ contents. For example, garnet-two mica schists from the Moine

Succession (Scotland) have high NH_4^+ contents, whereas biotite schists (muscovite and garnet free) may have negligible NH_4^+ contents (Boyd and Philippot, 1998). These features were taken as being good evidence for primary NH_4^+, formed by the in situ decomposition of indigenous organic matter, and also for the preservation of sedimentary features in amphibolite facies rocks.

If mineralogical and petrological controls can be used to show that the NH_4^+ in a metasedimentary rock is primary, then other components, such as grains of graphite or sulphide would also have been shown to be primary. However, if a sequence of rocks had been affected by secondary fluids then any mineralogical/petrological controls may have been totally disrupted, which may lead to disequilibrium mineral assemblages (in terms of the partitioning of ammonium and $\delta^{15}N$ between co-existing minerals). For example, micas and feldspars were grossly out of equilibrium in the chloritised granite (R20) studied by Boyd et al. (1993). For these reasons, future work on Precambrian metasediments will need to be detailed case studies, where the mineralogy and petrology of the rocks are taken into consideration in order to establish the origin of the NH_4^+.

6. The justification of uniformitarianism

The interpretation of stable isotope ratios often assumes uniformitarianism, where present day biological processes are considered to be similar to those that have acted in the past, and the justification for this is considered briefly. For nitrogen, not only does one need to consider the isotope ratios, but also the formation of NH_4^+. For example, can it be assumed that there were no abiogenic sources of NH_4^+ in the earliest Precambrian?

6.1. Abiogenic sources of NH_4^+ in the earliest Precambrian

The Hadean Earth would have witnessed a continual bombardment by meteorites, and larger objects. The carbonaceous meteorites are rich in amino acids (e.g. Shock and Schulte, 1990), and it is known that purely thermal processes can lead to the formation of NH_4^+ from organic matter (e.g. Williams et al., 1992). Thus, it is possible that abiogenic NH_4^+ may have been formed on the earliest Earth. In the presence of hydrothermal systems, this NH_4^+ may have been incorporated into crustal rocks (similar to 'secondary ammonium'), where it may have survived crustal processing. It is unlikely that any would remain today, but if so, it may not necessarily be present in metasediments, and may have unusual $\delta^{15}N$ values (e.g. Pizzarello et al., 1994).

6.2. Uniformitarianism and evolutionary biology

6.2.1. Carbon

The near constant partitioning of the carbon isotopes between organic matter and carbonate has been used as evidence for the antiquity of life (Schidlowski, 1988; Mojzsis et al., 1996). In particular, this interpretation implies the longevity of photosynthesis, and of the enzyme ribulose-1, 5-bisphosphate carboxylase oxygenase (rubisco), because the latter is responsible for the large fractionation of the carbon isotopes.

Many criticisms can be raised, because biological systems evolve with time, and inorganically precipitated graphite may have $\delta^{13}C$ values similar to graphite formed from the degradation of organic matter (e.g. Naraoka et al., 1996). However, one can appeal to aspects of evolutionary biology to begin to show why past and present organisms may give similar isotope variations. Consider the case of ancient organic matter and modern C_3 plants.

Photosynthesis in modern green plants occurs in chloroplasts, and leads to $\delta^{13}C$ values close to $-25‰$, similar to ancient values. Perhaps the most popular model for the origin of chloroplasts is that they resulted from the incorporation of cyanobacteria into larger prokaryotes (e.g. Margulis and Sagan, 1997; Margulis, 1998). This may have been by infection, or the cyanobacteria may have been 'eaten' and survived. The two organisms then established a symbiotic relationship with the waste products of one becoming the food for the other. Eventually the relationships became so intricate that they evolved into a single species. Evidence is based around the similarities between chloroplasts and modern eubacteria. For example, chloroplasts reproduce by splitting, reminiscent of fission in bacteria, and the DNA of chloroplasts is more similar to the DNA of modern bacteria, than the DNA in the nucleus of the host plant. Thus, one can begin to see why ancient and modern samples may be very similar. The basic biochemistry of photosynthesis was established early on in some common ancestor, and has become widely distributed during evolution. Indeed, rubisco is the probably the single most abundant protein in the biosphere (e.g. Williams, 1996).

6.2.2. Nitrogen

Similar reasoning can be applied to the nitrogen cycle because widely different organisms contain similar enzymes, and it is the enzymes that control the isotope composition of nitrogen. For example, nitrogen fixation occurs in a wide variety of organisms (e.g. Sprent, 1987; Sprent and Sprent, 1990), however all contain dinitrogenase, dinitrogenase reductase, glutamine synthetase (GS), and glutamine-2-oxoglutarate-amino-transferase (GOGAT), and again one can appeal to some common ancestor. If it can be shown that the basic biochemistry responsible for the fractionation of the nitrogen isotopes was established very early on, then all of the variations that one observes in Precambrian samples would be palaeo-environmental (water depth, atmospheric chemistry, season etc.).

The application of uniformitarianism to the formation of NH_4^+ in ancient sediments also needs consideration. Fig. 8A shows the basic requirements (in terms of enzymes) for the production of NH_4^+ in modern sediments. The formation of NH_4^+ (in cells) from nitrogen gas and dissolved nitrate implies the action of dinitrogenase and dinitrogenase reductase, and nitrate reductase and nitrite reductase, respectively. Incorporation of the NH_4^+ into carbon skeletons involves glutamate dehydrogenase, glutamine synthetase, glutamine-2-oxoglutarate-amino-transferase, and numerous other amino transferases. Assuming that the organic matter was degraded by heterotrophic bacteria, this would again imply numerous amino-transferases and glutamate dehydrogenase for the final deamination stage of mineralisation.

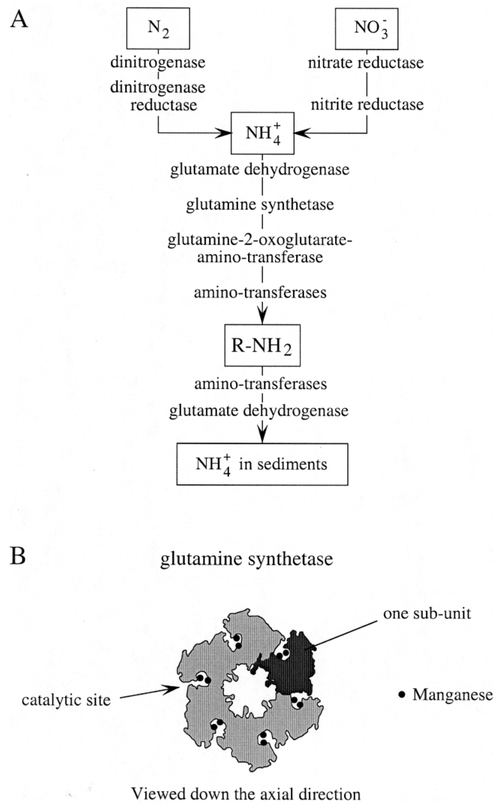

Fig. 8. A, the enzymes involved during the formation of organic matter, and its subsequent conversion to ammonium in sediments. B, the structure of glutamine synthetase.

Fig. 8B shows the complex structure of glutamine synthetase, which highlights that the application of uniformitarianism to the NH_4^+ in Precambrian rocks implies highly developed biological systems, as has already been noted for mildly altered Archean rocks (e.g. Schopf, 1993).

Further consideration of glutamine synthetase raises other considerations for a Hadean Earth. The enzyme is comprised of 12 sub-units (there are six beneath those shown in Fig. 8B), and each sub-unit consists of a polypeptide chain of 51 628 Da (Pelmont, 1995). Thus, glutamine synthetase is composed of strings of amino acids and is produced by living organisms. Clearly, complex enzymes such as glutamine synthetase could not have been present during the earliest days of the Earth, but have evolved with life. Therefore, the first amino acids were either formed in space, and brought to Earth in meteorites, or they were formed on Earth abiogenically, implying the action of inorganic catalysts in the prebiotic, Hadean world.

7. For the future

All aspects of nitrogen geochemistry and biogeochemistry remain under-developed. For crustal NH_4^+, part of the reason is that the analyses of silicate minerals are quite difficult (especially for isotopes), and that detailed case studies require a fairly large data set. A great advance would be the calibration of infra-red (FTIR) microscopes (Boyd, 1997) which would allow many samples to be analysed (50 per day) and would help when selecting grains for isotope analysis. Similarly, standard minerals for NH_4^+ analyses do not exist and one has to synthesise batches in the laboratory (Boyd and Pillinger, 1991). The characterisation of a set of international standards and the calibration of infrared microscopes could probably be achieved at the same time.

A better understanding of the present nitrogen cycle would be desirable, but this should not stop the continued analysis of Precambrian rocks, because so little is known. All aspects of the geochemistry of NH_4^+ in crustal rocks need to be considered, including

1. The partitioning of NH_4^+ and $\delta^{15}N$ between co-existing minerals in pristine rocks.
2. The mechanisms of nitrogen isotope fractionation during metamorphism.
3. The preservation of sedimentary features in metamorphic rocks.
4. The behaviour of NH_4^+ during partial melting (pegmatites, granites).
5. NH_4^+ in granulite facies rocks.
6. Establishing the links between NH_4^+ and mineralogy/petrology.
7. Establishing the links between NH_4^+ and other geochemical tracers including Sr, O, K, Al.
8. The recognition of primary and secondary NH_4^+.

It would be desirable to find several key geological settings where one could study the basic geochemistry of NH_4^+, and then apply the results to numerous Precambrian settings.

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