# Isotopic differences and paleoenvironmental significance of nitrogen contained in bulk sedimentary rocks, decarbonated aliquots and kerogen extracts

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## Abstract

The stable nitrogen isotopic composition ($\delta^{15}N$) of sedimentary rocks is an important tool for reconstructing the paleo-oceanic nitrogen cycle and has been widely used in palaeoenvironmental studies of the Precambrian and Phanerozoic. Currently, the commonly used parameters are the isotopic compositions of decarbonated samples ($\delta^{15}N_{DCN}$) and kerogen extracts ($\delta^{15}N_{kerogen}$). However, some studies have shown that there are differences between these two proxies. In addition, differences were found between $\delta^{15}N_{DCN}$ and the nitrogen isotopic compositions of untreated samples ($\delta^{15}N_{bulk}$). In order to explain these phenomena, we selected sedimentary rock samples from different time periods in the Phanerozoic and analyzed nitrogen isotopes after all three treatments (bulk rock, decarbonated rock, and kerogen extracts). We find that (1) $\delta^{15}N_{bulk}$ is greater than $\delta^{15}N_{DCN}$ in most samples by 0.6‰ on average, indicating that acid-soluble organic N with higher $\delta^{15}N$ values was lost preferentially during decarbonization; (2) $\delta^{15}N_{DCN}$ is greater than $\delta^{15}N_{kerogen}$ mainly in anoxic environments, which may be linked to ammonium accumulation in pore fluids or in the water column during deposition and/or diagenesis. For example, the anaerobic ammonia oxidation process and partial assimilation preferentially consume $^{14}NH_4^+$ and enrich $^{15}NH_4^+$ in seawater. Therefore, $NH_4^+$ fixed by clay minerals has a higher $\delta^{15}N$ than organic nitrogen; (3) $\delta^{15}N_{kerogen}$ greater than $\delta^{15}N_{DCN}$ was observed in a subset of samples and may reflect either preferential release of $^{14}NH_4^+$ from organic matter or biological production of isotopically light $NH_4^+$, followed by adsorption to clay minerals. In this case, the $\delta^{15}N$ of residual organic nitrogen would be relatively high compared to the released $NH_4^+$. However, this scenario is only retained in samples that have not undergone significant post-depositional alteration, which tends to lower

$\delta^{15}N_{kerogen}$ and increase $\delta^{15}N_{DCN}$. Differences between the three nitrogen parameters are in many cases small and would not alter overall paleoenvironmental interpretations; however, in some cases, they can be significant and carry additional information about diagenetic conditions that may be unlocked with additional studies on wider range of deposition environments.

**Keywords:** Nitrogen isotopes; Palaeoenvironment; Kerogen; Nitrogen cycle; Diagenesis

## 1. Introduction

Nitrogen is essential to all living organisms, because it is a major component of proteins and nucleic acids. Reconstructing the biogeochemical nitrogen cycle in deep time is therefore an important aspect of deciphering the evolution of life over Earth's history. The dominant processes in the marine nitrogen cycle are $N_2$ fixation, denitrification, assimilation of nitrate or ammonium, remineralization of biomass into ammonium, and nitrification (Altabet, 2006). $N_2$ fixation is the main source of nitrogen in the oceans and converts dissolved $N_2$ gas into organic-bound amines. Ammonification and remineralization transform organic N into inorganic ammonium. In the presence of $O_2$, ammonium is rapidly converted to nitrate ($NO_3^-$) via nitrification. Nitrate is thus the dominant form of nitrogen in the modern ocean and the major nutrient for plankton. Denitrification, which occurs under suboxic conditions in oxygen-minimum zones and sedimentary pore waters, converts nitrate back to $N_2$ gas and is the major mechanism of fixed N loss from seawater (Sigman et al., 2009). A small fraction of organic N escapes remineralization in the water column and gets buried in marine sediments. In anoxic settings where nitrate is scarce, this organic N may be derived from $N_2$-fixing or ammonium-assimilating organisms. The Black Sea and some anoxic lakes are examples of this scenario (Fulton et al., 2012). In contrast, under nitrate-replete conditions, such as the modern ocean, organic N is often derived from nitrate assimilators (Tesdal et al., 2013). In either case, ammonium is released during post-depositional diagenesis, which may be trapped in clay minerals. Sedimentary rocks therefore typically contain both organic amines and clay-bound ammonium (Mueller, 1977).

The various transformations of nitrogen forms are accompanied by isotopic fractionations recorded in the $^{15}N/^{14}N$ ratio (Altabet, 2006). The nitrogen isotopic composition (expressed in delta notation: $\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{air} - 1] \times 1000$) is therefore regarded as a key indicator for reconstructing environmental processes. The $\delta^{15}N$ value of sedimentary biomass typically reflects the isotopic composition of the major N nutrient. In the modern ocean, $\delta^{15}N$ thus captures variations in the isotopic composition of $NO_3^-$ in the water column (Altabet and Francois, 1994; Sigman et al., 2000; Casciotti et al., 2016), while in anoxic basins with limited nitrate, it reflects the isotopic composition of diazotrophs ($N_2$-fixers) (Fulton et al., 2012). In the past two decades, nitrogen isotopes have been widely used as important tracers of the global biogeochemical nitrogen cycle (Ader et al., 2016; Sun et al., 2019), the redox structure (Knies et al.,2013), the changes in marine primary productivity (Du et al.,2021), and the origin of key nitrogen metabolisms over Earth's history (Godfrey and Falkowski, 2009; Stüeken et al., 2021).

The nitrogen content is generally low in sedimentary rocks. The use of hydrochloric acid to remove carbonates can increase the nitrogen content in rock powders and reduce the weight of the sample required for analysis. Therefore numerous studies have measured the nitrogen

isotopic composition of decarbonated rock powders ($\delta^{15}N_{DCN}$) (e.g., Luo et al., 2018; Stüeken and Prave, 2022; Du et al., 2023). In addition, the nitrogen isotopic composition of kerogen isolates ($\delta^{15}N_{kerogen}$) has received increasing attention (Godfrey and Falkowski, 2009; Stüeken et al., 2015; Luo et al., 2016; Song et al., 2023). However, debate continues about how to interpret $\delta^{15}N$ values of various sample residues (Mettam and Zerkle, 2021; Fujisaki et al., 2022). Compared with untreated samples, DCN samples may have lost some of the N bound to acid-soluble clays; kerogen N only includes nitrogen compounds of insoluble organic matter. Recent studies found that the isotopic offset between $\delta^{15}N$ of kerogen and silicates increases with metamorphic grade (Stüeken et al., 2017) and during hydrothermal fluid alteration (Godfrey et al., 2013), but it may also be enhanced by early-diagenetic microbial process (Freudenthal et al., 2001).

To further elucidate this debate and identify the controls of these three proxies, we collected and analyzed sedimentary rock samples from different ages of the Phanerozoic. DCN samples and kerogen extracts were prepared and analyzed following standard protocols. We found that differences in the $\delta^{15}N$ between residues are influenced by the original sedimentary environment and diagenesis. Considering isotopic composition of nitrogen between the bulk samples and the two types of residues together may allow more accurate reconstruction of the original seawater nitrogen isotopic composition. Our preliminary results can facilitate future paleo-environmental studies.

## 2. Samples

The samples taken for this study represent different time periods in the Phanerozoic eon. These samples contain a variety of lithologies, and most of them have relatively high organic carbon (TOC) and total nitrogen (TN) content. Three shale samples come from the Lower Silurian Longmaxi Formation (e.g. Wang et al., 2016); one shale sample comes from the Lower Triassic Yue 101-89-X1 Well; three mudstone samples (which contain plant detritus) are from the Lower Triassic Chang 7 Member (e.g. Yuan et al., 2015); two shale samples are from the Lower Jurassic Da'anzhai Member (e.g. Xu et al., 2017); four lime mudstone samples come from the Upper Cretaceous Qingshankou Formation (e.g. Fu et al., 2022); two lime mudstone samples come from the Upper Cretaceous Nenjiang Formation (e.g. Liu et al., 2022). None of these sample sets have experienced significant metamorphism. More information is shown in Supplementary Table S1.

## 3. Methods

The extraction processes for different nitrogen proxies have been well studied and improved over the past decades. Based on the current research status, we provide a more complete route for the extraction of the three nitrogen proxies (Fig. 1). The acid treatment process mainly includes the rinse method and the capsule method (*in situ* acidification in a silver capsule to remove the carbonate, e.g. Brodie et al., 2011). During the acidification or drying processes in the capsule method, there is a risk that air-derived $NH_4^+$ may be adsorbed onto clay minerals within the sample (Fujisaki et al., 2022). In addition, the capsule method may produce a large number of inorganic chloride salts, which may impact the analyses. Therefore, the rinse method is preferable for $\delta^{15}N_{DCN}$, For $\delta^{15}N_{kerogen}$, we recommend referring to the process in GB/T 19144-2010 to obtain purer kerogen. This method can be used to

separate pure kerogen from a range of sedimentary rocks (mudstone, shale, carbonate).
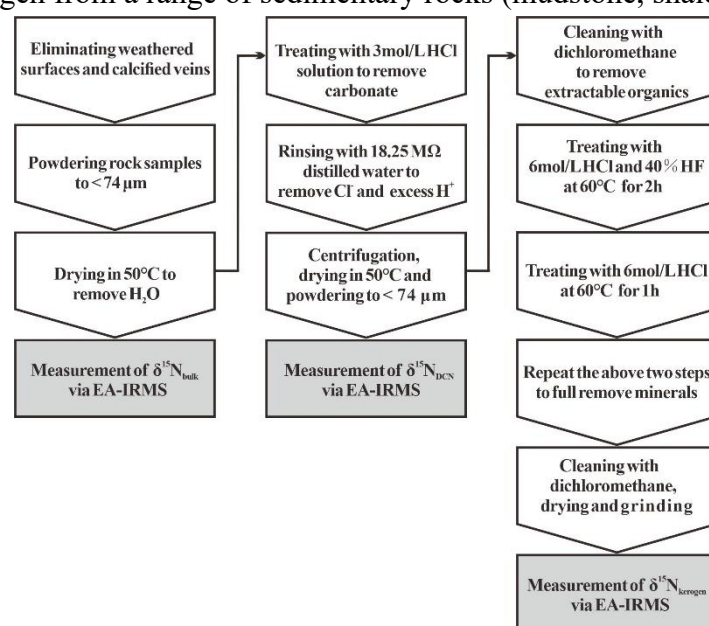


**Fig. 1. Flow-chart for the preparation of samples for nitrogen analyses in bulk rocks (left), decarbonated residues (middle) and kerogen isolates (right).**

### 3.1. Decarbonated process

For each rock sample, weathered surfaces were cleaned off before the rocks were powdered to < 74 μm using a ball mill. For decarbonation, 0.5~1 g of powder was weighed into a centrifuge tube and treated with 3 mol/L HCl. The acid was left to react overnight in the fume hood and then decanted. The decarbonated powder was rinsed multiple times with 18.25 MΩ/cm distilled water to remove excess acid. After each rinse, the samples were centrifuged at 3000 r/min before decanting the water. Finally, the samples were dried in an oven at 50°C.

### 3.2. Kerogen extraction

The method for kerogen extraction was adapted from the Chinese National Standard GB/T 19144-2010. Depending on the total organic carbon (TOC) content, approximately 30-50 g of powdered samples (< 74 μm) was added to the Soxhlet extractor to clean off extractable organics with dichloromethane. The cleaned samples were transferred to polytetrafluoroethylene beakers and soaked in distilled water for 4 hours. The samples were subsequently treated with 6 mol/L HCl and 40% HF to remove most minerals, including carbonate and most silicate phases. The powder sample has been fully decarbonated using hydrochloric acid in the previous steps (Fig. 1). The subsequent acid treatment in the Soxhlet extractor can be divided into four steps: 1) A mixture of 6 mol/L HCl and 40% HF was added into the beaker at a ratio of 2.4 mL HCl /3.6 ml HF for 1 g sample. The mixture was stirred at 60 °C for 2 h and then the acid solution was removed. The samples were rinsed with 1 mol/L HCl three times, and the supernatant was removed. 2) At a ratio of 6 ml HCl for 1 g of sample, 6 mol/L of HCl was added into the beaker while stirring. The mixture was stirred at 60 °C for 1 h and then the acid solution was removed. The samples were rinsed with 1 mol/L HCl three times and the supernatant was removed. 3) The first step was repeated but with an increased stirring time of 4 h. 4) Lastly, the second step was repeated. Finally, the samples were rinsed

with distilled water until the pH was approximately 7 and the supernatant was removed again. Subsequently, the samples were centrifuged at 3000 r/min and dried in an oven at 50 °C. The dried samples were cleaned again with dichloromethane in a Soxhlet extractor to remove soluble organic matter. The resulting kerogen residue was first air-dried and then thoroughly dried in an oven at 50°C, followed by weighing and homogenizing with a glass rod.

*3.3 Analytical methods*

Total nitrogen (TN), Total organic carbon (TOC), and nitrogen isotope ($\delta^{15}$N) analyses of untreated samples, decarbonated samples, and kerogen extracts were conducted at the State Key Laboratory of Biogeology and Environmental Geology (BGEG) of the China University of Geosciences, Wuhan. The concentrations (TOC and TN) of all samples were analyzed by a thermal conductivity detector of a Vario Macro Cube elemental analyzer (Elementar, Hanau, Germany) (Du et al., 2021). Uncertainties determined by duplicates of sulfanilamide are better than 5% relative error for TOC and TN. The $\delta^{15}$N was measured using Flash HT 2000 Plus coupled to a continuous-flow Delta V Advantage IRMS (Thermo Fisher Scientific) (Du et al., 2021). Briefly, 20-50 mg of powder was packed into tin capsules and combusted at 960°C. Standard reference materials USGS40 ($\delta^{15}$N$_{AIR}$ = –4.52‰) and IAEA-N-2 ($\delta^{15}$N$_{AIR}$ = +20.3‰) were used for $\delta^{15}$N calibration with a precision of duplicate analyses better than 0.2‰. The isotopic tests were repeated three times for each sample and $\delta^{15}$N was averaged for a better accuracy. For most samples, the differences between replicate analyses were less than ±0.2‰ (Supplementary Table S2).

**4. Results**

All data for TOC, TN and $\delta^{15}$N are shown in Supplementary Table S2. The range of TOC of the analysed samples from the Phanerozoic is 0.12-5.48 wt.% and the range of TN is 0.03-0.61 wt.% (Fig. 2a), covering a wide range of C and N content. There is no correlation between K content and TN in these samples (Fig. 2b). The $\delta^{15}$N$_{bulk}$ also has no correlation with either K content or Al/K (Fig. 2c-d). For most rock samples, decarbonated aliquots (treated with HCl) contain less nitrogen than untreated samples (Supplementary Table S2), and the proportion of nitrogen loss during acid treatment varies between 5.5% and 27.8% (average 13.5%). There is no correlation between nitrogen loss and carbonate or TOC contents in the samples (Fig. 2e-f). In the kerogen extracts, TOC ranges from 14.46 to 82.31 wt.% (average 50.74%) and TN ranges from 0.19 to 2.31 wt.% (average 1.03%). The reason for the lower TOC content in some of our kerogen extracts may be due to the presence of minerals that are difficult to remove by HF and HCl, such as pyrite and some heavy oxides (e.g. zircon). We note that these minerals do not affect the nitrogen isotopic compositions of the kerogen (Durand and Nicaise, 1980; Vandenbroucke and Largeau, 2007). For example, the kerogen with the lowest TOC in this study was from Chang 7 Member, which reportedly has high pyrite content (Yuan et al., 2015).

We found a large difference in C/N ratios (calculated as TOC/TN) between the kerogen samples and the decarbonated samples (7.2 times larger on average), which is expected given the fact that the HF treatment dissolves most silicate minerals and thus leads to the loss of silicate-bound NH$_4^+$ and elevated C/N.
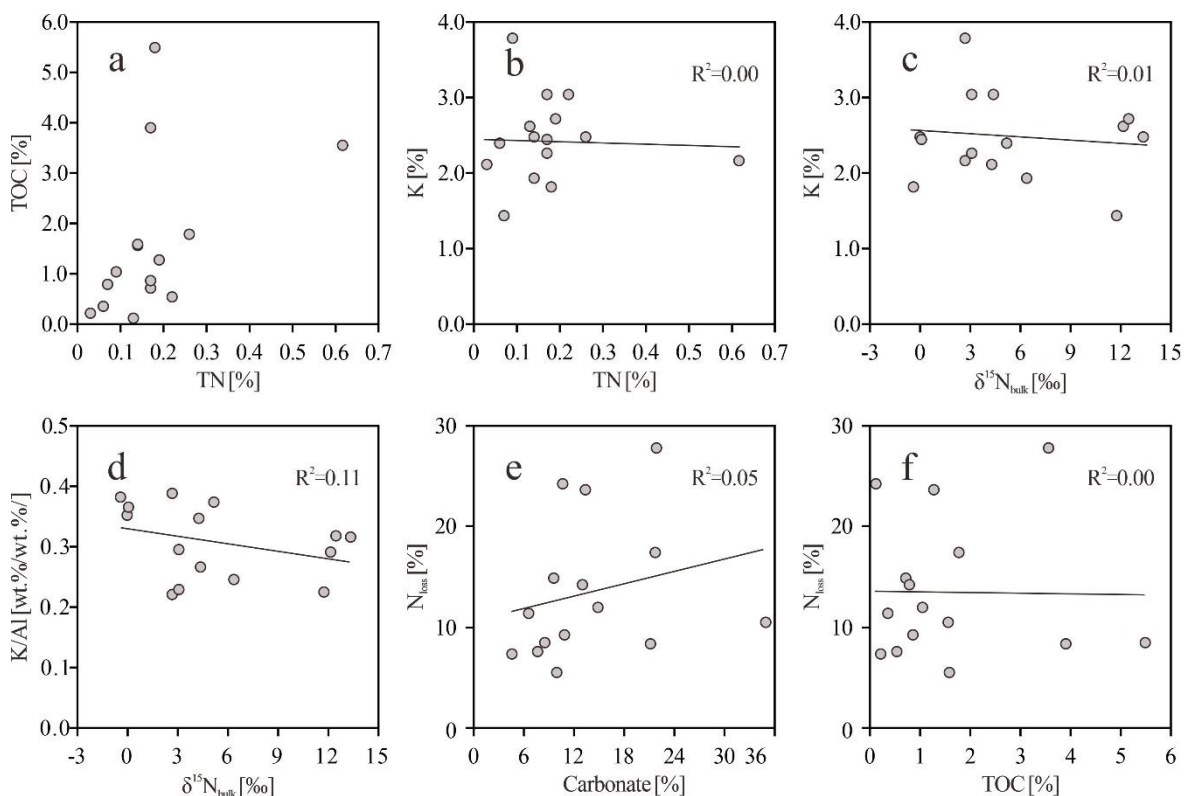
**Fig. 2. Cross-plots of geochemical data of the samples. Data show: (a) Total organic carbon (TOC) versus total nitrogen (TN), (b) K versus TN, (c) K versus $\delta^{15}N_{bulk}$, (d) K/Al versus $\delta^{15}N_{bulk}$, (e) $N_{loss}$ versus Carbonate, (f) $N_{loss}$ versus TOC.**

Our samples display a wide range of nitrogen isotope values, extending from -1.6‰ to +13.4‰ (Supplementary Table S2). There are differences in $\delta^{15}N$ between the bulk and two residues for the same sample as shown in Fig. 3. The average difference between DCN samples and bulk samples was 0.6‰, with the former slightly lower than the latter. The mean difference between kerogen and DCN samples was 1.9‰, where kerogen is mostly lower than DCN.
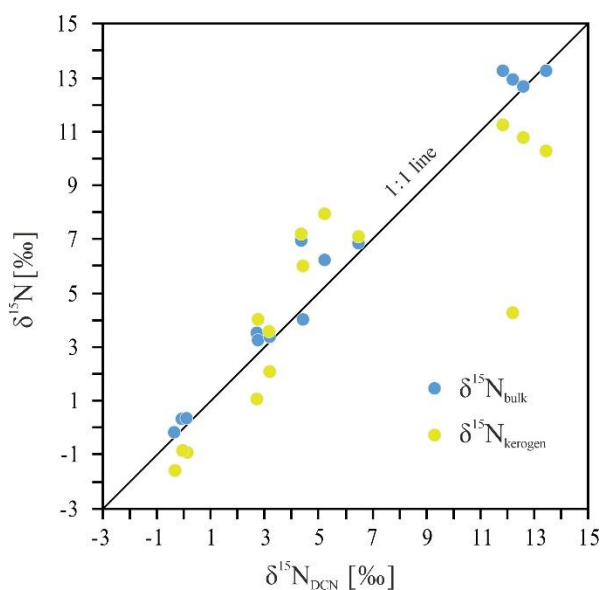


**Fig. 3. Nitrogen isotopic composition of the three nitrogen sample types.**

# 5. Discussion

## 5.1 Origin and evolution of nitrogen in sedimentary rocks

Nitrogen in sedimentary rocks exists mainly in two different forms, which are organic- (or kerogen-) bound amines and mineral-bound ammonium. The latter ($NH_4^+$) generally substitutes for $K^+$ in mineral lattices or is adsorbed on mineral surfaces, particularly clays. The possible sources of nitrogen in sediments thus include biomass burial, adsorption of ammonium (mostly derived from organic matter degradation *in situ*) onto clays, and detrital ammonium-bearing minerals. In organic-rich sediments, sinking organic matter is usually the most important nitrogen source, and this component evolves during biogeochemical and geological processes (Fig. 4). Understanding the sources of nitrogen in rocks is critical to identifying the original nitrogen signal of the paleo-ocean.

**Fig. 4. Major processes in the modern marine nitrogen cycle (adapted from Hutchins and Capone, 2022). Nitrogen isotope fractionations ($\varepsilon_{product-\ reactant} \sim \delta_{product} - \delta_{reactant}$) are from the compilations of Ader et al. (2016).**

Organic nitrogen in sedimentary rocks is derived from organic matter accumulated during sedimentation, mainly in the form of heterocyclic nitrogenous organic compounds. Patience et al. (1992) identified at least four nitrogen-containing functional groups in the surface sediments of the Peru upwelling region, including amino, pyrrole, pyridine and quaternary nitrogen ($R_4N^+$). These groups are derived from nitrogenous compounds such as proteins, nucleic acids and phytochromes. These primary forms of nitrogen are usually altered during early diagenesis, burial diagenesis and metamorphism (Ader et al., 2016). During early diagenesis, a portion of the nitrogenous organic matter is converted to inorganic ammonium and can accumulate to high concentrations within sedimentary pore waters (Prokopenko et al., 2006). Some of this ammonium may diffuse upwards and undergo reoxidation to nitrite and nitrate (Sigman et al., 2009). Thermal maturation of organic matter during burial diagenesis leads to further ammonium release and adsorption of ammonium onto clay minerals, particularly illite, which forms during late diagenesis (Williams et al., 1995; Schimmelmann and Lis, 2010). While organic nitrogen in sedimentary rocks of low metamorphic grade is predominantly in the form

of pyrroles or pyridines, the relative abundance of N-C$_3$ aromatic heterocyclic structures, where nitrogen is covalently bound to three carbon atoms, increases exponentially during metamorphism (Boudou et al., 2008). There are large differences in the properties of different types of nitrogen-containing organic molecules in sedimentary rocks. Soluble organic nitrogen mainly includes neutral pyrrole compounds and basic pyridine compounds (Richter et al., 1952), whereas kerogen holds insoluble nitrogenous organic matter.

The ammonium that is released and trapped in clays during organic matter degradation can constitute the major component of nitrogen in sedimentary rocks (Robinson et al., 2012). Hall (1999) divided inorganic sedimentary nitrogen into two forms: exchangeable-NH$_4^+$, which adsorbs onto organic and mineral surfaces or occupies interlayer sites in clay minerals through ion exchange reactions, and fixed-NH$_4^+$, which enters the crystal structure of silicate minerals. The exchangeable-NH$_4^+$ content is generally low and typically accounts for less than 1% of the total nitrogen in pelagic sediments (de Lange, 1992). When sediments undergo diagenesis and lithification, fixed-NH$_4^+$ is the most dominant form of inorganic nitrogen. Like organic-bound amines, some fixed-NH$_4^+$ can be converted to N$_2$ or NH$_3$ during metamorphic devolatilization, but a small fraction may be preserved even in high-grade metamorphic rocks in minerals such as micas and feldspars (Bebout and Fogel, 1992).

*5.2 δ$^{15}$N$_{bulk}$ and δ$^{15}$N$_{DCN}$*

In our study, δ$^{15}$N$_{bulk}$ represents the nitrogen isotopic compositions of untreated samples, and δ$^{15}$N$_{DCN}$ represents the nitrogen isotopic compositions of acid-treated samples. Acid treatment removes carbonate and thus allows measuring nitrogen and organic carbon isotopes. In this study, we expanded this approach to a suite of Phanerozoic rocks samples, and we found variable effects: the differences between δ$^{15}$N$_{bulk}$ and δ$^{15}$N$_{DCN}$ (defined as δ$^{15}$N$_{bulk}$ - δ$^{15}$N$_{DCN}$) of five samples are less than 0.2‰, which are within the analytical uncertainty of the measurement; the differences of four samples are between 0.3‰-0.4‰, which are slightly higher than the analytical uncertainty of our study, but within two standard deviations from each other; larger differences of 0.5‰-2.6‰ occur in six our samples (Fig. 5). For comparison, Wang et al. (2018) analysed untreated samples and HCl acid-treated samples from the Siduping section (TOC ranges from 0.82 to 4.14 wt.%) and Wuhe section (TOC ranges from 0.47 to 1.39 wt.%) for nitrogen isotopic composition and found a difference in δ$^{15}$N of 1‰-3‰ between these two kinds of samples. The reason for this slightly larger difference compared to our results could be that Wang et al. (2018) used the fumigation method.

Both inorganic and organic nitrogen may be lost during acid treatment. Inorganic nitrogen (NH$_4^+$) mainly exists in silicate minerals, such as illite, montmorillonite and mica. The treatment with strong acids may cause the silicate minerals to dissolve or change in structure (Terry, 1983), leading to NH$_4^+$ loss. For example, biotite in 2 mol/L HCl at 31℃ can show a structural collapse and high solubility (Gastuche and Fripiat, 1962). In addition to silicate minerals, Wang et al. (2018) suggested that the loss of carbonate-associated N during acidification and rinse was also a possible reason; however, this explanation would primarily be applicable in carbonate rocks and is therefore probably not relevant to our study, which was focused on siliciclastic sediments (the carbonate content of our samples is 5%~35%). Fujisaki et al. (2022) suggested that acid-soluble nitrogenous organic matter may also be lost during acid treatment. The acid-soluble organic matter in rocks is defined as bitumen (Durand and

Nicaise, 1980), and soluble organic nitrogen may have a high content in immature samples. The main basic nitrogen-containing group in rock samples is pyrrole, and substances containing pyrrole groups may be soluble in acid treatment.
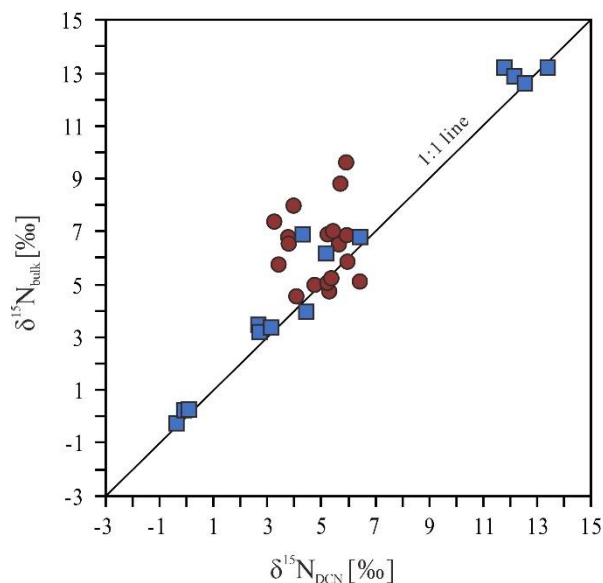


**Fig. 5. $\delta^{15}N_{bulk}$ versus $\delta^{15}N_{DCN}$. Blue squares represent data from this study and red circles represent data from Wang et al. (2018).**

Most of the samples have higher $\delta^{15}N_{bulk}$ than $\delta^{15}N_{DCN}$ (Fig. 4), which indicates that the nitrogen fraction lost during acid treatment is slightly enriched in $^{15}N$. $^{14}NH_4^+$ tends to be released preferentially during remineralization and organic matter maturation, making early diagenetic silicate minerals isotopically lighter, as they absorb some of this isotopically light $NH_4^+$ (Sigman and Casciotti, 2009; Schimmelmann and Lis, 2010). Hence if these early diagenetic clays had been lost during HCl treatment, this should have caused the opposite effect to the actual result. During metamorphism, the $\delta^{15}N$ of fixed-$NH_4^+$ increases (Stüeken et al., 2017), meaning that the loss of such slightly higher-grade clays could potentially explain the results. However, the rock samples in this study were not significantly affected by metamorphism, making this explanation unlikely. Instead, the most plausible reason for the isotopic difference between untreated and decarbonated powder aliquots is the loss of organic nitrogen present in the acid-soluble bitumen. For example, two samples (XT-14 and XT-15) from the Nengjiang Formation have 1‰ and 2.6‰ offsets between $\delta^{15}N_{bulk}$ and $\delta^{15}N_{DCN}$ respectively. These samples have relatively high bitumen content (Fu et al., 2021). This process would be more significant in immature samples with a higher bitumen content, because these samples may contain more nitrogen-rich materials, such as amino acids (Brodie et al., 2011).

Due to the differences in $\delta^{15}N_{bulk}$ and $\delta^{15}N_{DCN}$ of some samples, it is worth considering which nitrogen isotopic composition can be chosen as a proxy for the original paleo-ocean environment. In cases where there are isotopic differences between bulk samples and DCN samples, this may affect the palaeoenvironmental information obtained. For bulk sample analyses, only weathering surfaces and veins are removed, and there is essentially no loss of nitrogen during this process. Therefore, bulk samples contain all kinds of nitrogen present in sedimentary rocks. The biggest problem with bulk samples is the low nitrogen content, which

can in some cases be difficult to analyse. Furthermore, potential surface contaminants may not be washed off as effectively. Therefore, $\delta^{15}N_{DCN}$ (i.e., decarbonated powders) is currently more commonly used in paleoenvironmental studies (Ader et al., 2016; Stüeken et al., 2017; Wang et al., 2018). Compared to bulk samples, DCN samples can lose some of their nitrogen during the acid treatment. DCN samples thus contain mainly fixed-$NH_4^+$ in silicate minerals and nitrogen present in organics that are insoluble in acids. Therefore, some studies have concluded that acid treatment is not necessary for measuring $\delta^{15}N$ (Fujisaki et al., 2022).

At present, The $\delta^{15}N_{DCN}$ is currently used more frequently in palaeoenvironmental studies in the Precambrian and Phanerozoic (Stüeken et al., 2017; Wang et al., 2018; Du et al., 2021). Our results suggest that decarbonation can be detrimental for nitrogen isotope studies of immature rock samples. This conclusion is supported by previous studies which also shown greater alteration during acid treatment of thermally immature sedimentary rocks (Fernandes and Krull, 2008; Kennedy et al., 2005). Meanwhile, it is possibly less of a concern for rocks of higher metamorphic grade that contain relatively more acid-insoluble organic matter. However, we stress that the partial dissolution of silicate minerals (such as biotite) could affect nitrogen isotopes in higher-grade rocks, and this process requires further investigation. In the meantime, we conclude that analyses of paired $\delta^{15}N_{bulk}$ and $\delta^{15}N_{DCN}$ would be advantages when using nitrogen isotopes for paleoenvironmental reconstruction to make the study results more reliable. However, it is also important to note that the small isotopic differences between bulk rocks and decarbonated residues that we found would in many cases not necessarily alter qualitative paleoenvironmental interpretations.

### 5.3 $\delta^{15}N_{DCN}$ and $\delta^{15}N_{kerogen}$

Stüeken et al. (2017) measured nitrogen isotope values of paired kerogen and decarbonated bulk rocks in samples spanning from the Mesoarchean to the Permian and found that the differences between $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{DCN}$ increased with metamorphic grade. The data in our study show the same trend (Fig. 6), with eleven of the fifteen samples from the Phanerozoic having a difference between $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{DCN}$ of more than 1‰ and three samples having a difference between 0.6‰ and 0.8‰. The three samples (XT-1, XT-2 and XT-3) from the lower Silurian Longmaxi Formation analysed in this study show a relatively light nitrogen isotopic composition, and although the difference between $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{DCN}$ averages 1‰, all $\delta^{15}N$ values fall within the range of −2‰ to +1‰, which is typically interpreted as a result of biological $N_2$ fixation. Hence, in this case, the isotopic offset between the two types of sample residues does not alter the overall trend in Figure 6. A similar interpretation was reached by Koehler et al. (2019) who investigated Ordovician-Silurian rocks in southern Scotland. The difference between $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{DCN}$ in their study exceeds 1‰, but most of the samples have $\delta^{15}N$ in the range from −2‰ to +1‰, suggesting that the ocean at that time was dominated by the process of biological $N_2$ fixation due to limited nitrate availability. However, this rule may not apply to all samples. For example, one sample (XT-4) analysed in this study has a $\delta^{15}N_{kerogen}$ of +1‰ and a $\delta^{15}N_{DCN}$ of +2.7‰, where the former falls within the $N_2$ fixation window while the latter could reflect nitrate uptake. Hence using only one particular nitrogen isotope value alone may lead to biased results. Therefore, the simultaneous measurements of $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{DCN}$ for paleoenvironmental reconstruction have been used in many studies (Luo et al., 2016; Zerkle et al., 2017; Kipp et al., 2018; Yang

et al., 2019; Wang et al., 2021). We selected samples from these studies that had both $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{DCN}$, and then plotted these data together with the data from this study (Fig. 6). This analysis shows that there is a significant difference between $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{DCN}$ for most of the samples. From our compilation it appears that the overall average difference between $\delta^{15}N_{DCN}$ and $\delta^{15}N_{kerogen}$ is 1.9‰, which is higher than the difference between $\delta^{15}N_{DCN}$ and $\delta^{15}N_{bulk}$ (0.6‰ on average). One possible reason is the utilization of high concentrations of HF (40%) in the process of kerogen extraction, which may lead to more loss of soluble organic nitrogen. Another possibility is that this isotopic difference reflects environmental processes and conditions during sediment deposition and diagenesis (Ader et al., 2016).
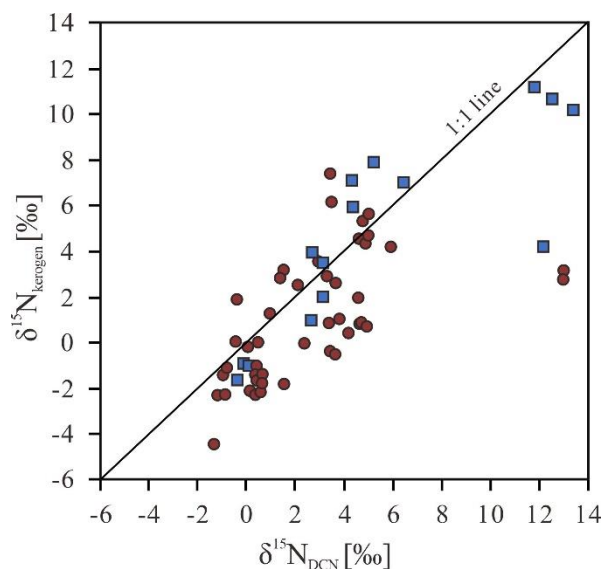


**Fig. 6. The data of $\delta^{15}N_{DCN}$ and $\delta^{15}N_{kerogen}$. Blue squares represent data from this study and red circles represent data from previous studies (Luo et al., 2016; Stüeken et al., 2017; Zerkle et al., 2017; Kipp et al., 2018; Yang et al., 2019; Wang et al., 2021) (2017).**

A number of scenarios could explain why $\delta^{15}N_{DCN}$ is higher than $\delta^{15}N_{kerogen}$ in rocks (Fig. 7a-d). Lack of oxygen in the water column and within sediments is perhaps the main reason. Based previous studies, the samples we collected were deposited in anoxic environments (Li et al., 2021; Chen et al., 2022; Fu et al., 2022; Qiu and He, 2022; Shi et al., 2022). On average, diagenesis of organic matter under anoxic conditions has been shown to not discriminate between nitrogen isotopes (Robinson et al., 2012). However, the rate of nitrification is weaker in anoxic environments, while denitrification and anammox are enhanced. Anammox in particular could potentially explain the observed isotopic effect. $NH_4^+$ and $NO_2^-$ react during anammox, and the resulting $N_2$ is released from the ocean. In this process, $^{14}NH_4^+$ ispreferentially involved in this process, that leads to the increase of $\delta^{15}N$ in the remaining $NH_4^+$ pool (Brunner et al., 2013). This isotopically enriched $NH_4^+$ may become fixed in clay minerals (Prokopenko et al., 2006, 2013), leading to the elevated $\delta^{15}N_{DCN}$ values that we observed (Fig. 7a). As for our sample, the Longmaxi Formation perhaps experienced a higher anammox rate in the nitrogen cycle, leading to the observed isotopic offset (Li et al., 2021).

Another possibility is that $^{14}NH_4^+$ is used preferentially during biological assimilation, leading to$^{15}NH_4^+$ enrichment in seawater. When primary productivity is high in the anoxic

ocean, a large amount of ammonium may accumulate in the water column, derived from biomass decomposition. Subsequent re-assimilation with a preference for $^{14}NH_4^+$ may result in isotopically light organic matter (Papineau et al., 2009). When the residual $^{15}$N-enriched ammonium in seawater is fixed by clay minerals, it leads to $\delta^{15}N_{DCN}$ higher than $\delta^{15}N_{kerogen}$ (Fig. 7b).

In addition, the preferential degradation of $^{15}$N-enriched nitrogenous organic matter during anoxic diagenesis is also a possibility (Koehler et al., 2017). This process results in the release of heavy $NH_4^+$ into the pore water and its preservation in clay minerals. The residual nitrogen in organic matter would be relatively lighter (Fig. 7c). The DCN samples with nitrogen isotope values between -2‰ and +1‰ in this study may follow this pattern. Here, bulk samples and kerogen isolates of the same samples are also in this range. However, this diagenetic mechanism is perhaps unlikely, given that on a global average no systematic diagenetic effects on the isotopic composition of N were observed in anoxic settings (Robinson et al., 2012).

With ongoing research on the palaeoenvironmental nitrogen cycle more potential causes of elevated $\delta^{15}N_{DCN}$ relative to $\delta^{15}N_{kerogen}$ are revealed. Recently, researchers have focused on the partial nitrification of ammonium (Stüeken and Prave, 2022). During early diagenesis, $NH_4^+$ released from the microbial mats into the pore water may be partially oxidized to produce isotopically lighter $NO_2^-$/$NO_3^-$ at the sediment-water interface, leaving the remaining $NH_4^+$ pool enriched in $\delta^{15}N$. The isotopically lighter $NO_2^-$/$NO_3^-$ may be used by organisms or washed away while $NH_4^+$ with isotopically heavy is trapped by clay minerals, leading to higher $\delta^{15}N_{DCN}$ than $\delta^{15}N_{kerogen}$ (Fig. 7d). In addition, empirical data suggest that metamorphism (Stüeken et al., 2017) and hydrothermal alteration (Godfrey et al., 2013) further increase the difference between kerogen- and silicate-bound nitrogen, possibly due to equilibrium fractionation effects that tend to lower $\delta^{15}N_{kerogen}$ and increase $\delta^{15}N_{silicate}$.

Some samples showed the opposite pattern, where $\delta^{15}N_{kerogen}$ was higher than $\delta^{15}N_{DCN}$. One possible explanation is that this can also occur in anoxic or suboxic environments (Fig. 7e), if $^{14}NH_4^+$ is preferentially released by the decomposition of organic matter. If this $NH_4^+$ pool with isotopically light is fixed by the clay minerals, it may lead to lower isotopic values in DCN samples compared to organic matter. This phenomenon has also been described in parts of the modern ocean (Li and Jia, 2011). Another possibility is that the $NH_4^+$ with isotopically light is generated by dissimilatory nitrate reduction to ammonium (DNRA), which associated with a large isotopic fractionation (McCready et al., 1983) (Fig. 7f).

There is an ongoing discussion as to which of the two residue types ($\delta^{15}N_{DCN}$ or $\delta^{15}N_{kerogen}$) is closer to the primary marine N signal. In early diagenesis, $^{14}NH_4^+$ is preferentially released during organic matter mineralization (Macko and Estep, 1984). When part of this isotoipally light $NH_4^+$ is re-adsorbed by clay minerals (and therefore retained in the bulk sample), the nitrogen isotope fractionation caused by organic matter decomposition is reduced, and therefore $\delta^{15}N_{DCN}$ may be close to that in the primary of organic matter formed during sedimentation (Mettam and Zerkle, 2021). Kerogen is defined as the insoluble organic fraction dispersed in sedimentary rocks (Durand and Nicaise, 1980). There are many nitrogen-containing compounds in sediments that are covalently bonded to C, such as tetrapyrroles, which have a relatively stable structure (Ohkouchi et al., 2006). Some studies have shown that the nitrogen isotopic composition of kerogen is not significantly changed during the thermal maturation of organic matter (Williams et al., 1995; Rivera et al., 2015). There may be a

significant loss of nitrogen during metamorphism, but in a study of meta-anthracites and graphite, the nitrogen isotopic composition of the organic matter did not change significantly (Ader et al., 2006). Therefore, some researchers have suggested that the nitrogen isotopic composition of the kerogen is closer to the primitive ancient seawater signals (Godfrey and Falkowski, 2009). However, the focus on kerogen-bound N only misses out on any of the primary ammonium that was transferred from organic matter to clay minerals but technically belongs to the originally buried biomass. When using nitrogen isotope values for paleoenvironmental reconstruction, a combined discussion of these three nitrogen sample types (bulk rock, decarbonated residues, kerogen isolates) can yield may help with deciphering primary signals. Based on our data and compilations from the literature, we find that an offset between $\delta^{15}N_{DCN}$ and $\delta^{15}N_{kerogen}$ is common. Therefore, an integrated discussion of the $\delta^{15}N_{DCN}$ and $\delta^{15}N_{kerogen}$ of sedimentary rocks is the best solution.

We are currently not able to describe the exact mechanisms that led to the observed isotopic offsets between silicate-bound and organic-bound nitrogen in each sample. Independent evidence on redox conditions, productivity and organic matter maturity would be needed to evaluate the potential reasons. However, our review highlights the diversity of processes that can potentially affect isotopic compositions of differing nitrogen reservoirs in sedimentary rocks.
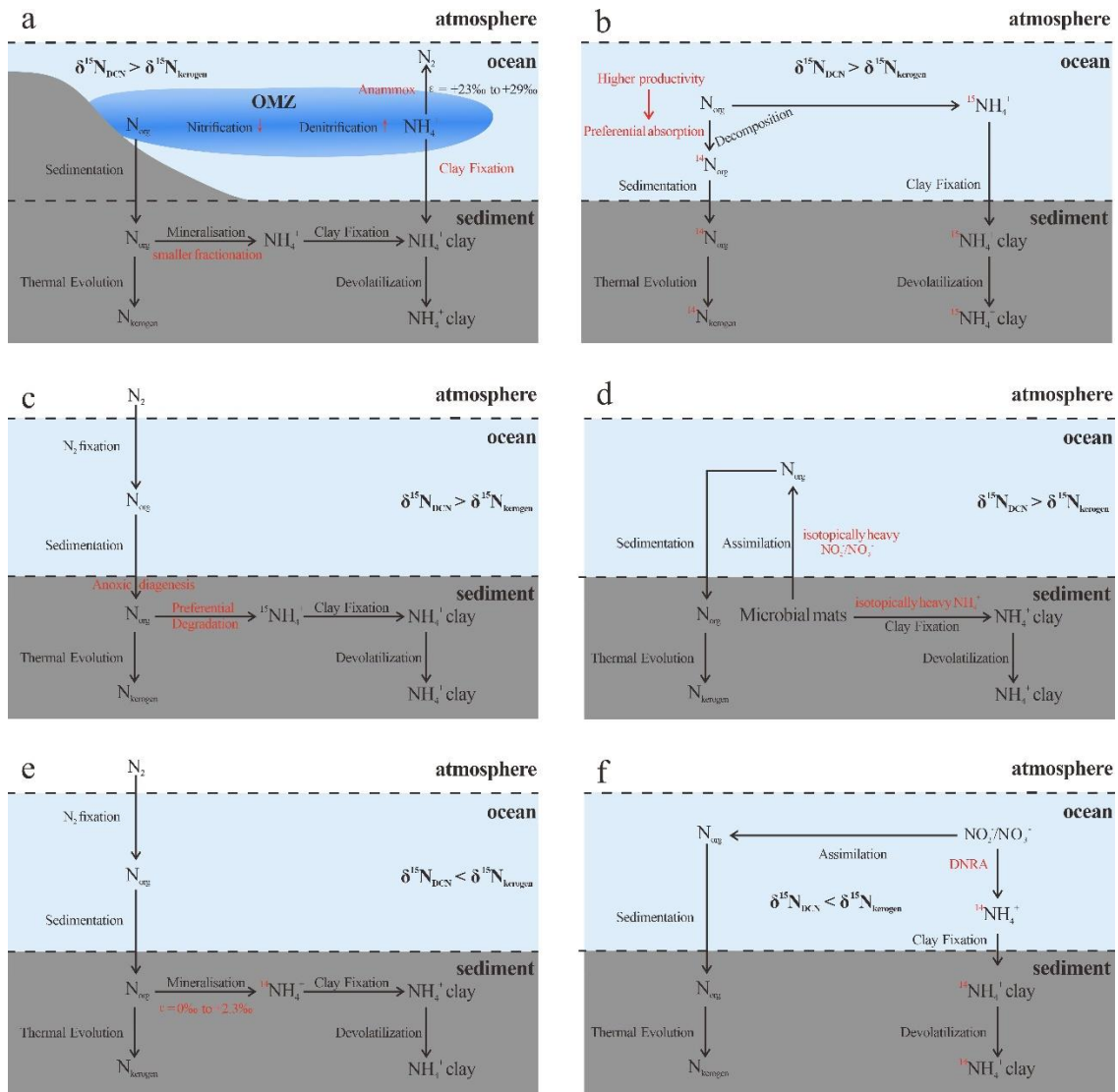
**Fig. 7. Reasons for differences in δ$^{15}$N$_{DCN}$ and δ$^{15}$N$_{kerogen}$ due to different marine environments. Dominant factors are marked in red. Nitrogen isotope fractionations ($\varepsilon_{\text{product- reactant}} \sim \delta_{\text{product}} - \delta_{\text{reactant}}$) are from the compilations of Ader et al. (2016)**

## 6. Conclusions

Analyses of nitrogen isotope were performed on rock samples from different periods of the Phanerozoic, focusing on three nitrogen proxies, δ$^{15}$N$_{bulk}$, δ$^{15}$N$_{DCN}$, and δ$^{15}$N$_{kerogen}$. We found minor differences between these three fractions, which are in part explicable by methodological effects and partly due to primary environmental processes that led to a divergence in nitrogen isotopic rations between different nitrogen reservoirs. For most of the samples, δ$^{15}$N$_{DCN}$ values are lower than δ$^{15}$N$_{bulk}$ values, indicating the preferential loss of $^{15}$N acid-soluble organic nitrogen due to the acid treatment. This process may be more severe for thermally immature rocks. The relationship between δ$^{15}$N$_{DCN}$ and δ$^{15}$N$_{kerogen}$ is likely more complex and influenced by the redox environment, biological productivity, and the degree of metamorphism. Therefore, we suggest that these three nitrogen proxies should be measured simultaneously when using nitrogen isotopes for palaeoenvironmental reconstruction to better unravel the complex history of Earth's nitrogen cycle.

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1