

NOTE

Stepwise combustion analyses of distinct nitrogen isotopic compositions on Paleoproterozoic organic matter

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Nitrogen isotopic analyses were conducted on two kerogenous samples from the Gunflint Formation (*ca.* 1.9 Ga) using the stepwise combustion technique to evaluate a potential analytical problem for the carbonaceous samples and to assess if this method is appropriate for the analysis of ancient rocks. Two discriminated $\delta^{15}\text{N}$ plateaux are identified for each sample with mean values of +5.0‰ and +7.3‰ for sample 0708, and +6.1‰ and +5.2‰ for sample 0704, respectively. The direction of the $\delta^{15}\text{N}$ shift is opposite in each sample. This characteristic excludes the possibility of analytical artifact as the source of isotope fractionation and metamorphism isotope fractionation. The two $\delta^{15}\text{N}$ plateaux observed for each of the samples are characterized by different activation energies for the co-released carbon. These results suggest that similarly aged sedimentary rocks may contain at least two types of organic matter that record different source information for $\delta^{15}\text{N}$.

Keywords: nitrogen isotopic composition, Paleoproterozoic, stepwise combustion method, kerogen, Gunflint Formation

INTRODUCTION

The nitrogen (N) isotopic compositions of Precambrian organic matter (OM) may provide information on microbial N cycling during the early Earth's history (e.g., Beaumont and Robert, 1999; Shen *et al.*, 2006). Previous studies have focused on bulk rock or bulk kerogen samples. Only a few studies have determined N isotopic composition using the stepwise combustion method (e.g., Boyd *et al.*, 1993; Krooss *et al.*, 2005).

Partial extraction of the analyte during combustion may be associated with isotopic fractionation. For example, a strong fractionation effect has been reported for N during stepwise extraction from a less-combustible host phase (Pinti *et al.*, 2007).

Most Precambrian OM has been subjected to some degree of metamorphism. Previous investigators proposed that ammonia loss during metamorphism is associated with a shift to a relatively positive N isotopic composition (Haendel *et al.*, 1986). However, it is still uncertain whether all relatively high $\delta^{15}\text{N}$ values characterizing Precambrian OM are the result of metamorphism. To test

this possibility, we investigate N isotopic composition changes during the stepwise combustion of Precambrian OM.

MATERIALS AND METHODS

Carbonate-rich sandstones (samples 0708 and 0704) were collected from outcrop of the Gunflint Formation, Ontario, Canada (sample 0708: 48°29'24.4" N, 89°11'34.2" W; sample 0704: 48°29'24.6" N, 89°11'35.3" W). Samples contain 0.34 and 0.23wt% organic carbon. The estimated age for the Gunflint Formation is *ca.* 1.9 Ga (Fralick *et al.*, 2002), and its metamorphic grade is considered to be sub-greenschist facies. Kerogen was extracted using standard method (Vandenbroucke, 2003). Organic solvent treatment was omitted because bitumen was present in the samples at only negligible levels.

Elemental and isotopic analyses were performed on the Balzers QMG420 quadrupole mass spectrometer at Osaka University, Japan, following the method described by Yamamoto *et al.* (1998) and Pinti *et al.* (2007). The platinum-wrapped sample is heated for 30 minutes during each combustion step in the O₂ atmosphere. Nitrogen contamination associated with the O₂ gas is typically ~0.02 ng. The pressure of the O₂ atmosphere during each analysis was 0.45Torr for sample 0708 and 0.85Torr for sample 0704.

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Table 1. $\delta^{15}\text{N}$ values and $F(\text{N}_2/^{40}\text{Ar})$ ratios for the air standard

Standard ID	$\delta^{15}\text{N}$ (‰)	1 σ error	$F(\text{N}_2/^{40}\text{Ar})$
#1	-0.8	0.6	1.12
#2	0.5	0.4	1.13
#3	-0.1	0.5	1.08
#4	-0.9	0.8	1.05
#5	-0.4	0.7	1.11
#6	0.2	0.5	1.11
#7	0.4	1.2	0.98
#8	-0.8	0.7	1.08
#9	0.6	0.8	1.07
#10	1.0	1.0	0.97
#11	-0.1	0.7	1.09
#12	1.8	1.0	1.06
#13	-0.5	0.5	1.00
#14	-0.4	0.5	1.05
#15	-0.4	0.5	1.04
#16	0.3	0.6	1.04
#17	0.7	0.8	0.99
#18	0.9	0.5	0.99
#19	0.3	0.7	1.04
#20	-0.2	0.7	0.99
#21	-0.0	0.5	1.00
#22	-0.8	0.8	1.00
#23	0.3	0.8	1.00
S.D	0.68		

Note: $F(\text{N}_2/^{40}\text{Ar})$ denotes the $\text{N}_2/^{40}\text{Ar}$ ratio obtained by each analysis, normalized by the mean $\text{N}_2/^{40}\text{Ar}$ ratio of the standard air.

Nitrogen isotopic compositions are expressed relative to atmospheric N_2 ($^{15}\text{N}/^{14}\text{N} = 0.00367$) in the standard delta notation as follows:

$$\delta^{15}\text{N} = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{air}} - 1] \times 1000.$$

The reproducibility of N isotopic measurements was estimated by replicate measurement of the air gas standard (Table 1). Quantities of carbon (C) and hydrogen (H), converted into CO_2 and H_2O during the combustion, were measured using a pressure gauge.

RESULTS

Table 2 presents the quantity of released N and its $\delta^{15}\text{N}$ values for samples during each combustion step together with C and H concentrations.

Sample 0708

At $<500^\circ\text{C}$, a small amount of N (87 ppm) was characterized by particularly negative $\delta^{15}\text{N}$ (-7.5‰ to -4.5‰). The source for those N is most likely from contamination and/or residual silicate bonded N, but not kerogen. Therefore, we excluded in later discussion these low-tempera-

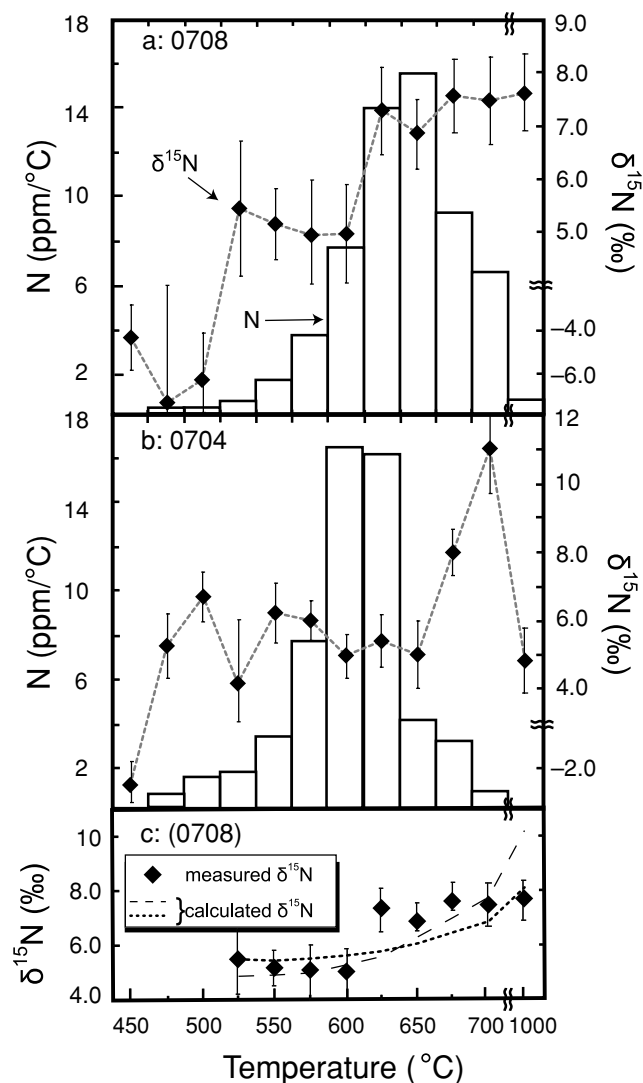


Fig. 1. Nitrogen (N) concentrations (white bars) and $\delta^{15}\text{N}$ values (black diamonds) for organic matter during combustion of samples 0708 (a) and 0704 (b). (c) Comparison between measured $\delta^{15}\text{N}$ values for sample 0708 (black diamonds) and Rayleigh distillation curves. The Rayleigh distillation curves assume simple mass dependent isotopic fractionation effects where ^{14}N is released faster than ^{15}N at constant rates (α). The fractionation factor (α) assumed for the dashed line is 1.00213‰. In this case, the measured and theoretical $\delta^{15}\text{N}$ value agree when the average $\delta^{15}\text{N}$ values taken from the two temperature ranges, 525–600 °C and 625–1100 °C, are compared. The dotted line represents the fractionation at $\alpha = 1.001\text{‰}$, where the same initial $\delta^{15}\text{N}$ value with measured value is assumed.

ture fractions, which also appeared in sample 0704.

The combustion of major C-bearing materials and corresponding N release started at 525 °C. The four temperature steps between 525 °C and 600 °C showed rela-

Table 2. Elemental (C, H and N) concentrations and $\delta^{15}\text{N}$ values for organic matter in carbonate-rich sandstone samples 0708 and 0704

Temp. (°C)	C (ppm)	H (ppm)	N (ppm)	C/N (atomic)	$\delta^{15}\text{N}$ (‰)	1 σ error
<i>0708 (0.033 mg)</i>						
450	39638	46	66	701	-4.5	1.5
475	15001	b.l.	10	1785	-7.5	5.8
500	18286	24	11	1984	-6.4	2.1
525	29317	b.l.	19	1848	5.4	1.3
550	51774	b.l.	42	1437	5.1	0.7
575	83582	b.l.	93	1044	4.9	1.0
600	125347	b.l.	192	763	5.0	0.9
625	162598	30	349	544	7.3	0.8
650	141617	27	389	424	6.8	0.7
675	91436	26	230	463	7.6	0.7
700	45616	b.l.	165	323	7.5	0.8
1100	42278	b.l.	407	121	7.6	0.7
Total	846490	152	1973	496	6.9	0.3
<i>0704 (0.047 mg)</i>						
450	51705	84	32	1903	-2.8	0.9
475	26033	44	18	1715	5.3	0.9
500	35771	40	36	1150	6.7	0.7
525	53399	31	40	1545	4.2	1.8
550	97618	50	83	1376	6.2	0.9
575	168086	22	193	1015	6.0	0.6
600	215046	26	416	603	5.0	0.6
625	147072	35	408	421	5.4	0.8
650	20395	17	102	234	5.0	1.0
675	3137	b.l.	78	47	8.0	0.7
700	2363	b.l.	19	142	11.0	1.3
1100	22937	16	43	626	4.9	1.0
Total	843563	365	1467	671	5.5	0.3

Note: Temp. = combustion temperature; b.l. = blank level. Blank nitrogen level associated with the gas-extraction system ranges from <0.001 ng at <900°C, to 0.03 ng at 1100°C. The detection limits for CO₂ and H₂O pressures on this analytical line are $\sim 3 \times 10^{-10}$ mol.

tively constant $\delta^{15}\text{N}$ values, between +4.9‰ and +5.4‰ (Fig. 1a). In this temperature range, 18% of the total sample N and 34% of the total sample C were released. The peak combustion occurred at temperatures between 625°C and 1100°C, where 77% of the total sample N and 57% of the total sample C were released. The $\delta^{15}\text{N}$ values (+6.8‰ to +7.6‰) exhibited by the samples from the four combustion steps between 625°C and 1100°C fall in a relatively narrow range and are significantly different from those observed for samples combusted between 525°C and 600°C. Sample analyses using the stepwise combustion method identified the presence of two distinct $\delta^{15}\text{N}$ (Fig. 1a), with mean values of $+5.0 \pm 0.6\%$ and $+7.3 \pm 0.4\%$.

Sample 0704

The $\delta^{15}\text{N}$ values for the five consecutive combustion steps between 475°C and 575°C exhibited no significant variation with mean value of +6.1‰ (within 1 σ -errors, Fig. 1b). In this temperature range, 25% of the total sample N and 45% of the total sample C were released. The

$\delta^{15}\text{N}$ values of the following three combustion steps, between 600°C and 650°C, fall within a relatively narrow range between +4.9‰ and +5.4‰ with mean value of +5.2‰. Interestingly, the direction of the shift in the $\delta^{15}\text{N}$ value near 600–625°C is different between the two samples. For sample 0708, the $\delta^{15}\text{N}$ value increased by 2.3‰, whereas for sample 0704, the $\delta^{15}\text{N}$ value decreased by 0.9‰. A progressive increase was observed in the $\delta^{15}\text{N}$ value from 675°C to 700°C in sample 0704; this increase was not observed for sample 0708. The second plateau appears at $\sim 25^\circ\text{C}$ lower than that observed for sample 0708. This lower temperature may be the result of the higher O₂ pressure during the combustion.

DISCUSSION

The preferential release of ¹⁴N during combustion may result in relatively low $\delta^{15}\text{N}$ values for sample fractions combusted in earlier steps and relatively high $\delta^{15}\text{N}$ values for sample fractions combusted in later steps (Boyd *et al.*, 1993). The expected isotope shift by the Rayleigh-

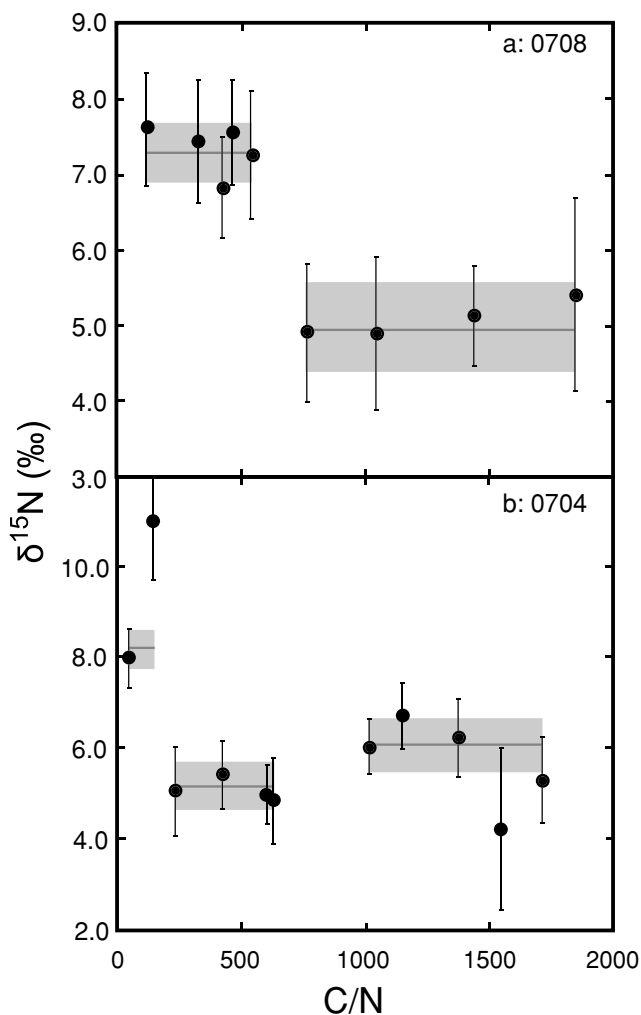


Fig. 2. Plot of $\delta^{15}\text{N}$ vs. C/N for the stepwise combustion of samples 0708 (a) and 0704 (b). (a) $\delta^{15}\text{N}$ values and C/N ratios differ between the temperature ranges 525–600°C and 625–1100°C. (b) $\delta^{15}\text{N}$ values and C/N ratios are divided into three groups: 475–575°C, 600–650°C and 1100°C, and 675–700°C. The results for the sample combusted at 675°C and 700°C plot in an extremely C-poor and/or N-rich area. This result suggests the existence of different phases. The solid horizontal lines and the gray squares show the mean $\delta^{15}\text{N}$ values and the error on the mean for each temperature group, respectively.

type isotope fractionation is calculated from the released N in sample 0708, assuming two α -factors ($\alpha = 1.00213$ and $\alpha = 1.001$; detailed information are described in Fig. 1c). It is confirmed that both patterns did not match the measured $\delta^{15}\text{N}$ values. Therefore, the $\delta^{15}\text{N}$ change with temperature cannot be explained by Rayleigh-type isotopic fractionation.

For sample 0704, a small shift in the $\delta^{15}\text{N}$ value is observed after combustion at 575°C. The $\delta^{15}\text{N}$ values observed between 600°C and 650°C are lower than the

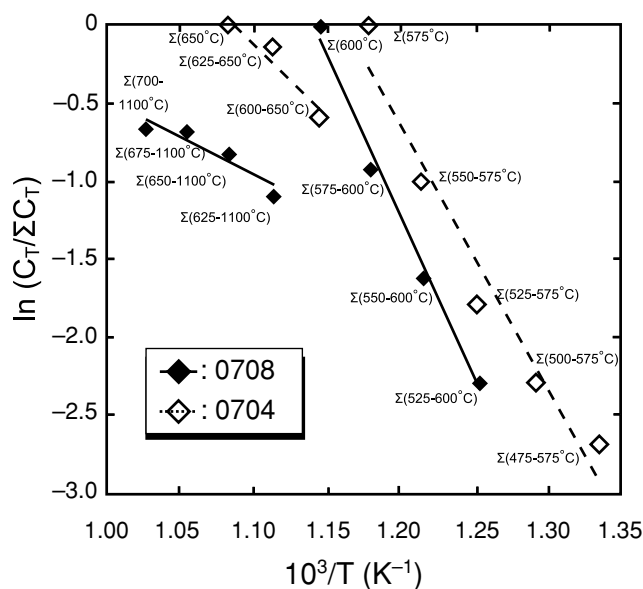


Fig. 3. Plot of the logarithm of the release amounts of carbon vs. the inverse of the combustion temperature for samples 0708 and 0704. The black diamonds and solid lines represent the observed values for sample 0708 and their best-fit curves respectively. The white diamonds and dashed lines are the corresponding data for sample 0704, respectively. Data are plotted only for temperature range 525–1100°C for sample 0708, and 500–650°C for sample 0704, in which the major release of the OM occurred. Plots are divided into two groups, at 625°C for sample 0708, and at 600°C for sample 0704, based on the phase change of $\delta^{15}\text{N}$. Inclinations (activation energies) for each group are 174 (kJ/mol) for the lower temperature range, and 42 (kJ/mol) for the higher temperature range for sample 0708. Inclinations for each group are 141 (kJ/mol) for the lower temperature range and 77 (kJ/mol) for the higher temperature range for sample 0704.

$\delta^{15}\text{N}$ values at lower temperature fractions. The isotope shift from 575 to 600°C cannot be explained by Rayleigh-type fractionation during the analyses. High $\delta^{15}\text{N}$ values are observed for the sample combusted between 675°C and 700°C. The increase in the $\delta^{15}\text{N}$ value between 650°C and 675°C is accompanied by a significant decrease in the C/N ratio, from 234 to 47 (Table 2). This suggests that the relatively high $\delta^{15}\text{N}$ values observed between 675°C and 700°C are hosted by a N-rich carrier, which is independent from the phases observed during combustion at lower temperatures (Fig. 2b). This carrier does not appear to be present in sample 0708 (Fig. 2a).

The Arrhenius plots for the C combustion rates for both samples suggest two carbonaceous components that are characterized by different $\delta^{15}\text{N}$ values. A prominent change in the trends are observed where the $\delta^{15}\text{N}$ value shifts at 625°C for sample 0708 and at 600°C for sample 0704, respectively (Fig. 3). A change in the activation

energy may occur for combustion of even a single carbonaceous phase, potentially associated with a change in the rate-determining process for the combustion (Luo *et al.*, 2004). If different N isotopic fractionation occurred when the combustion takes place through different pathways, it may result in apparently different $\delta^{15}\text{N}$ values observed at respective temperature ranges corresponding to the different combustion pathways. However, in such a case, the $\delta^{15}\text{N}$ values would exhibit Rayleigh-type isotope fractionation profiles; which is not the case observed in our samples. The two distinct $\delta^{15}\text{N}$ plateaux for samples 0708 and 0704 suggest the presence of two N-bearing host phases with distinct $\delta^{15}\text{N}$ values and different C structures. These different structures may be inherited from different behaviors of organic molecules during thermal maturation associated with metamorphism.

Implications of the distinct $\delta^{15}\text{N}$ plateaux

The geological implications of the distinct $\delta^{15}\text{N}$ plateaux observed for the samples are discussed here. A positive shift in the $\delta^{15}\text{N}$ value, similar to that observed for sample 0708, may result from the preferential release of ^{14}N during metamorphism. Alternatively, this may also be derived from different sources of organic material initially deposited in the sediment. Samples 0708 and 0704 were collected from sites within a few meters of each other, and have identical mineralogy. Therefore, metamorphic grades of both samples are thought to be the same. If metamorphism were responsible for the observed shifts in the $\delta^{15}\text{N}$ values, the shifts for both samples would be in the same direction (Haendel *et al.*, 1986).

Accordingly, the two $\delta^{15}\text{N}$ plateaux for sample 0708 more likely originate from the presence of different types of OM characterized by distinct N isotopic compositions. Microbial N cycling and associated nitrification-denitrification in ancient age may result in different N isotopic compositions for the OM and may help to explain the $\delta^{15}\text{N}$ values observed for samples 0708 and 0704.

CONCLUSIONS

The N isotopic compositions of OM from the Gunflint Formation were measured using the stepwise combustion method. Two well-discriminated $\delta^{15}\text{N}$ plateaux were observed for each sample. These plateaux do not appear to be produced by analytical artifacts; rather, their compositions represent those of OM that survived diagenesis and metamorphism. The reaction rate of C oxidation changed during the same combustion step as the $\delta^{15}\text{N}$ gap. These differences in oxidation rate suggest that the N components characterized by unique $\delta^{15}\text{N}$ values are hosted in carbonaceous compounds with different

compositional and probably structural profiles. The characteristic $\delta^{15}\text{N}$ of Gunflint kerogen may be intrinsically related to microbial N cycling. A detail investigation of the $\delta^{15}\text{N}$ profiles using the stepwise combustion method may provide unique information on Precambrian OM, which would not be assessed using classical analyses of bulk organic samples.

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