A Refinement of Nitrogen Isotope Analysis of Coal Using Elemental Analyzer/Isotope Ratio Mass Spectrometry and the Carbon and Nitrogen Isotope Compositions of Coals Imported in China

Lianjun Feng,* Hongwei Li, and Detian Yan

Abstract: The ability to accurately analyze nitrogen (N) isotopes of coal is important for evaluating its contribution to NO\textsubscript{X} emissions to the atmosphere via coal combustion. Although an elemental analyzer/isotope ratio mass spectrometer is highly efficient for analyzing the N isotopes of coal, it requires large amounts of organic matter (>3 mg) to produce enough N\textsubscript{2} to enable N isotope measurements due to the high organic carbon contents of coal with relatively low N contents. Therefore, to completely oxidize the organic matter, more oxidant matter is required to enhance coal combustion in a reactor tube in an elemental analyzer through injecting O\textsubscript{2} during the combustion process. One reference material (RM) (GBW11104) was used to determine the effect of amounts of O\textsubscript{2} on the accuracy of nitrogen isotope values obtained. Our results show that small amounts of O\textsubscript{2} injected into the EA resulted in incomplete coal combustion, which yielded a lower N content and more positive N isotope ratio for RM (GBW11104) than those obtained by complete combustion. Thus, to ensure the complete combustion of coal, large O\textsubscript{2} injection amounts are required. The refined method was applied to provide the N isotope values of coals imported from Southeast Asia, Russia, and Australia. Combined with the carbon isotope values, the imported coals from three coal-producing regions (Southeast Asia, Russia, and Australia) display distinct characteristics.

Introduction

Fossil fuel combustion, such as the burning of coal, is known to be the main source of NO\textsubscript{X} emissions into the atmosphere.\textsuperscript{1} The nitrogen (N) isotope ratio is known to be effective for discriminating between nitrogen sources,\textsuperscript{2,3} and the contribution from coal combustion can be estimated if its N isotope composition is known. The isotopic composition of nitrogen in a sample is conventionally expressed as $\delta^{15}\text{N} (\%e) = \left(\frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}/^{14}\text{N}}_{\text{sample}} / \frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}/^{14}\text{N}}_{\text{air}} - 1\right) \times 1000$. An increasing amount of N isotope data from coal is being reported,\textsuperscript{4,5} and the continuous-flow isotope ratio mass spectrometer has become a popular method used to analyze N isotopes,\textsuperscript{4,6–8} mainly due to its high efficiency, rather than the use of conventional labor-intensive methods, such as the Dumas combustion method\textsuperscript{9,10} and Kjeldahl method.\textsuperscript{11} However, although more data are being reported, few studies are being conducted to evaluate analytical methods employed. Our previous work suggested that, when using the continuous-flow elemental analyzer/isotope ratio mass spectrometry (EA-IRMS) method, the accuracy of determining the N isotope of organic-rich shale is closely related to the amount of oxidant matter employed,\textsuperscript{12} and our research suggested that, if enough oxidant matter, such as O\textsubscript{2}, is supplied, highly accurate N isotope values can be obtained. As with organic-rich materials such as shales, there are potential problems in determining the N isotopes of coal that is enriched in organic matter. In this paper, therefore, we selected easily purchased coal reference material (RM) (GBW11104) to determine how varying O\textsubscript{2} injection amounts can affect the accuracy of N isotope measurements obtained. In addition, 39 imported coals, mainly from Southeast Asia, Russia, and Australia, were analyzed to obtain their N isotope values. Furthermore, combined with carbon isotope of the coals, which is largely influenced by the local environmental conditions at the time of formation,\textsuperscript{13} we try to obtain the isotopic characteristics from the different coal-producing regions.

Results and Discussion

Oxygen Injection and Analysis of Coal N Isotopes.

The EA/IRMS method was used to analyze the N isotopes of organic matter (OM). In the reactor tube, OM is first combusted, and NO\textsubscript{X} is simultaneously released. During the combustion process, partial combustion due to a limited supply of oxidant results in the occurrence of isotopic

*Corresponding author.

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fractionation, which has been observed for organic-rich shales.\textsuperscript{12} Therefore, to ensure that the N isotope of organic-rich rocks is accurately identified, it is necessary to supply enough oxidant substances, such as O$_2$. To analyze the N isotope of organic-rich shale, three oxidant matter types, CuO, V$_2$O$_5$, and O$_2$, were selected to test how the oxidant substances enhanced the complete oxidation of OM and to determine their use in obtaining N isotope values.\textsuperscript{12} The results showed that the use of O$_2$ more efficiently resulted in the complete combustion of OM compared to other oxidants such as CuO and V$_2$O$_5$. Therefore, in the study, we used O$_2$ as the oxidant matter.

To evaluate how O$_2$ influences the analysis of the N isotope, varying volumes of O$_2$ gas (8.75–40 mL) were injected into the elemental analyzer during the combustion of coal. As the volume of O$_2$ injected during combustion increased, the N contents of the RM (GBW11104) showed a clearly increasing trend (Figure 1). The N isotope contents of coal became invariant (1.15\%) within a standard error when the O$_2$ volume was higher than 20 mL (Figure 1, Table 1). In contrast, the N yield was the lowest (75.8\%), and the most positive N isotope of organic-rich shale, three oxidant matter types, CuO, V$_2$O$_5$, and O$_2$, were selected to test how the oxidant substances enhanced the complete oxidation of OM and to determine their use in obtaining N isotope values.\textsuperscript{12} The results showed that the use of O$_2$ more efficiently resulted in the complete combustion of OM compared to other oxidants such as CuO and V$_2$O$_5$. Therefore, in the study, we used O$_2$ as the oxidant matter.

Table 1. Replicate Analyses of $\delta^{15}$N of RM GBW11104

| weight (mg) | O$_2$ (mL) | N content $\pm$ SD (wt \%) | $\delta^{15}$N $\pm$ SD (\textit{air}) | $n$ |
|---|---|---|---|---|
| 0.5 | 30 | 1.10 $\pm$ 0.05 | 5.05 $\pm$ 0.18 | 4 |
| 1 | 30 | 1.09 $\pm$ 0.05 | 4.63 $\pm$ 0.07 | 3 |
| 2 | 30 | 1.09 $\pm$ 0.02 | 4.33 $\pm$ 0.08 | 3 |
| 3 | 30 | 1.12 $\pm$ 0.02 | 4.28 $\pm$ 0.09 | 3 |
| 5 | 30 | 1.13 $\pm$ 0.01 | 4.69 $\pm$ 0.16 | 3 |
| 7 | 30 | 1.13 $\pm$ 0.05 | 4.81 $\pm$ 0.14 | 3 |
| 3 | 8.75 | 0.87 $\pm$ 0.14 | 7.12 $\pm$ 0.32 | 3 |
| 20 | 3 | 1.10 $\pm$ 0.01 | 5.70 $\pm$ 0.36 | 3 |
| 25 | 1.14 $\pm$ 0.01 | 4.75 $\pm$ 0.29 | 4 |
| 40 | 1.15 $\pm$ 0.02 | 4.26 $\pm$ 0.13 | 3 |

The $\delta^{15}$N values of the RM showed a decreasing trend (Figure 1) when the volume of O$_2$ injected was higher than 25 mL, and the N isotope became invariant. It is of note that, when the default amount (8.75 mL) of O$_2$ for the EA was injected, the N yield was the lowest (75.8\%), and the most positive N isotope value was obtained (7.12 $\pm$ 0.32 \%). In summary, the amount of O$_2$ involved in combustion directly relates to the ability to obtain accurate measurements of the N isotopes of coal. Limiting the amount of O$_2$ injected could result in an incomplete reaction and thus large fractionation, and these results are consistent with previous research conducted on organic-rich shales.\textsuperscript{12}

We also tested the ability to determine N isotope values with respect to the sample size used. With sample sizes of 2 and 3 mg and 30 mL of O$_2$ injected, the N isotopes and content were both consistent with the results obtained from complete combustion (Figure 2, Table 1). However, the use of small sample sizes (0.5, 1 mg) and large sample sizes (5, 7 mg) all showed slightly positive N isotope values relative to values obtained by complete combustion (4.33, 4.28\%). The relatively positive N isotope values obtained from small sample sizes are possibly related to the contribution of the blank. Although the signal of the blank cannot be directly observed during the combustion process, the N isotope values for small sample sizes can easily be affected by the blank. This was also observed in previous studies.\textsuperscript{14–16} The slightly positive $\delta^{15}$N values from large samples (5, 7 mg) were related to incomplete combustion, which occurred with respect to the larger amount of reducing matter employed.

In this study, the possible discrepancy between N isotopes obtained with and without adequate amounts of O$_2$ gas can be as much as 3\%. The incomplete combustion of coals will lead to inaccurate data. However, it is noted that, in this study, the injection time was set as 6 s (ca. 30 mL of O$_2$) for EA because a longer injection time decreases the lifetime of the reactor tube due to rapid Cu oxidation.

Nitrogen and Carbon Isotope Characteristics of Coals Imported in China. The optimal conditions for analyzing the N isotope values of coal were obtained, as previously mentioned. Sample weight should be at least 2 mg to exclude possible contributions from blank. In addition, to ensure complete combustion, 30 mL of O$_2$ was injected during the combustion process in EA. In this study, the 39 imported coal samples were analyzed for organic carbon (C) and N isotopes, and results are provided in Table 2.

With respect to wide investigations conducted on $\delta^{15}$N values of coal, the N isotope compositions of coals from Southeast Asia and Russia have not previously been obtained. In this study, the $\delta^{15}$N values of coal from Indonesia ranged from 0.38 to 2.32\%, with average values of 1.23 $\pm$ 0.51\%, and the two Philippine and Malaysian coals were 0.88 and 1.22\%, respectively. It is thus considered likely that the coal-producing region of Southeast Asia is characterized by uniform light $\delta^{15}$N values. Only a few N isotopes of Russian coal have previously been reported, and this study shows a wide distribution of $\delta^{15}$N values (3.00 $\pm$ 0.92\%) for Russian coals. The Australian coals
show similarly heavy values (average $2.98 \pm 0.36\%$), which is concordant with a previous report ranging from 0.3 to $3.7\%$.\(^{17}\) The wide distribution in nitrogen isotope of coals is also seen in the previous report ($ca. 0-5\%$).\(^{5,13,18,19}\)

The C isotope analysis results for Indonesian coals (average $-27.8 \pm 0.5\%$) were consistent with those of previous results and showed light isotope values (average $-27.4 \pm 0.8\%$).\(^{20}\) In addition, the two coals from the Philippines and Malaysia were also found to be characterized by light isotope values ($-27.81$, $-27.33\%$). In contrast, the carbon isotope values of coals from Australia and Russia were characterized by the relatively heavy values (average $-23.22 \pm 1.24$, $-25.55 \pm 0.82\%$), which is also consistent with prior research results.\(^{20}\) The $\delta^{13}C$ values of imported coals range from $-28$ to $-22\%$, which is consistent with the bulk coal samples with a range of $-27$ to $-22\%$.\(^{13}\)

In summary, the coals imported from three coal-producing regions (Southeast Asia, Australia, and Russia) have distinct isotopic compositions (Figure 3). In our results, Southeast Asia coals have the lightest nitrogen and carbon isotope values. This study reports a greater number of N isotope signatures, which can be entered into the database for N isotope research relating to coal.\(^{15}\)

**CONCLUSIONS**

Using the EA-IRMS method, the C and N isotopes of organic-rich coals were effectively analyzed. However, when conducting an evaluation using the N isotope standard (GBW11104), N isotope values were affected by the amounts of oxidant matter. The limited supply of oxidant matter, such as O$_2$, results in the incomplete combustion of coal, and heavy N isotope values are subsequently obtained. By obtaining the optimum conditions for the EA-IRMS method in this study, accurate N isotope values can be obtained. Coals from the main coal-producing regions (Russia, Australia, and Southeast Asia) were investigated. Coals from Southeast Asia were first investigated and showed the lightest nitrogen and carbon isotope values compared to those from Australian and Russia. The combined data of $\delta^{15}N$ and $\delta^{13}C$ from the imported coals from Indonesia, Australia, and Russia show distinct characteristics.

**EXPERIMENTAL SECTION**

**Instruments and Methods Employed.** Continuous-flow analyses were conducted using a Flash 2000 HT elemental analyzer with a MAS 200R autosampler coupled to a Delta V Advantage isotope ratio mass spectrometer via a ConFlo IV universal interface (all Thermo Fisher Scientific). The EA parameters were 1.2 bar helium (He) with a 100 mL/min flow rate of carrier gas and a 180 mL/min flow rate of reference gas and 1.0 bar O$_2$ with a flow rate of 175−300 mL/min and an injection end time (duration of O$_2$ injection) of 3−8 s. The sample powder was weighed in a tin capsule and then sealed. Samples were dropped by the autosampler into a high-temperature reactor consisting of a heated quartz tube filled.
with Cr$_2$O$_3$, reduced copper (Cu) wire, and silvered CoO–Co$_2$O$_3$, which was held at 980 °C. The sample was processed in the presence of excess O$_2$ by flash combustion. The gaseous products were carried in a He flow through reduced Cu wire held. This reduction step converted N oxides into N$_2$ and trapped excessive O$_2$. Halogens and/or SO$_2$ from gas mixtures were trapped by silvered CoO–Co$_2$O$_3$, and H$_2$O and CO$_2$ were removed by a Carbosorb and magnesium perchlorate trap. The gas products were separated in a Porapak Q gas chromatography column (4 m, 50 °C, from Agilent Technologies, USA) before entering the mass spectrometer. In this study, organic carbon (C) isotopes of coal samples were also analyzed, and the above EA configuration was unchanged (except for the removal of Carbosorb in the water trap).

Isotope ratio analyses of every individual sample were conducted in different runs and in triplicate. To avoid the disturbance of reduction fluctuation with increasing consumption of Cu, all tests were conducted using the first 80 samples of newly filled reaction tubes. The analytical procedure was verified after every sixth analysis using the zero blank. In the analysis sequence, every sample was followed by a blank sample. The instrument stability was also checked by analyzing the working standard after every sixth measurement. All raw measurements were made relative to pulses of the N$_2$ and CO$_2$ working gas, and data were analyzed using Isodat 3.0 software (Thermo Fisher Scientific). Raw δ$^{15}$N and δ$^{13}$C values were corrected using multiple-point linear regression based on certified reference materials run during the same sequence.

**Experimental Materials.** Chromium oxide (Cr$_2$O$_3$), silvered cobaltous-cobaltic oxide (CoO–Co$_2$O$_3$), reduced Cu wire (0.7 mm), quartz wool, quartz glass tubes (18.5 mm × 450 mm), Carbosorb, magnesium perchlorate, and tin capsules for solids (3.3 mm × 5 mm) were purchased from Thermo Fisher Scientific (Bremen, Germany). High-purity gases, including He, O$_2$, N$_2$, and CO$_2$ (purity >99.999%; all obtained from Air Products, Beijing, China) were used as the carrier gas, oxidizer, and working standard gas, respectively. Urea (IVA Analysentechnik, Meerbusch, Germany), USGS34 (KNO$_3$), USGS64 (C$_2$H$_5$NO$_2$), and USGS65 (C$_2$H$_5$NO$_2$) (from USGS, Reston, USA) were used in the analysis of the N isotope, and GBW04407 and urea (IVA Analysentechnik, Meerbusch, Germany) were used in the analysis of the organic carbon (C) isotope.

**Coal Samples.** Coal RM (GBW11104) was selected to determine the optimum EA conditions for conducting N isotope analysis. GBW11104 was purchased from the China National Standards, China. In addition, 39 coal samples were supplied by the Shanghai Customs District, China. The coals were imported into China from three coal-producing regions including Southeast Asia (Indonesia n = 26, Malaysia n = 1, and Philippines n = 1), Australia (n = 5), and Russia (n = 6). Detailed information can be found in Table 2.

## AUTHOR INFORMATION

**Corresponding Author**

Lianjun Feng — Key Laboratory of Mineral Resources, Institute of Geology and Geophysics and Innovation Academy for Earth Science, Chinese Academy of Sciences, Beijing 100029, China; orcid.org/0000-0002-0325-3789; Email: ljfeng@mail.iggcas.ac.cn

**Authors**

Hongwei Li — Key Laboratory of Mineral Resources, Institute of Geology and Geophysics and Innovation Academy for Earth Science, Chinese Academy of Sciences, Beijing 100029, China

Detian Yan — Key Laboratory of Tectonics and Petroleum Resources of Ministry of Education, China University of Geosciences, Wuhan 430074, China

**Notes**

The authors declare no competing financial interest.

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