Asian Journal of Chemistry; Vol. 24, No. 12 (2012), 5453-5456

ASIAN JOURNAL OF CHEMISTRY

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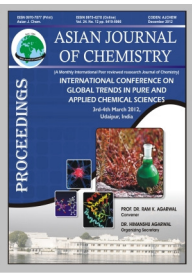

Latitude Effect on Carbon, Nitrogen and Oxygen Stable Isotope Ratios in Foliage and in Nitric-oxide Ions of Aerosols†

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AJC-11665

In this study, aerosol samples (PM 4.5) and foliage samples were collected in Singapore and in Fairbanks, Alaska in 2009 and 2010. Ion chromatography, gas chromatography-mass spectrometry and element mass spectrometry were used to measure anion concentrations and nitrogen and oxygen stable isotope ratios in nitrogen oxide ions of the aerosol samples, as well as to measure carbon and nitrogen stable isotope ratios in the foliage samples. In both Singapore and Fairbanks, it was observed that values of delta $^{15}N/^{14}N$ in nitric-oxide substances from aerosols were correlated with declination. The value of $\delta\ ^{15}N/^{14}N$ in nitric-oxide substances from aerosols in Fairbanks increased with increasing declination due to more active conversions from ^{14}N to ^{14}C by neutron bombardment. This study implies that at least one of the reason of increasing concentration of carbon dioxide in the atmosphere past 2 centuries may be affecting by cosmic-ray bombardment to nitrogen in the atmosphere.

Key Words: Cosmic rays, Nitric-oxide substances, Variations of stable isotope ratios.

INTRODUCTION

To date, there have been a considerable number of reports and investigations regarding accounts of stable isotopic fractionations and variation of stable isotope ratios. These descriptions depend only on biological activities, a little bit of differences of kinetic ratios of chemical reactions and a little differences of physical development. Although the relationship between the phenomena of variation of stable isotope ratios and cosmic-ray bombardment (spallation effect) also has never been considered. The object of this investigation is to discover the reason for variations in isotopic ratios in the environment to adapt the previous studies as follows. Furthermore the previous studies of production of ^{7}Be by nuclear spallation reactions were the study focused on the product of nuclear spallation reactions. However this investigation is focused on the reactant of nuclear spallation reactions.

Neutron bombardment from cosmic radiation (spallation effect): Nitrogen stable isotopes of ^{14}N (atomic number: 7, mass number: 14) have been known following neuclear chemical reactions in the atmosphere by neutron bombardment from cosmic radiation (spallation effect).

$$ {}^{1}_{0}n(fast)+{}^{14}_{7}N \rightarrow {}^{12}_{6}C+{}^{3}_{1}H \quad (1) $$

$$ {}^{1}_{0}n(slow)+{}^{14}_{7}N \rightarrow {}^{14}_{6}C+{}^{1}_{1}H \quad (2) $$

Large amounts of radioisotoe ^{3}H (tritium) (atomic number: 1, mass mumber: 3) are formed in the atmosphere through nuclear reaction[1] between fast neutrons and ^{14}N. The yield for this reaction is known about 2500 atoms radioisotoe ^{3}H (tritium) per second per square meter of the earth's surface; the global inventory is therefore about 2.12×10^{-6} mol/sec. ^{3}H (tritium) has half-life of 12.33 years, decaying by weak β emission to ^{3}He (eqn. 3)

$$ {}^{3}_{1}H \rightarrow {}^{3}_{2}He + e^{-}(\beta-ray)+(\gamma-ray) \quad (3) $$

It is rapidly incorporated in water, entering the global hydrological cycle. Rain water contains between 4 and 25 tritium atom per 10^{18} hydrogen atoms, lower at equatorial zone and increasing with latitude.

The other hand the nuclear chemical reaction between thermalized neutrons (slow neutrons) from cosmic radiation and ^{14}N make radioisotope ^{14}C (atomic number: 6, mass number: 14)[2] (eqn. 2) (spallation effect). This reaction is known to occur with a yield of approximately 22000 atoms ^{14}C formed per

†Presented as invited lecture to the International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

second per square meter of the earth's surface; the global inventory is therefore about 1.86×10^{-5} mol/sec. ^{14}C has half-life of 5730 years, decaying by soft β emission to ^{14}N (eqn. 4).

$$^{14}_{6}C \rightarrow ^{14}_{7}N + e^{-}(\beta - ray) + (\gamma - ray) \quad (4)$$

Hence one of source of ^{14}N is radioisotope ^{14}C with decaying by soft β emission to ^{14}N.[4] In addition it is known that following nuclear chemical reactions for another source of ^{14}N (eqns. 5-7).

$$^{12}_{6}C + ^{1}_{1}H \rightarrow ^{13}_{7}N + (\gamma - ray) \quad (5)$$

$$^{13}_{7}N \rightarrow ^{13}_{6}C + e^{-}(\beta^{-} - ray) + e^{+}(\beta^{+} - ray) + \nu_{e} \quad (6)$$

$$^{13}_{6}C + ^{1}_{1}H \rightarrow ^{14}_{7}N + (\gamma - ray) \quad (7)$$

Thus nevertheless ^{14}N atoms are consumed by cosmic radiation (spallation effect), ^{14}N atoms are supplied by these nuclear chemical reactions.

The production rate k of a nuclide is:

$$k = \phi\sigma N_t \quad (8)$$

where, φ is the neutron flux (neutron of appropriate energy per cm^2/sec), σ the reaction cross section (at the given neutron energy, in cm^2) and N_t the number of target atoms with reaction cross section σ. The reaction cross section of ^{14}N σ is 0.075 barn and the reaction cross section of ^{15}N σ is 0.000024 barn for the neutron velocity at 2200 m/sec (energy 0.0253 eV, 300 K). Therefore if other parameters are same, ^{14}N has more than 312 times probabilities of neutron bombardment than ^{15}N.

This deference may contribute variation of stable isotope ratios for $\delta\ ^{15}N/^{14}N$.

Unlike charged particles, no coulomb barrier hinders neutrons from reaching the target nucleus. This leads to generally higher reaction cross-sections for neutrons, particularly at very low energies. We have seen that the geometric cross-section of a target nucleus is in the order of 1 barn (b) or 10^{-28} m^2. Experimentally, the cross-section for capture of energetic (FAST) neutrons (≧ 1 MeV) are often close to 1 barn (b) or 10^{-28} m^2. However for neutrons whose kinetic energy is in the 1-100 eV region (SLOW neutrons), some nuclei show very large cross-section as high as 10^5 barn (b) or 10^{-23} m^2.

Therefore estimated values on these descriptions depend on neutron velocity *i.e.* it is difficult to calculate these estimated values correctly because neutron velocity is effected by lots of factors such as *e.g.* weather condition and amount of cosmic-ray in troposphere and stratosphere[1]. Though, that the neutron bombardment from cosmic radiation has been deeply involved in the variation of stable isotope ratios is no doubt.

Oddo-Harkins rule: In order to understand the effects of neutron bombardment on stable isotopes, it is necessary to refer to the laws governing the binding of the atomic nucleus[2].

There are certain nucleons (2, 8, 20, 28, 50, 82, 126) that are more tightly bound than others; this is the origin of the shell model.

Even numbers of nucleons are more tightly bound than odd numbers of nucleons.

Hence ^{14}N is more easily broken than ^{15}N. The proton number and the neutron number of ^{14}N are both 7. The proton number of ^{15}N is also 7, but its neutron number is 8 (Table-1).

TABLE-1
CHARACTERIZATIONS OF CARBON (C), NITOROGEN (N) AND OXYGEN (O) STABLE ISOTOPES FOR THIS STUDY

Stable isotope	^{12}C	^{13}C	^{14}N	^{15}N	^{16}O	^{18}O
Atomic number = proton number	6	6	7	7	8	8
Mass number	12	13	14	15	16	18
Neutron number	6	7	7	8	8	10

Thus a nuclear chemical reaction in which ^{14}N and a neutron (n) produce the ^{14}C radioisotope is known to occur in the atmosphere, especially at altitudes between 30,000 feet and 50,000 feet (9000 -15,000 m)[3-6].

$$^{1}_{0}n + ^{14}_{7}N \rightarrow ^{14}_{6}C + ^{1}_{1}H \quad (9)$$

In contrast, there is no known nuclear chemical reaction between ^{15}N and a neutron (n) because ^{15}N is more tightly bound than ^{14}N (due to the fact that ^{15}N has a neutron number of 8). Therefore only ^{14}N is affected by neutron bombardment from the sun and from cosmic rays. Thus ^{14}N is converted into the ^{14}C radioisotope and the relative amount of ^{15}N in the stable isotope ratio is increased. The latitude effect on nitrogen stable isotope ratios (both in the foliage and in the nitric-oxide substances within the aerosol samples) should be affected by these principles. Lower latitudes such as Singapore tend to have higher atmospheric temperatures than do higher latitudes such as Fairbanks, Alaska. Higher atmospheric temperatures generate stronger updrafts, allowing aerosols to climb to higher altitudes. At these higher altitudes, neutrons are more abundant than at lower altitudes. Consequently, at lower latitudes there are more active conversions from ^{14}N to ^{14}C by neutron bombardment. This is the mechanism by which nitrogen stable isotope ratios (δ 15/14N), both in foliage and in nitric-oxide substances within the aerosol samples, are increased at lower latitudes.

Previous study of Production of ^{7}Be by nuclear spallation reactions: ^{7}Be (Beryllium isotope mass number: 7) is produced by *e.g.* following nuclear spallation reactions between high energy cosmic-rays and atmospheric nuclei.

$$^{1}_{1}p + ^{14}_{7}N \rightarrow 2^{7}_{4}Be + ^{1}_{0}n \quad (10)$$

This phenomenon has been used for various purposes in the field of geoscience[7,8]. These previous studies were the study focused on the product of nuclear spallation reactions.

EXPERIMENTAL

Aerosol samples (PM 4.5) were taken at the National University of Singapore in Singapore (Latitude: 1°18' N; Longitude: 103°46' E; altitude: 67.0 m) in 2009 and 2010 and at Fairbanks International Airport in Fairbanks, Alaska, U.S.A. (Latitude: 64°50.116' N; Longitude: 147°49.747' W; Altitude: 143.3 meters) in 2010.

The $\delta^{15}N/^{14}N$ and $\delta^{18}O/^{16}O$ isotope ratios in NO_3^- were measured using the denitrifier method[9,10]. Anion concentrations and isotope ratios were measured at the laboratory of social biogeochemistry (Laboratory of Professor Muneoki YOH and Associate Professor Keisuke KOBA), Tokyo University of Agriculture and Technology (TUAT), Building #2, Rooms 328 and 2N-101, 5-8, Saiwai-Cho 3-Chome, Fuchu-Shi, Tokyo 183-8509, Japan. The calibration curves for these isotopic analyses were constructed using the international standards

USGS32, USGS34, USGS35 and IAEA. The stable isotope ratio delta was calculated with the following eqn. 11.

$$\left[\frac{R_{SAMPLE} - R_{STANDARD}}{R_{STANDARD}}\right] \times 1000 \text{‰} = \delta = \text{delta} \quad (11)$$

Abies firma (Momi or Japanese fir) was selected as the source of foliage samples in Fairbanks, Alaska, U.S.A. Samanea saman (rain tree) was selected as the source of foliage samples in Singapore. Sampling was performed in Fairbanks Alaska, U.S.A. and in Singapore in 2010.

In the laboratory, collected foliage was dried at 80 ºC to constant weight. All foliage ground samples were analyzed for delta $^{15}N/^{14}N$ and delta $^{13}C/^{12}C$ using an elemental analyzer. Calibrated DL-α-alanine (δ $^{13}C/^{12}C$= -23.45 [per mil]; δ $^{15}N/^{14}N$= -1.66 [per mil]), glycine (δ $^{13}C/^{12}C$= -34.89 [per mil]; δ $^{15}/^{14}N$= 10.04 [per mil]) and histidine (δ $^{13}C/^{12}C$= -9.94 [per mil]; δ $^{15}N/^{14}N$= -7.96 [per mil]) were used as internal standards. The stable isotope ratio delta was calculated using eqn. 11.

RESULTS AND DISCUSSION

It is generally known that δ $^{15}N/^{14}N$ in foliage decreases with increasing latitude[12]. It was found that the average value of delta $^{15}N/^{14}N$ in foliage in Fairbanks (latitude 64.84º N) was -1.84 [per mil] whereas the average value of δ $^{15}/^{14}N$ in foliage in Singapore (latitude 1.3º N) was -1.3 [per mil], clearly following the expected trend. However, no such latitudinal trend was apparent for δ $^{13}C/^{12}C$ in foliage: in Fairbanks the average value was -23.18 [per mil] and in Singapore the average value was -24.1 [per mil]. Trends for δ $^{15}N/^{14}N$ in aerosols were similar to those in foliage: the average value of δ $^{15}N/^{14}N$ in the nitrogen oxides substances within the aerosol samples in Fairbanks was -2.70 [per mil], whereas in Singapore the average value was +7.61 [per mil], showing a clear increase with decreasing latitude. However, δ $^{18}O/^{16}O$ in aerosol samples did not show a latitudinal trend: the average value of δ $^{18}O/^{16}O$ in the nitrogen oxides substances within the aerosol samples in Fairbanks was +42.97 [per mil], very similar to the average value in Singapore, which was +46.36 [per mil]. In summary, comparison of the Fairbanks samples and the Singapore samples only showed a latitude effect for nitrogen stable isotopes (both in foliage and in nitrogen oxides substances within the aerosol samples).

In Singapore, day length as well maximum and minimum temperature remain nearly constant throughout the year. If δ $^{15}N/^{14}N$ was correlated with these factors only, it should not show substantial change throughout the year (Fig. 1, Figs. 3-5). However, δ $^{15}N/^{14}N$ in Singapore does vary considerably over the course of a year. These variations in δ $^{15}N/^{14}N$ in nitrogen oxides substances within Singapore aerosol samples were clearly correlated with declination. δ $^{15}N/^{14}N$ in nitrogen oxides substances within the aerosol samples reached maximum values at declinations approximately 20º N and 20º S. Minimum values were reached at approximately 0º N and S (Fig. 2). Singapore is located at 1.3º N, almost at the equator. Therefore, similar declination values indicate similar positions of the sun from Singapore. This allowed us to confirm the correlation between declination and delta $^{15}N/^{14}N$ in nitrogen oxides substances within aerosols. Another mechanism by which latitude affects stable isotope ratios concerns the deflection of cosmic rays. Cosmic radiation decreases with decreasing latitude, reaching a minimum at the equator. This is because the earth's geomagnetic field (specifically the Van Allen radiation belt) deflects cosmic rays most effectively at the equator[13]. When declination approaches 0º N and S, cosmic radiation to Singapore decreases. Therefore conversion from ^{14}N into ^{14}C decreases and thus the relative amount of ^{15}N in the stable isotope ratio also decreases. On the other hand, as declination approaches 20º N and S, cosmic radiation to Singapore increases and accordingly the relative amount of ^{15}N in the stable isotope ratio also increases. The results of this study were closely aligned with these explanations of the relationship between declination and values of δ $^{15}N/^{14}N$ in nitrogen oxides substances within the aerosol samples.

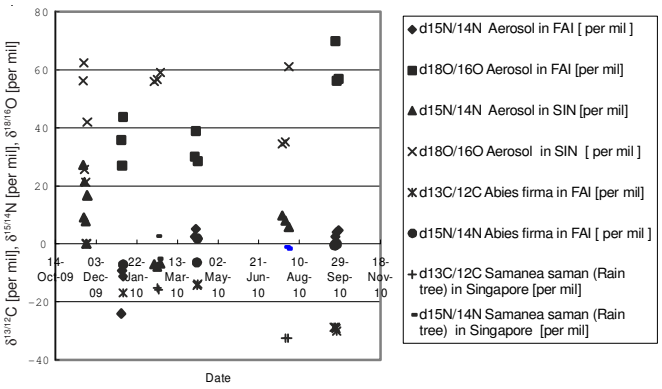

Fig. 1. Date *Vs.* Isotope Ratios; (FAI: Fairbanks, Alaska; Latitude: 64.84º North); (SIN: Singapore; Latitude: 1.3º North)

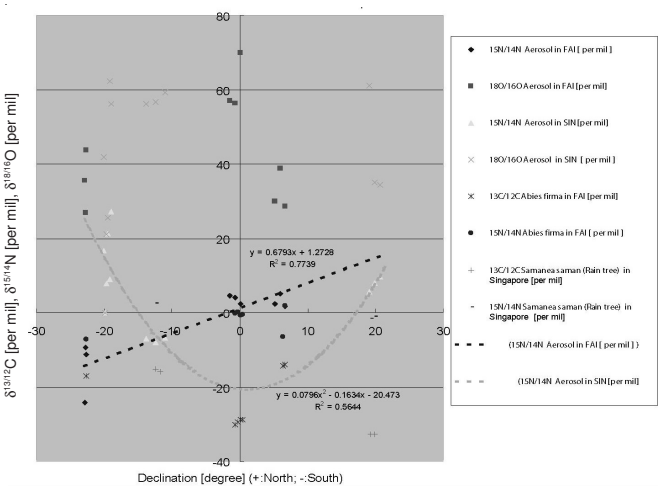

Fig. 2. Declination *vs*. Isotope Ratios; (FAI: Fairbanks, Alaska; Latitude: 64.84º North); (SIN: Singapore; Latitude: 1.3º North)

Fig. 2. shows a significant positive linear relationship between declination and δ $^{15}/^{14}N$ in nitrogen oxides substances from the aerosol samples in Fairbanks. However, unlike Singapore, Fairbanks also showed distinct trends for maximum and minimum atmospheric temperature and day length. In higher-latitude regions such as Fairbanks, declination has a greater effect on maximum and minimum atmospheric temperature and day length than it does in lower-latitude regions such as Singapore. Longer day lengths in Fairbanks contribute to higher atmospheric temperatures, which in turn propel nitrogen oxides substances within the aerosol to higher altitudes

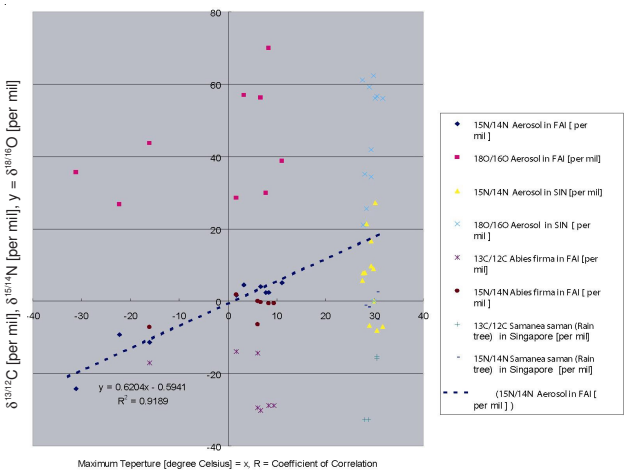

Fig. 3. Maximum temperture *vs*. isotope ratios; (FAI: Fairbanks, Alaska; Latitude: 64.84º North); (SIN: Singapore; Latitude: 1.3º North)

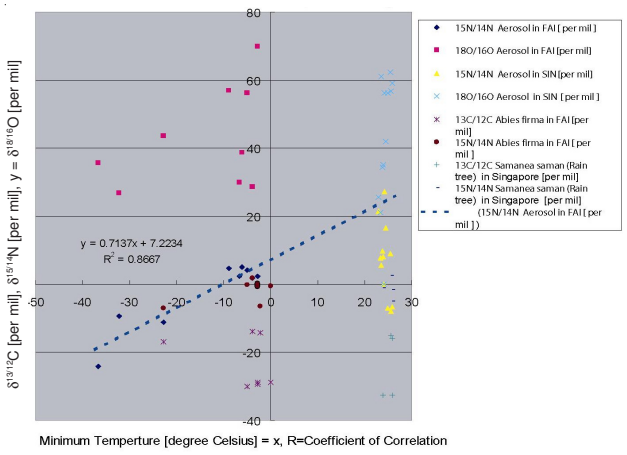

Fig. 4. Minimum temperature *vs*. isotope ratios; (FAI: Fairbanks, Alaska; Latitude: 64.84º North); (SIN: Singapore; Latitude: 1.3º North)

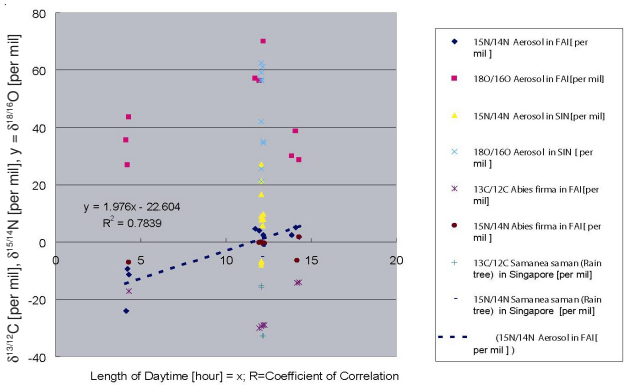

Fig. 5. Length of daytime vs. isotope ratios; (FAI: Fairbanks, Alaska; Latitude: 64.84º North); (SIN: Singapore; Latitude: 1.3º North)

where they are exposed to greater numbers of neutrons. Consequently, it was observed that the value of $\delta\ ^{15}N/^{14}N$ in nitrogen oxides substances within the aerosol samples in Fairbanks increased with increasing declination, due to more active conversions from ^{14}N to ^{14}C by neutron bombardment.

If variation of $\delta\ ^{15}N/^{14}N$ in Singapore was correlated with photochemical reactions, value of $\delta\ ^{15}N/^{14}N$ should be maximum at when declination was at the equator. Because Singapore is located at 1.3º North, almost the equator and it receives maximum lightning from the sun when declination is at the equator. However actual data in Singapore does not indicate that maximum value of $\delta\ ^{15}N/^{14}N$ does not appear at declination at the equator. Furthermore in Singpore it had been never observed nitrate concentrations decrease in atmosphere.

Conclusion

It is known general tendency as a latitude effect that nitrogen stable isotope ratios $\delta\ ^{15}N/^{14}N$ in the foliage in lower latitude has higher than that of in higher latitude. Average value of $\delta\ ^{15}N/^{14}N$ in foliage in Fairbanks (Latitude: 64.84º North) was -1.84 [per mil] *versus* average value of $\delta\ ^{15}/^{14}N$ in foliage in Singapore (Latitude: 1.3º North) was -1.3 [per mil]. It was subjected to this latitude effect clearly. However average value of $\delta\ ^{13}C/^{12}C$ in foliage in Fairbanks was -23.18 [per mil] *versus* average value of $\delta\ ^{13}C/^{12}C$ in foliage in Singapore was -24.1 [per mil]. It was unclear tendency for $\delta\ ^{13}C/^{12}C$ in foliage between Fairbanks and Singapore. In Singapore it was also observed that values of $\delta\ ^{15}N/^{14}N$ in nitrogen oxides substances within the aerosol samples were clearly correlated with declination. The value of $\delta\ ^{15}N/^{14}N$ in nitrogen oxides substances within the aerosol samples in Fairbanks increased with increasing declination due to more active conversions from ^{14}N to ^{14}C by neutron bombardment.

To date majority of people has believed that the reason of increasing concentration of carbon dioxide in the atmosphere past 2 centuries is anthropogenic emission by fossil fuel burning. However this study implies that at least one of this reason may be affecting by cosmic-ray bombardment to nitrogen in the atmosphere. It is time to reconsider the real intention of control of reduction of carbon-dioxide emissions by the some developed nations.

ACKNOWLEDGEMENTS

It was my great pleasure to attend ICGTCS-2012 (International Conference on Global Trends in Pure and Applied Chemical Sciences) conducted by Asian Journal of Chemistry in Udaipur, India from 3 to 4 March 2012, in the world's largest population in democratic nations as an invited speaker by the convener Dr. Ram K. Agarwal with supporting by Organization for the Prohibition of Chemical Weapons (OPCW).

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