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The Atomic Weight and Isotopic Composition of Nitrogen and Their Variation in Nature*

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I. Introduction

Two stable isotopes of nitrogen exist in nature, ^{14}N and ^{15}N. The less abundant isotope, ^{15}N, was discovered in 1929 by Naude[1], who studied the band spectra of nitric oxide, NO. However, the main source of a standard for this element is the air in our atmosphere, which is made up of approximately 78% N_2. In section II, we will review the measurements of the isotopic composition in air and its variation around the world. In section III, we will investigate the variation of the isotopic composition in the various compounds or sources of nitrogen compared to the value in air. Section IV will review the data on the atomic weight and section V will be concerned with the non-terrestrial data for nitrogen. Section VI will address some comments on the problem of the nitrogen atomic weight.

II. Nitrogen Isotopic Composition in Standard Air

Naude's discovery of ^{15}N came from a search of the absorption band spectrum of nitric oxide produced from $NaNO_2$. Urey and Murphy[2] were the first to report measurements of the isotopic composition of air nitrogen. Since then, there has been a long series of such measurements as indicated in Table I. It should be noted that the first measurement which attempted to calibrate the instrument for the problem of mass discrimination was that of Nier[3], in 1950. Junk and Svec[4] also performed a calibrated measurement of nitrogen in air in 1958. These measurements are consistent and the value of Junk is recommended. In Table I, use has been made of the measurement by Nier[3] of the oxygen isotopic composition in air in order to convert the ratio. $^{15}N^{16}O/^{14}N^{18}O$, to a value for $^{14}N/^{15}N$.

Air has been used as a laboratory standard for nitrogen and attempts have been made over the years to investigate the variations in the isotopic composition of atmospheric nitrogen. Table II lists the results of the various studies performed to date. Basically, atmospheric nitrogen is invariant, at least to the level of accuracy of the present measurements, both for locations around the world as well as for the height at which the air sample was collected.

This property of invariance around the world aids in the study of variations of various nitrogen compounds, as described in the next section. These variations

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are referenced to the standard of nitrogen in air, and result in complete isotopic composition and atomic weight values being calculated for each of the compounds. The effect of these variations on the value that IUPAC recommends for the atomic weight can be seen in section IV. These will be discussed in section VI.

Table I. $^{14}N/^{15}N$ Values in Air

Author (Year)	Ref.	$^{14}N/^{15}N$
Urey (31)	2	270.
Urey (31)	2	270.
Murphy (32)	5	269. ± 3.
Vaughn (34)	6	265. ± 8.
Nier (50)	3	273. ± 1. ****
White (50)	7	268.5 ± 1.4
Smith (51)	8	268.9 ± 0.4
Soloway (51)	9	260.8 ± 0.7
Junk (58)	4	272.0 ± 0.3 ****
Palmer (60)	10	270.0 ± 0.3 #
Pilot (63)	11	273.2
Chatterjee (73)	12	265.1
IUPAC Mean Value (85)	13	271.

**** Calibrated Measurement

Possible Carbon Monoxide Interference

Table II. Variations of Nitrogen Isotopic Composition in Air

Author (Year)	Ref.	Variation	Source
McQueen (50)	14	$^{14}N/^{15}N$ varies by (3.9 ± 0.4)%	Air 41.4 km. – 58.8 km.
Dole (54)	15	Constant to 1 Part in 650	Air to 51.6 km.
Junk (58)	4	Constant to 1 Part in 7000	Air to 11 km.
Hoering (58)	16	Constant to 4 Parts in 10,000	Various Samples – USA
Mariotti (83)	17	Constant to 1 Part in 25,000	Austria, Canada, France, Mexico, Caribbean, USA

III. Variation of the Isotopic Composition in Terrestrial Compounds

The isotopic composition of nitrogen in rocks, minerals, oil, coal, natural gases, atmospheric compounds, nitrogen in soil and dissolved or suspended in water and from biological processes have been extensively studied and reported in the literature. The variations are usually reported as per mil (1/1000) deviations in the ratio $^{15}N/^{14}N$ of the sample relative to some standard, usually nitrogen in atmospheric air. This deviation takes the usual form as indicated below:

$$\delta^{15}N = 1{,}000 \times [(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard} / (^{15}N/^{14}N)_{standard}]$$

Thus, positive deviations correspond to an excess of ^{15}N in the sample, while negative deviations correspond to a deficiency of ^{15}N in that sample. Table III lists some $\delta^{15}N$ values for various types of samples of nitrogen found in nature and they are all reported relative to a standard of nitrogen in air.

From Table III, it can be seen that most of the terrestrial sources have extreme values which exceed the new limits placed on the variation by the latest IUPAC value and uncertainty as recommended in 1985, i.e. $\delta^{15}N$ = −15.4 to +23.0. The very large value for the depleted ^{15}N variation in the case of atmospheric compounds corresponds to exhaust from a nitric oxide plant. If we should eliminate such airborn pollution sources, this extreme value would be reduced to −13.7, rather than −150, as listed in Table III.

Table III. Nitrogen Isotopic Abundance Variations in Various Terrestrial Materials

Source	$\delta^{15}N$ – Mean Value (Range)	Ref.
Distilled Water	+0.85 ± 0.10	18
Tank N_2	−3.38	4,9,19
Rocks, Minerals	−15.6, +30.9	11,20,21,22,23,24
Coal, Oil, Gas	−24., +27.5	8,11,12,16,20,21,25 26,27,28,29,30,31
Atmospheric Compounds	−150., +21.4	28,32,33.34,35
Soil Nitrogen	−23.4, +28.6	21,28,36,37,38,39 40,41,42,43,44
Biological Processes	−49., +54.7	20,28.34.42.43.45,46.47 48,49,50,51,52,53,54,55
Organic Matter in Water Oxides in Water	−15., +29.	56,57,58,59,60,61,62,63.64,65.66

IV. Atomic Weight Values and Their Variation in Terrestrial Materials

The atomic weight value of 14.01 was recommended by the Atomic Weight Commission in 1907 based on the measurement of gaseous densities of nitric oxide and nitrogen by Gray[67] and his analysis of the oxide. In 1920, the Commission adjusted this value to 14.008, without comment. These values were based on the scale of oxygen = 16. When the atomic weight scale was changed to ^{12}C = 12. in 1961, the Commission changed the recommended value of the nitrogen atomic weight to 14.0067±0.0001, based on the calibrated measurement of the isotopic composition of nitrogen in air by Junk and Svec[4] and the 1960 Atomic Mass Table of Mattauch[68]. In 1985, the Commission changed their rule on quoted uncertainties to allow all digits from 1 to 9. The atomic weight of nitrogen was shifted to the mid-point of the range of measured terrestrial values known to the Commission, corresponding to 14.00674±0.00007.

In 1983, the Commission had added a footnote 'g' to account for the fact that one known extreme variation at the high end just fell outside the uncertainty limits of 14.0067 ± 0.0001 at 14.00681. However, with the change made by the Commission in 1985, this extreme was now covered and the 'g' should have been removed. As it turns out, the Commission could argue that all of the deviations in Table III that fall outside of the present limits were intended to be covered by this failure to remove the footnote. This brings up the matter of exactly what does the 'g' denote and what does the Commission mean by geologically exceptional samples? If we accept the variations as listed but eliminate the airborn pollution sources as noted earlier, the atomic weight values for the extreme variations become: 14.00654 and 14.00692.

V. Isotopic Abundance Variations in Various Non-Terrestrial Materials

The isotopic composition of nitrogen in various non-terrestrial materials have been measured on meteorites for many years. Measurements on other planets, stars and in solar flares are of comparatively recent vintage. The values obtained for these materials are significantly different from the values measured here on Earth in many cases, as can be seen in Table IV. The range of atomic weight values, which correspond to these $\delta^{15}N$ values listed in the Table, are shown in Table V.

VI. Discussion

As can be seen from an inspection of the various Tables, the atomic weight of nitrogen as presently recommended does not include the various extreme values as reported in the literature. The Commission will have to decide how they wish to handle such variations. Nitrogen can be considered as a test case, since there are no doubt similar problems with many other elements, mostly concentrated among the light elements. It is to be expected that even wider variations will be discovered and reported in the future. What are meaningful variations? Until the Commission decides on that question, we can not begin to decide how to treat the known data.

Table IV. Nitrogen Isotopic Abundance Variations in Various Non-Terrestrial Materials

Source	$\delta^{15}N$ – Mean Value (Range)	Ref.
Moon	−190., +156.	69,70,71,72,73
Mars	+739.	74
Venus	0. ±280.	75,76
Jupiter	+632. ±272.	77
Sun (Solar Flares)	+1176., (−184. to +3696.)	78
Stars	−472.	79
Cosmic Rays	(−110,520. to +189,400.)	80,81,82
Instellar System – Plane	−286., (−167. to −375.)	83
Instellar System – Center	−500., (−286. to −615.)	83
Meteorites	−326., +1033.	84,85,86,87,88,89 90,91,92,93,94
Earth	−150., +54.7	For Comparison

Table V. Nitrogen Atomic Weight Values in Various Non-Terrestrial Materials

Source	Atomic Weight – Mean Value (Range)
Moon	14.00603 – 14.00729
Mars	14.00940
Venus	14.00563 – 14.00764
Jupiter	14.00803 – 14.01005
Sun (Solar Flares)	14.01099, (14.006056 – 14.020703)
Stars	14.0050048
Cosmic Rays	14.293 – 14.414
Instellar System – Plane	14.00536 – 14.00612
Instellar System – Center	14.00448 – 14.0057
Meteorites	14.00554 – 14.01047
Earth	14.006548 – 14.006925 (Airborn Pollution – 14.00318)

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