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The Atomic Weight and Isotopic Composition of Boron and Their Variation in Nature[a]

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Abstract

The boron isotopic composition and atomic weight value and their variation in nature are reviewed. Questions are raised about the previously recommended value and the uncertainty for the atomic weight. The problem of what constitutes an acceptable range for normal material and what should then be considered geologically exceptional is discussed. Recent measurements make some previous decisions in need of re-evaluation.

I. Introduction

Two stable isotopes of boron exist in nature, ^{10}B and ^{11}B, as was first shown by Aston[1]. Although Aston[2] implied that there might be a variation in the ratio of the two stable isotopes in nature, Thode[3] was the first to prove it experimentally over forty years ago. There was subsequent speculation that this variation was the cause for the differing values of the thermal neutron absorption cross section standard (at room temperature) used at various nuclear laboratories.

There are boron standards in NBS-Standard Reference Material-SRM-951 and CBMN-IRM-611. Unfortunately, they were not available when much of the early work on variations in the boron isotopic composition was being performed. This makes it difficult to intercompare the results from those various experimenters. There was a synthetic standard used at McMaster University which allows experimental results at that location to be compared. There was also a synthetic boron standard used at the New Brunswick Laboratory of the Atomic Energy Commission.

This report deals primarily with the variations in the boron isotopic composition in nature. This will have an impact on the uncertainty in the recommended value of the atomic weight and also question the procedure used to select the mean value and the uncertainty range.

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II. Boron Isotopic Standards

A standard reference material of boric acid[4], SRM-951, has been produced with a certified $^{11}B/^{10}B$ value of 4.044 ± 0.003, or an abundance value for ^{10}B of 19.83 atom %. In addition, Searles Lake borax has been measured relative to a standard source to have a $^{11}B/^{10}B$ ratio of 4.040 to 4.045. McMaster University had a synthetic boron standard[5] with a $^{11}B/^{10}B$ of 3.956. Searles Lake borax was measured to be 4.040 ± 0.008 for the $^{11}B/^{10}B$ ratio on the basis of this standard. The Atomic Energy Commission laboratory at New Brunswick used a synthetic boron standard[6] from the Knolls Atomic Power Lab with a ratio $^{11}B/^{10}B$ = 3.661 ± 0.007. The procedure used here has been to normalize values to the standard used in the experiment and if no standard was available to normalize the Searles Lake borax value to 4.044 and to determine other boron compositions correspondingly. Even with this procedure, some problems persist, which will be discussed later.

There has recently been another isotopic reference material prepared[7], CBMN-IRM-611, which has a certified $^{11}B/^{10}B$ value of 4.044 ± 0.005 or an abundance value of ^{10}B = 19.824.

III. Measured Boron Isotopic Compositions

The isotopic composition of boron had been controversal for many years, with the ^{10}B atom percentage thought to be 18.6% to 18.8%. This was thought to be due to the lack of a boron standard and to the use of BF_3, which causes a 'memory' effect in a mass spectrometer. With the introduction of synthetic standards for boron by the early 1960's, the measured ^{10}B abundance rose to a value of 19.8% for California borax (see Table I). Most of the recent experiments include values for the SRM-951 standard. Table II lists measurements on standards.

There is a question about the boron mean value because of the variations in composition. The Commission on Atomic Weights and Isotopic Compositions usually defines the mean value as that which would be commonly found in science and industry. Searles Lake borax would fall into this category with Italian and Turkish borax as additional common sources, which have ^{10}B abundance values 1.8% below and 2.0% above Searles Lake value, respectively. In addition, the Searles Lake borax ^{10}B value is almost at the mid-point of the range of compositions for all terrestrial boron materials.

IV. The Problem of Boron Isotopic Variations

Although there were some earlier results on the isotopic composition of boron in the literature, the first indication of the variation in different materials was the work of Thode and co-workers[3] in 1948. He found a 3.5% variation in various minerals. Although Oberghaus[8] did not find any variations, Parwell[9] did note a two tenths of one percent positive variation in seawater compared to minerals in the $^{11}B/^{10}B$ ratio, i.e., seawater is heavier or has a higher atom percent of ^{11}B. However in agreement with Oberghaus, Parwell did not find any variation in the ratio for boron in minerals above the few per mil (parts per thousand) level. Schiuttse[10] noted a 3.5% variation between Italian boron and central Asiatic boron. During the 1960's further work left no doubt that the variation in the boron isotopic composition was real. The only question became how large is this variation and what are the relative values for the various minerals.

In 1969, DeBievre[11] reported a large source of boric acid was available which would allow some intercomparison between measurements at the various laboratories. An intercomparison by Debus[12] showed that the boron neutron cross section measurements on natural boron disagreed because of this natural variation in the atom percent of the two isotopes. In the case of boron, one of these isotopes, ^{10}B, has an extremely large value for the absorption of the neutron at thermal energies (room temperature). The variation in the abundance of ^{10}B leads to a discrepancy in the cross section when two different sources of boron were used as standards in the measurements.

The isotopic composition of boron in rocks, minerals, and water have been extensively studied and reported in the literature. The variations are usually reported as per mil (1/1000) deviations in the ratio $^{11}B/^{10}B$ of the sample relative to some standard. This deviation takes the usual form as indicated below:

$$\delta^{11}B = 1{,}000 \times [(^{11}B/^{10}B)_{sample} - (^{11}B/^{10}B)_{standard}] \,/\, (^{11}B/^{10}B)_{standard}$$

Thus, positive deviations correspond to an excess of ^{11}B in the sample, while negative deviations correspond to a deficiency of ^{11}B in that sample. Table III lists some $\delta^{11}B$ values for various sea-water and brine samples found in nature.

V. Recommended Isotopic Composition of Boron

When you have an element such as boron, which has significant variations in the various minerals in which it is found, one has to decide what is meant by the natural isotopic composition of that element. We usually mean by that term the isotopic composition of the most common sources which would be available to science and industry for that element. However, this interpretation is what led to the problem with the neutron cross section community. The major sources were boric acid; from Searles Lake, California for the USA nuclear labs; maybe from Turkey in the case of European nuclear laboratories. Unfortunately, there was a very significant variation in the isotopic composition of boron even for the same mineral material from two different areas of the world.

As can be seen from Table IV, older Turkish boric acid measurements are from 1.5% to 1.8% lighter than the Searles Lake boric acid. This leads directly to the same difference in the boron cross sections. In fact, a 1.4% difference had been measured[12] by Debus with an uncertainty amounting to 0.3%. There is a recent measurement of Turkish borax which is only 0.5 % lighter. That could be a problem for solution to the cross section. The isotopic composition for the boric acid of common sources can be calculated from Table III to be 19.8% ± 0.3% for the atom percent of ^{10}B. The full range of isotopic compositions found in nature is from ^{10}B = 19.0 atom % (Dead Sea brines) to 20.4 atom % (tin bearing silicate). This leads to a value 19.8% ± 0.8% for the atom percent of ^{10}B, if the full range was included. If a restricted range is used, one must justify why a given mineral is considered normal and another with minimally larger isotopic abundance must be considered geologically exceptional. See sections VI and VII.

VI. The Isotopic Variations of Terrestrial Boron Sources

The isotopic composition of boron in rocks, minerals, brines, water and even biological samples have been extensively studied and reported in the literature. The per mil variations are reported in Tables IV and V. It can be seen that there is a problem with the Searles Lake borax and the seawater values in Shima's measurement[13], which used the McMaster University synthetic standard On the other hand, many of the other values measured by Shima appear to agree with subsequent measurements. It would almost appear that the values for the borax and sea-water had been interchanged in the various tables, except that there are two slightly different values for the borax and two separate values for Pacific Ocean sea-water and Tokyo Bay water. Sea-water was a problem. Both Shima and Agyei[14] found similar values slightly enriched in ^{11}B, while Schwarcz[15] found sea-water boron to be significantly enriched. This led the Commission to exclude sea-water boron as a normal source for the range or uncertainty in the atomic weight value and to treat it as a 'g' footnote, i.e.; a geologically exceptional material. As can be seen in Table II, Schwarcz's value has received support in more recent measurements. In addition, the range between the $\delta(^{11}B)$ values for the highest mineral and the sea-water decreased from + 23.7, + 40.6, which formed a natural break, to + 32.7, + 38.6. It has now become an almost continuous range of $\delta(^{11}B)$ values, to be discussed later.

VII. Atomic Weight Values and Their Variation in Terrestrial Materials

The atomic weight value of 11. for boron was recommended by the Atomic Weight Commission in their first Table in 1902. In 1906, the value was changed to 11.0, without comment. In 1919, the Commission adjusted this value to 10.9 and in 1925, to 10.82. In each case, the value was based on chemical measurements, and on a standard of O = 16. In 1961 when the atomic weight scale was changed to $^{12}C = 12.$, the Commission changed the recommended value of the boron atomic weight to 10.811 ± 0.003, based on the measurement of the isotopic composition of boron in Searles Lake borax by McMullen[5] and the 1960 Atomic Mass Table of Everling[16]. This value took into account the variations measured by Thode[3] and McMullen[5]. In 1969, the Commission reduced the number of significant digits to 10.81 ± 0.01 on the basis of Finley[6] and Schwarcz[15] measurements of the boron variation in nature. In 1983, the Commission changed their rule on quoted uncertainties to allow all digits from 1 to 9. The atomic weight of boron was shifted to the mid-point of the range of measured terrestrial values (with the exception of sea-water boron) known to the Commission. This corresponded to an atomic weight of 10.811 ± 0.005. There was a question raised about the Schwarcz measurement, so the sea-water boron value was treated as geologically exceptional material and a footnote 'g' was to be added. It was mistakenly left out of the table, and added finally in 1985.

From the data in Table III, the Searles Lake borax atomic weight value is 10.812, while that for Italian borax is 10.815 and for Turkish borax is 10.809.

However, the NBS measurement for Turkish boron would be 10.811 and would imply that the source of boron in European nuclear labs was of some unknown origin. These values are all within the quoted mean value and uncertainty in the atomic weight value recommended by the Commission. However, the value for sea-water[17] of 10.819 is outside that range since the Commission specifically excluded it. If one calculates the value for ulexite, hilgardite and boracite as measured by Swihart[18], the values of 10.8168, 10.8164 and 10.8162 are also excluded. In the past, the Commission included all mineral values and specifically excluded the questionable value for sea-water. New measurements now extend the range of mineral values almost up to that of sea-water. We are left with an uncertainty in the atomic weight value for boron which treats minerals as normal material or as geologically exceptional material depending upon whether or not the boron isotopic ratio falls within an arbitrary range. Since the sea-water value has now been established without question, it no longer makes sense scientifically to introduce the smaller range but should include the almost continuous range of boron variations. This would lead to an atomic weight of 10.812 ± 0.008. The value of 10.811 corresponds to a ^{10}B abundance value of 19.9 atom %. There had been no mineral with this abundance value, only a reference material from CBMN. This value was originally chosen to split the difference between Searles Lake borax and Turkish borax. Now this might correspond to the Turkish borax value and the European source may be some unknown material. This whole question should be readdressed along with the range interpretation.

VIII. Isotopic Abundance Variations in Various Non-Terrestrial Materials

The isotopic composition of boron in various non-terrestrial materials have been measured on meteorites. Measurements on cosmic rays provide the only other non-terrestrial source. The values obtained for the meteorites are close to the terrestrial values but the cosmic ray data are considerably different. The data can be seen in Table VI. The range of atomic weight values are shown in Table VII, for terrestrial as well as non-terrestrial material.

IX. Discussion

As can be seen from an inspection of the various Tables, the atomic weight of boron as presently recommended does not include the various extreme values as reported in the literature. The footnote "g" for exceptional specimens is being applied to sea-water, which covers three quarters of the earth's surface. The Commission will have to decide how they wish to handle such variations in a manner which is consistent from one element to another. As had been discussed some years ago in the report on nitrogen[19], 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. No action has been taken by the Commission on this problem. Hopefully, the Lisbon meeting will be different.

Table I. $^{11}B/^{10}B$ Ratio and ^{10}B Atom % Values

Author	$^{11}B/^{10}B$	^{10}B (atom %)	Comment
Elliot[20]	3.63 ± 0.02	21.6	Band Spectra, BO, Chilian Boron
Aston[2]	3.85	20.6	BF$_3$ source
Paton[21]	4.86 ± 0.15	17.1	Band Spectra, BH source
Ornstein[22]	4.43	18.4	Band Spectra
Inghram[23]	4.31	18.83 ± 0.02	BF$_3$ source
Watson[24]	3.88	20.5	BF$_3$ source
Thode[3]	4.37	18.62	Searles Lake borax
McNamara[25]	4.18	19.31	Searles Lake borax
Oberghaus[8]	4.11	19.57 ± 0.08	KBF$_4$ source
Shuittse[10]	4.106 ± 0.002	19.57	BCl$_3$ source
Panchenkov[26]	4.44 ± 0.05	18.38 ± 0.17	BF$_3$ source
Sevryugova[27]	4.11	19.5	BCl$_3$ source
Palmer[28]	4.09	19.65	Commercial sodium borate
Newton[29]	4.06–4.09	19.65–19.76	Borax
Semenov[30]	4.15	19.42	Boric oxide
Bentley[31]	4.19	19.27 ± 0.13	BF$_3$ source
Kolchin[32]	4.13	19.49	Borax
Zonov[33]	4.17	19.34	Boric acid
McMullen[5]	4.040	19.84 ± 0.08	Searles Lake borax
Finley[6]	4.070	19.72	Boric oxide
Goris[34]	4.00	20.0	Boric oxide
Shima[35]	4.020	19.92	Tokyo Seawater
Shima[13]	4.248	19.05	California Borax
Shergina[36]	4.231 ± 0.004	19.12	Reagent grade borax, Russian?
DeBievre[11]	4.044 ± 0.005	19.824 ± 0.020	Boric Acid, Merck
Schwarcz[15]	4.029 ± 0.018	19.88 ± 0.07	Average Terrestrial Rocks
Gensho[37]	4.04 ± 0.04	19.8 ± 0.2	Reagent boric acid
Rein[38]	4.0560 ± 0.0087	19.78 ± 0.04	Boron Carbide Pellets
Hannaford[39]	4.00 ± 0.04	20.0 ± 0.2	Atomic Absorption Spectrometry
Mamer[40]	4.07 ± 0.11	19.74 ± 0.41	Sodium Tetraborate
Gregoire[41]	4.177 ± 0.014	19.32 ± 0.06	NASS-1, ref.seawater
Kakihana[42]	4.087 ± 0.008	19.66 ± 0.04	Hot spring water, Japan
Spivack[43]	4.2037 ± 0.0004	19.217 ± 0.002	Seawater

Table II. $^{11}B/^{10}B$ Ratio and ^{10}B Atom % Values in Reference Standards

Author	$^{11}B/^{10}B$		^{10}B (atom %)		Comment
McMullen[5]	4.249		19.05		ORNL-A Standard
McMullen[5]	3.936		20.26		ORNL-B Standard
Finley[8]	3.664		21.4		KAPL Standard
Shima[13]	3.950,3.958		20.2		ORNL-B Standard
Agyei[14]	4.243,4 287		18.9–19.1		ORNL-A Standard
Agyei[14]	3.932,3.969		20.1-20.3		ORNL-B Standard
DeBievre[11]	4.044	± 0.005	19.824	± 0.020	Boric Acid, Merck
Catanzaro[4]	4.0436	± 0.0033	19.827	± 0.013	Boric Acid, Ref. Material, SRM-951
Nomura[44]	4.043	± 0.003	19.83	± 0.01	NBS-SRM-951
Tamura[45]	4.042	± 0.005	19.83	± 0.03	
Kanzaki[46]	4.045	± 0.005	19.82	± 0.02	NBS-SRM-951
Nomura[47]	4.046,4.050		19.80–19.82		NBS-SRM-951
Ramakumar[48]	4.045	± 0.002	19.82	± 0.01	NBS-SRM-951
Swihart[19]	4.0447	± 0.006	19.82	± 0.02	NBS-SRM-951
Spivack[17]	4.04558	± 0.00033	19.819	± 0.001	NBS-SRM-951
Duchateau[49]	4.023	± 0.010	19.91	± 0.04	CBMN-IRM-011
Xiao[50]	4.05037	± 0.00022	19.801	± 0.001	NBS-SRM-951
Oi[51]	4.0432	± 0.0020	19.829	± 0.008	NBS-SRM-951
Swihart[52]	4.040,4.045		19.82–19.84		NBS-SRM-951
Musashi[53]	4.044–4.047		19.81–19.83		Geol.Survey(Japan) Rock Ref.Std.
Palmer[54]	4.0456	± 0.0012	19.819	± 0.005	NBS-SRM-951
Zhang[55]	4.0428	± 0.0003	19.83		CBMN-IRM-011
Lamberty[7]	4.055	± 0.005	19.82	± 0.04	CBMN-IRM-611

Table III. Boron Isotopic Abundance Variations in Waters

Author	$\delta^{11}B$;Value or Range	Standard	Comment
Parwell[9]	+ 0.2	No standard;rel minerals	Sea-water
Shima[13]	+ 7.7	McMaster standard	Tokyo Bay
Agyei[14]	+ 0.25	McMaster standard	Tokyo Bay
Schwarcz[15]	+ 43., + 47.	McMaster standard	Arctic, Atlantic, Pacific
Nomura[44]	+ 38., + 40.	NBS-SRM-951	Pacific
Spivack[43]	+ 39.5	NBS-SRM-951	Atlantic + Pacific Ocean
Nomura[47]	4.200,4.207[a]	McMaster standard	Pacific Ocean
Kakihara[42]	4.087[a]	NBS-SRM-951	Hot Springs water, Japan
Palmer[54]	− 9.3, + 4.4	NBS-SRM-951	Yellowstone Hot Springs
Palmer[56]	+ 29.7, + 39.0	NBS-SRM-951	Red Sea Hydrothermal fluids
Vengosh[57]	+ 38.4	NBS-SRM-951	Eastern Australia Bay Water
Vengosh[58]	+ 55.7, + 57.4	NBS-SRM-951	Dead Sea Brines
Vengosh[59]	+ 51.7, + 54.9	NBS-SRM-951	Dead Sea Hot Springs

[a] $^{11}B/^{10}B$ ratio listed

Table IV. Boron Isotopic Abundance Variations in Various Terrestrial Minerals

Author	δ^{11}B;Value or Range	Standard	Source
Thode[3]	4.37 [a]	no standard	Borax (Calif.)
McMullen[5]	4.040[a]	McMaster standard	Borax Searles Lake
Shima[13]	4.248[a]	McMaster standard	Borax Searles Lake
Swihart[18]	+ 0.32	NBS-SRM-951	Borax Boron
Oi[51]	+ 2.3	NBS-SRM-951	Boron Borax
Oi[51]	+ 8.5, + 10.2	NBS-SRM-951	Searles Lake Borax
Xiao[50]	4.045[a]	NBS-SRM-951	Borax (Calif)
Thode[3]	− 18.1	Searles Lake borax	Turkish borax
Agyei[14]	− 8.7, − 14.6	McMaster standard	Turkish borax
Xiao[50]	− 4.9	NBS-SRM-951	Turkish borax
Thode[3]	+ 10.5	Searles Lake borax	Italian boric acid
Agyei[14]	+ 13.1, + 20.0	McMaster standard	Italian boric acid
Agyei[14]	+ 8.2	McMaster standard	Ulexite (Turkish)
Swihart[18]	− 4.45	NBS-SRM-951	Ulexite (Turkish)
Oi[51]	− 1.4, − 1.1	NBS-SRM-951	Ulexite (Turkish)
Swihart[18]	+ 31.7	NBS-SRM-951	Ulexite (USSR)
Swihart[18]	− 16.0	NBS-SRM-951	Ulexite (Calif.)
Oi[51]	− 3.1	NBS-SRM-951	Ulexite (Calif)
Thode[3]	− 22.9	Searles Lake borax	Ulexite (Argentina)
Finley[6]	− 30.4	KAPL standard	Ulexite (Argentina)
Agyei[14]	+ 7.2	McMaster standard	Ulexite (Argentina)
Shima[13]	− 9.4	McMaster standard	Ulexite (Argentina)
Finley[6]	− 12.4	KAPL standard	Colemanite (Calif.)
Agyei[14]	− 12.1	McMaster standard	Colemanite (Calif.)
Oi[51]	− 12.8, − 4.9	NBS-SRM-951	Colemanite Boron, Death Valley
Finley[6]	− 12.4	KAPL standard	Colemanite (Turkish)
Agyei[14]	− 11.6, − 12.1	McMaster standard	Colemanite (Turkish)
Swihart[18]	− 15.8	NBS-SRM-951	Colemanite (Turkish)
Oi[51]	− 9.8, − 6.8	NBS-SRM-951	Colemanite (Turkish)
Agyei[14]	+ 1.2	McMaster standard	Colemanite (Argentina)
Finley[6]	+ 23.7	KAPL standard	Inyoite (USSR)
Swihart[18]	+ 24.19	NBS-SRM-951	Inyoite (USSR)
Swihart[18]	− 11.8	NBS-SRM-951	Inyoite (Calif.)
Swihart[18]	+ 31.48	NBS-SRM-951	Hilgardite (La)
Swihart[18]	+ 28.4	NBS-SRM-951	Boracite (La)
Gregoire[41]	3.906, 4.026[a]	NASS-1	Tin-bearing silicate

[a] $^{11}B/^{10}B$ ratio listed

Table V. Boron Isotopic Abundance Variations in Other Terrestrial Materials

Author	$\delta^{11}B$;Value or Range	Standard	Source
Shima[13]	4.104	McMaster standard	Sea-water sediment
Gregoire[41]	4.027, 4.128[a]	NASS-1	Sea-water sediment
Spivack[59]	4.027, 4.108[a]	NBS-SRM-951	Sea-water sediment
Swihart[52]	- 22. - + 2.2	NBS-SRM-951	Tourmaline
Slack[60]	- 23.1 - - 17.2	NBS-SRM-951	Tourmaline
Palmer[61]	- 22.8 - + 18.3	NBS-SRM-951	Tourmaline
Chaussidon[62]	- 29.3, - 2.2	NBS-SRM-951	Tourmaline
Nomura[63]	3.965, 4.013[a]	NBS-SRM-951	Coal (Canada,China,USA,South Africa)
Nomura[63]	4.177	NBS-SRM-951	Coal (Japan)
Musashi[64]	- 0.5, - 2.2	NBS-SRM-951	Rock (Japan Hot Spring)
Smith[65]	0.79 - 0.836[a]	NBS-SRM-951	Blood Plasma
Smith[65]	0.39 - 0.47[a]	NBS-SRM-951	SRM-909, Human Serum
Smith[65]	0.76 - 0.82[a]	NBS-SRM-951	SRM-1571, Orchard Leaves
Smith[65]	0.87 - 0.91[a]	NBS-SRM-951	SRM-1548, Total Diet
Kanzaki[46]	4.053- 4.077[a]	NBS-SRM-951	Fumarolic Gases
Kanzaki[46]	4.040- 4.073[a]	NBS-SRM-951	Sassolites
Nomura[47]	4.07 - 4.13[a]	NBS-SRM-951	Fumarolic Condensates

Table VI. Boron Isotopic Abundance Variations in Various Non-Terrestrial Materials

Source	$\delta^{11}B$ - Mean Value (Range)	Ref.
Meteorites	- 55.6, - 21.0	Shima[13]
Cosmic Rays	+ 53.9	Mewaldt[66]
High Energy Cosmic Rays	- 208.5	Krombel[67]
High Energy Cosmic Rays	- 613.3	Bjarle[68]
High Energy Cosmic Rays	- 891., - 901.	Gibner[69]
Earth	- 30.4, + 57.	For Comparison
Atomic Weight Commission	- 35.6, + 27.1	For Comparison

Table VII. Boron Atomic Weight Values in Various Materials

Source	Atomic Weight - Mean Value (Range)
Cosmic Rays (High Energy)	10.298 - 10.772
Meteorites	10.8026 - 10.8084
Earth	10.8062 - 10.8200
Terrestrial Boron in Minerals	10.8062 - 10.8168
Terrestrial Boron in Sea-water	10.8176 - 10.8190
Atomic Weight Commission	10.806 - 10.816

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