different electrolyte was non-reducible. An equation was derived for the polarograms obtained and for estimation of the standard potential of the electron electrode from polarograms of salt solutions.

2. Two different types of measurements gave values of −1.86 and −1.92 volts for the standard potential of the electron electrode *versus* the standard potential of the hydrogen electrode at −36°. These values are roughly in agreement with a theoretical value of −2.04 volts calculated by Makishima.

3. A relationship between the solubility of metals in liquid ammonia and the standard potential of the electron electrode was presented.

URBANA, ILL. RECEIVED APRIL 15, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCMASTER UNIVERSITY]

Natural Variations in the Isotopic Content of Boron and its Chemical Atomic Weight

BY H. G. THODE, J. MACNAMARA, F. P. LOSSING AND C. B. COLLINS

Introduction

Several years ago it was suggested by W. J. Whitehouse and B. Pontecorvo that small variations in the isotopic abundances of boron might explain discrepancies in neutron capture crossection measurements made by different investigators using boron as a standard. As a result of this suggestion, seven or eight boron mineral samples were collected from various parts of the world with the object of determining the variation, if any, in the abundances of the boron isotopes with a mass spectrometer. However, interest in the neutron capture crossection aspect of the problem decreased and the problem was dropped for a while because of other work. The problem was again taken up during the past year because of general interest in the abundances of the boron isotopes. Inghram[1] made a careful study of the isotopic content of boron, but unfortunately did not publish information on the sources of his samples. Other investigators have demonstrated variations in the isotopic content of carbon,[2] and oxygen[3] in nature, and it would not be surprising to find some variations in the isotopic content of boron.

Urey and Greiff[4] first showed from thermodynamic considerations that the isotopes of the light elements did differ slightly in chemical properties. These differences in chemical properties result in some fractionation of the isotopes in natural processes. Isotopic exchange constants involving the isotopes of carbon, nitrogen, oxygen and sulfur have been calculated by the methods of statistical mechanics and checked by experiments.

Recently Urey[5] made a further study of the thermodynamic properties of isotopic substances and reviewed the theoretical and experimental results obtained to date. The boron exchanges which have been investigated from a theoretical point of view are limited to the boron halides. Exchange processes involving these particular compounds cannot readily be realized experimentally at normal temperatures. Of particular interest is the predicted difference in vapor pressures of isotopic boron chlorides. These differences predicted in the thermodynamic properties of isotopic boron compounds suggest that some isotopic exchange process might occur in nature which would result in a slight fractionation of the isotopes.

A change in the ratio of the boron isotopes can, of course, be effected by neutron irradiation. However, neutron intensities in the earth's surface due to cosmic ray and other sources would seem at the present time to be too low, especially in geological deposits below the surface, to account for possible variations in the isotopic ratios. To date, nine samples of boric acid, eight of known origin, prepared from boron minerals obtained from widely separated geological deposits, have been investigated. These samples were converted to boron trifluoride gas and the ratio B^{11}/B^{10} determined with a mass spectrometer. The results obtained for the nine samples are reported in this paper.

Experimental

Preparation of Samples.—The boron trifluoride samples used in the mass spectrometer investigations were prepared by a method described previously.[6] Stoichiometric quantities of potassium fluoborate, anhydrous boric oxide and concentrated sulfuric acid are mixed together in a flask and the mixture is heated strongly *in vacuo*. The boron trifluoride produced is bubbled through concentrated sulfuric acid saturated with boric oxide to remove hydrogen fluoride and moisture. The boron trifluoride is condensed by means of liquid air and is further purified by distilling from one ampoule to another, discarding the first and last portions. Care was taken at this point to avoid possible fractionation of the isotopes.

The anhydrous boric oxide used is prepared by dehydrating boric acid in a vacuum oven for two hours at 200° and the potassium fluoborate is prepared by treating boric acid with hydrogen fluoride to produce fluoboric acid which is converted to form the potassium salt by titration with 5 *N* potassium hydroxide. The boron samples came in the form of boric acid. All of these but one were prepared from borates by the usual treatment with sulfuric acid. The potassium salts are crystallized out first at elevated temperatures, after which the temperature is reduced to bring out the borax. (The borax is then treated with sulfuric acid to produce boric acid.) The boron sample obtained from Tuscany in Italy is ob-

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[1] Inghram, *Phys. Rev.*, **70**, 653 (1946).

[2] Nier and Gulbransen, THIS JOURNAL, **61**, 697 (1939).

[3] Murphy and Nier, *Phys. Rev.*, **59**, 771 (1941).

[4] Urey and Greiff, THIS JOURNAL, **57**, 321 (1935).

[5] Urey, *J. Chem. Soc.*, Part 2, 562 (1947).

[6] "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 21.

tained as boric acid directly. The boric acid vapors come out of rock fissures with volcanic gases and are collected in water lagoons and concentrated.

Mass Spectrometry.—Two mass spectrometers were used in the investigation. One is a 180° direction focussing instrument of the Nier type,[7] the other a 90° sector type.[8] In both cases ion current measurements were made with linear inverse feedback amplifiers coupled to a Leeds and Northrup Speedomax recorder.[9] The ratio of the boron isotopes B^{11}/B^{10} was obtained both from the BF_2^+ ions, masses 48 and 49, and the B^+ ions, masses 10 and 11.

The nine samples considered were first investigated on a relative basis. This is done by comparing each sample to a standard. The procedure is to record ion currents in the mass ranges mentioned above for a standard sample, quickly repeat this procedure with a sample, and return to the standard. The three sets of four ratios each can be obtained in about ten minutes. If the two sets of results for the standard sample agree within the limits of precision for a single set, then the comparison with the middle set is considered satisfactory. Although the ratio of the boron isotopes obtained will vary by as much as one-half per cent. from day to day, due to variations in the operation conditions of the mass spectrometer, the relative values obtained by the above procedure are good to 0.1 per cent.

Results

Figures 1 and 2 show typical recordings obtained with the 90 degree and 180 degree instrument, respectively. The ion current records in Fig. 1 were obtained using an automatic shunt selector[9] and the three shunt zeros are shown at the bottom by the dotted lines. The results of Fig. 2 were obtained with a manual shunt selector. In this case the zero is traced out by the pen between the peaks.

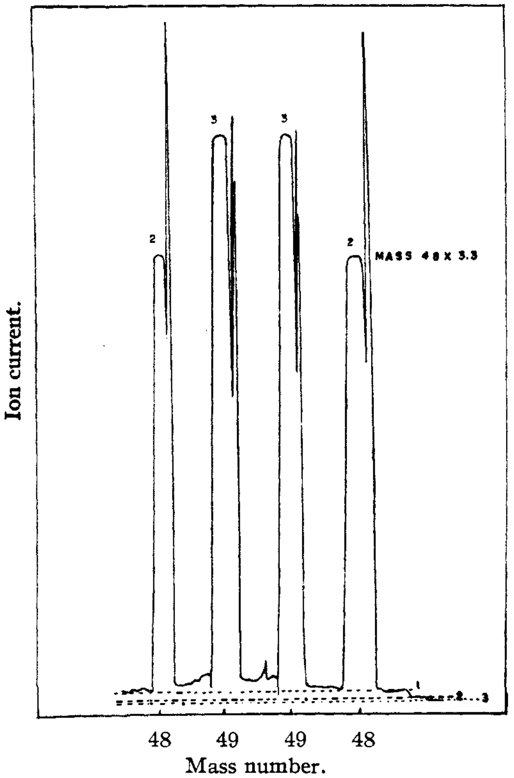

Fig. 1.—Recorded mass spectrograms of BF_2^+ ion currents obtained with a 90° sector type mass spectrometer. Shunts are selected automatically.

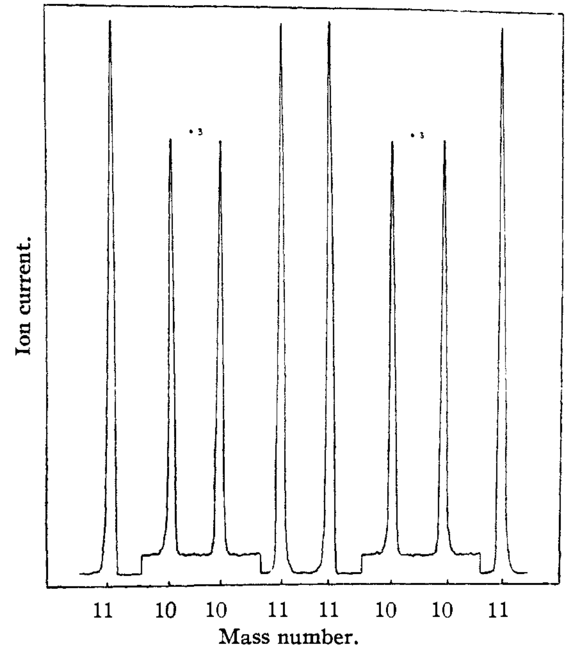

Fig. 2.—Recorded mass spectrograms of B^+ ion currents obtained with a 180° deflection mass spectrometer. Shunts are selected manually.

Table I gives the relative mass spectrometer B^{11}/B^{10} ratios for nine samples of boron trifluoride prepared from nine different samples of boric acid. These results were obtained by the method described above and could be checked relative to each other within the limits of the precision indicated. For example, two sets of values are given for sample 8. In each case the sample was compared with a standard. The two results, however, were obtained several days apart. The relative accuracy in regard to the mass spectrometer determinations is, therefore, about 0.1%. Sample 3 was arbitrarily chosen as the standard. The relative values obtained were ratioed to the value 4.370 which was found to be the average for the standard.

The results indicate that the ratio of the B^{11}/B^{10} varies from sample to sample by as much as 3 per cent, the two samples with a high ratio being prepared from boric acid obtained from Tuscany and Stassfurtite, and the sample with the lowest ratio being prepared from Argentine Ulexite.

Absolute Ratios.—The absolute value of the B^{11}/B^{10} ratio for a given sample cannot, of course, be determined with the same accuracy as can relative values. However, a careful study has been made of the factors which would affect the abso-

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[7] Thode, Graham and Zeigler, *Can. J. Research*, **23**, 40 (1945).

[8] Graham, Harkness and Thode, *J. Sci. Instruments*, **24**, no. 5, 119 (1947).

[9] Lossing, Shields and Thode, *Can. J. Research*, **25**, 397 (1947).

TABLE I

ISOTOPIC CONSTITUTION OF BORON SAMPLES FROM NATURAL SOURCES[a]

Sample no.	Mineral and geological deposit	Boric acid prepared by	Mass spectrometer Ratio B^{11}/B^{10}
1	Sultantchair, Turkey	Hopkins and Williams, London, Eng.	4.291 ± 0.008
2	Rasorite, Boron, Cal.	Pacific Coast Borax Co.	4.322 ± .004
3	Borax, brine of Searles Lake, Cal.	American Potash and Chemical Corp.	4.370 ± .005
4	Sample of boric acid	From unknown commercial source	4.369 ± .004
5	Stassfurtite, Stassfurt, Germany	Borax Consolidated, London, Eng.	4.422 ± .004
6	Ulexite, Tres Morros, Argentine	Borax Consolidated, London, Eng.	4.270 ± .001
7	Tincal, hot springs of Tibet	Borax Consolidated, London, Eng.	4.326 ± .004
8	Boric acid vapors, Tuscany, Italy	Borax Consolidated, London, Eng. (1)	4.416 ± .004
		(2)	4.411 ± .003
9	Pandermite, Sultantchair, Turkey	Borax Consolidated, London, Eng.	4.297 ± .01

[a] 180° mass spectrometer, magnetic scanning.

TABLE II

COMPARISON OF ABSOLUTE VALUES OF B^{11}/B^{10} OBTAINED WITH DIFFERENT INSTRUMENTS UNDER DIFFERENT CONDITIONS

Sample[a]	90° sector mass spectrometer, magnetic scanning, ratio $B^{11}F_2/B^{10}F_2$	180° mass spectrometer electrostatic scanning, $B^{11}F_2/B^{10}F_2$	180° mass spectrometer magnetic scanning, B^{11}/B^{10} Table I	Average ratio B^{11}/B^{10}
1	4.292 ± 0.019	4.256 ± 0.002	4.291 ± 0.008	4.280 ± 0.01
2	4.291 ± .008	4.359 ± .005	4.322 ± .004	4.324 ± .02
3	4.340 ± .013	4.358 ± .002	4.370 ± .005	4.356 ± .01
4	4.360 ± .004	4.358 ± .005	4.369 ± .004	4.362 ± .01
5	4.483 ± .010	4.371 ± .004	4.422 ± .004	4.425 ± .04
6	4.320 ± .009	4.278 ± .003	4.270 ± .001	4.289 ± .02
7	4.295 ± .002	4.369 ± .005	4.326 ± .004	4.330 ± .03

[a] Separate preparation of samples 1–7 of Table I. Each sample analyzed separately.

lute ratio. These included the effect of pressure and electron ionizing current on the ratio, as well as the linearity of the amplifier and recording unit, and the constancy of the grid leak as a function of signal. Table II shows the results obtained with two completely different set-ups, a 180 degree deflection, and a 90 degree sector type instrument.

From a study of the factors mentioned above and from a consideration of the results of Table II, the absolute accuracy of the ratios would seem to be good to ±0.5 per cent. or better. Impurities and compound formation in the mass spectrometer tube may account in part for this small variation. Moisture combining with boron trifluoride forms hydrofluoric acid which in turn produces silicon fluoride compounds with the glass apparatus. When the ratio of the boron isotopes was obtained from BF_2^+ ions, masses 48 and 49, a 47 mass peak was recorded which was found to be due to $Si^{28}F^+$. Therefore Si^{29} and Si^{30} would give SiF^+ peaks, masses 48 and 49, which would add to the BF_2^+ peak heights. In some cases when a large 47 peak occurred, a correction factor brought the ratio into agreement with former results, but in most cases the correction was negligible. No impurities giving ions corresponding to masses 10 and 11 were found. It is interesting to note that the absolute ratio of 4.311 obtained by Inghram[1] for an unknown sample falls in the range of values found for the different samples.

The Chemical Atomic Weight of Boron.—The isotopic weights of boron 10 and boron 11 obtained from mass spectra doublets have been given by Bainbridge and Jordan.[10] These are 10.016287 ± 72 and 11.012847 ± 78, respectively. Taking the lowest B^{11}/B^{10} ratio found of 4.27, sample 6, Table I, and using the factor 1.000274 to convert from the physical to the chemical scale, one obtains a chemical atomic weight of 10.82078 as compared to 10.82580 calculated for sample 8, Table I, which has a high B^{11}/B^{10} ratio. In other words, the chemical atomic weight of boron varies by 0.005.

Briscoe[11] is the only one to report slight variations in the chemical atomic weight of boron. Table III gives the atomic weights as found by Briscoe for three different samples. These are compared with values calculated from our mass spectrometer data for samples obtained from the same geographical areas.

TABLE III

Briscoe		Present work	
Source	Chemical at. wt.	Source	Chemical at. wt.
California	10.840	California, Pacific Coast Borax Co.	10.822
		American Potash and Chemical Co.	10.824
Tuscany	10.825	Tuscany	10.826
Asia Minor (Turkey)	10.818	Turkey	10.822

Results obtained for the Tuscany and Turkey samples are in close agreement with those of Bris-

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(10) Bainbridge, Paper presented at Seventh Solvay Congress, Sept. 21, 1947.

(11) Briscoe, *J. Chem. Soc.*, **127**, 150, 696 (1925).

coe. We do not check, however, the high value for the California sample. It is possible, of course, that some variation in the isotopic content of boron may occur within the California deposits. This possibility is being investigated.

Discussion

The boron samples investigated to date are all from secondary geological deposits with the possible exception of the boric acid vapors from Tuscany, which are of volcanic origin. Even in this case fractionation may occur in the vaporization process. Laboratory experiments are being carried out to determine the isotope fractionation, if any, in the steam distillation of boric acid. Other samples of boron from primary geological deposits are being collected. These include Tourmaline which contains 1–2% of boron and is a volcanic mineral. Finally, further secondary samples will be investigated to determine the variation in isotopic content of boron in different layers and at different depths in various California deposits.

Acknowledgments.—We wish to thank W. J. Whitehouse who first suggested this investigation and collected the samples, and M. Lounsbury who assisted with some of the mass spectrometer measurements. Further, we wish to thank the American Potash and Chemical Company, the Pacific Coast Borax Company, and Consolidated Borax, Limited, for their information regarding the mineral and geological deposits of boric acid samples. Finally we wish to acknowledge financial assistance from the National Research Council of Canada.

Summary

A mass spectrometer investigation has been made of the isotopic constitution of boron obtained from various mineral deposits in the earth's crust. This investigation involved the use of boron trifluoride gas which was prepared from boric acid. Both the BF_2^+ and B^+ ions were considered in the determination of the B^{11}/B^{10} ratios. Automatic recording equipment used with the mass spectrometers made it possible to determine the relative ratios of B^{11}/B^{10} for the different samples with a precision of ±0.1%, and an absolute accuracy of ±0.5% or better.

The ratio of B^{11}/B^{10} was found to vary from 4.27 to 4.42, or about 3.5%, depending on the source of the boron. Corresponding variations in the chemical atomic weights have been calculated using the latest mass data for the isotopes.

HAMILTON, ONTARIO, CANADA RECEIVED MARCH 19, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Photolysis of Persulfate. II. The Quantum Yield in Water and the Effect of Sodium Chloride in Dilute Alkaline Solution

BY LAWRENCE J. HEIDT, JOSEPH B. MANN AND HILDA R. SCHNEIDER

The persulfate ion, $S_2O_8^=$, in water absorbs ultraviolet light and is photochemically reduced to sulfate ions.[1,2,3] The over-all reaction is $S_2O_8^= + h\nu + H_2O = 2SO_4^= + {}^1/_2O_2 + 2H^+$. It is not known whether the oxygen produced in the reaction was originally part of the water, persulfate or hydroxyl ion. Hydrogen peroxide has not been found in any of the photolyzed solutions[3] so it is probably not an intermediate product in the photochemical reaction although it is made by the thermal hydrolysis of persulfates. The photochemical oxidation of the oxygen, therefore, appears to be the transfer of two electrons from divalent oxygen to the photon-activated persulfate anion.

The quantum yield, ϕ, of the reaction has been measured by R. H. Crist[2] and by L. J. Heidt[3] over a wide range of conditions. The value of ϕ is a maximum in neutral solution; it decreases rapidly as the acidity is increased but alkali has a smaller depressing effect. Maximum quantum yields of unity[2] and six-tenths[3] have been reported for the reaction produced by light of λ 254 mμ.

The value of unity reported by Crist[2] was obtained by measuring the sulfate produced in the reaction by precipitating and weighing it as barium sulfate. His quantum yields would be larger than the real values if other material came down with the barium sulfate.

The value of six-tenths reported by Heidt[3] was obtained by measuring the change in the concentration of persulfate. This was done by reducing the persulfate in a mixture of sulfuric and phosphoric acids with excess ferrous iron followed by titration of the excess ferrous with permanganate solution. His quantum yields would be smaller than the real values if any product of the reaction oxidized ferrous iron. This product was not hydrogen peroxide because separate tests[3] showed it to be absent; neither was it oxygen because it was shown that air[1] and oxygen[3] did not affect the quantum yields obtained by this method. However, if chloride ions contaminated the solutions, hypochlorite is a possible product of the reaction and would oxidize the ferrous iron thereby lowering the quantum yields. The laboratory supply of

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[1] J. L. R. Morgan and R. H. Crist, THIS JOURNAL, **49**, 960 (1927).

[2] R. H. Crist, *ibid.*, **54**, 3939 (1932).

[3] L. J. Heidt, *J. Chem. Phys.*, **10**, 297 (1942).