BORON ISOTOPES IN TERRESTRIAL AND EXTRA-TERRESTRIAL MATERIALS

ISOTOPIC AND ELEMENTAL COMPOSITION OF BORON IN METEORITES, TEKTITES AND TERRESTRIAL MATERIALS

By

EMMANUEL KENNETH AGYEI, B.Sc., M.Sc.

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
October 1968

DOCTOR OF PHILOSOPHY (1968)
(Physics)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Isotopic and Elemental Composition of Boron in Meteorites, Tektites and Terrestrial Materials

AUTHOR: Emmanuel Kenneth Agyei, B.Sc. (Lond.) (University of Ghana)
M.Sc. (McMaster University)

SUPERVISOR: Professor C. C. McMullen

NUMBER OF PAGES: x, 161

SCOPE AND CONTENTS:

The absolute B^{11}/B^{10} ratios of meteorites, tektites and terrestrial materials have been determined mass spectrometrically with a precision of 0.17 per cent (two standard errors) for one complete analysis, an accuracy of 0.05 per cent and a reproducibility of the mean of 0.08 per cent (half range).

Separation of boron was by cyclic pyrohydrolysis and the quantity determined by curcumin colorimetry with a precision of 9 per cent (two standard deviations), an accuracy (relative to isotope dilution) of 1 per cent and a reproducibility of 5 per cent.

The results indicate that there are no differences between the average terrestrial and meteoritic ratios. The slightly high value for Bruderheim (M) is probably due to latter-stage cosmic irradiation. Absorption of marine boron by certain clays produces a 4.8 per cent enrichment of B^{11} in sea water. Tektites appear to have a sedimentary rather than a chondritic or igneous origin.

Mean values of B^{11}/B^{10} ratios and boron content for meteorites and the planets are estimated.

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to my supervisor, Dr. C. C. McMullen, under whose direction, inspiration and keen interest this research was made possible. Thanks are also due to Drs. W. B. Clarke, H. P. Schwarcz and H. G. Thode for their many helpful suggestions, the first two of whom served on the supervisory committee.

I also wish to take this opportunity of thanking those mentioned elsewhere in the thesis who made samples available for my research, Mr. Edward M. Beaver for installing the new electronic units of the mass spectrometer, and Mrs. Stella Smith for typing this thesis.

Financial support for this work was provided by the National Research Council of Canada, to whom I am very much indebted.

Finally, I would like to thank the University of Ghana for awarding me a postgraduate scholarship which enabled me to undertake this research.

TABLE OF CONTENTS

Page

Page

LIST OF TABLES

Table No. Page

LIST OF ILLUSTRATIONS

PHOTOGRAPHS OF SAMPLES

CHAPTER I

INTRODUCTION

1. INTRODUCTION

Since the discovery of the isotopes of boron, their relative abundance in nature has been studied for a variety of reasons. They were first investigated as part of the general accumulation of nuclear data in order to develop suitable theories about the atomic nucleus. More researchers joined the investigation when it was discovered that the isotopic ratio was not constant in nature, and the studies became even more intensified as a result of the role played by boron in reactor physics. After several years of less activity in this field, it now appears that a new interest is being aroused by the work of nuclear astrophysicists who would like to know how boron, together with the light nuclei, lithium, beryllium and deuterium were originally synthesized. This has made it necessary to study boron in a wider variety of materials.

The present work involves studies of the amount of boron and its isotopic abundance in meteorites, tektites, and a variety of terrestrial materials. The rationale for analyzing the particular samples will be given in this thesis in the appropriate places.

2. PREVIOUS WORK

(a) Discovery of B^{11}/B^{10} Variations in Nature

When Aston (1920) discovered the two stable isotopes of boron at masses 11 and 10 with a mass spectrometer, he also made the first estimate of their abundance using photometry. Eleven years later, Aston (1931) made another isotope abundance measurement on a boron sample, probably of European origin. B^{11}/B^{10} ratios were also measured by Elliott (1930, 1931) using photometry on the band spectra of BO (Chilean boron) and by Paton and Almy (1931) also using photometry on the band spectra of BH.

Prior to 1946 a great deal of work had been done on the neutron capture cross-section and the isotopic ratio of boron because of the role this element played in reactor physics. Thode and co-workers observed during preliminary studies of the boron isotopes variations in the ratio of B^{11}/B^{10}. This led Whitehouse and Pontecorvo (1948) to suggest that isotopic variations might account for the discrepancies in cross-sectional values.

Inghram (1946) made a very careful determination of the isotopic ratio of boron in a sample of unknown origin. Two years later Thode et al. (1948) completed more extensive measurements of B^{11}/B^{10} for nine natural samples having different geological origins. They detected a variation of about 3.5 per cent, in agreement with the suggestion of Whitehouse and Pontecorvo that small variations in the measured values of the slow neutron capture cross-section of boron from laboratory to laboratory was due to a variation in the natural abundance of the boron isotopes.

The theoretical argument for the observed variations had already been given by Urey and Rittenberg (1933), and Urey and Greiff (1935), who calculated using thermodynamic considerations, the equilibrium constants, vapour pressures and isotopic enrichment factors of chemical reactions involving the isotopes of the light elements, lithium, carbon, nitrogen, oxygen and sulphur. These theoretical results were in good agreement with experimental observations, e.g. the work on carbon dioxide by Weber et al. (1935). Simple physical processes such as diffusion, evaporation, distillation, centrifuging, thermal diffusion and electrolysis may also give rise to isotope fractionation. Natural isotopic variations of up to 3 per cent were also observed by Dole and co-workers (1936, 1940, 1944) for oxygen; and up to 5 per cent by Thode et al. (1949) for sulphur. It was observed by Nier and Gulbransen (1939), and by Nier and Murphy (1941) that the C^{13} content was higher in inorganic sources than in organic systems.

(b) Improved Method of Analysis

Until 1960 all mass spectrometric work on boron used gaseous samples such as boron trifluoride, trimethyl boroxine and boron hydrides. Conflicting results of early workers were mainly due to memory effects left by adsorption of the sample gas on the walls of the gas inlet system of the mass spectrometer, and to isotopic fractionation due to inadequate chemical preparation of the samples. Another source of error in gas source mass spectrometers of low resolving power is the possibility of hydrocarbon backgrounds contributing to isotopic peaks.

Attempts were made by Bentley (1960) to reduce the BF_3 adsorption by carefully redesigning the gas inlet system, and correcting for instrumental error by calibrating the mass spectrometer with a prepared standard of a known B^{11}/B^{10} ratio. Unfortunately the instrumental discrimination did not remain constant during a series of analyses. A considerable advance was made towards solving these problems when the solid source techniques of mass spectrometry were applied to boron isotope measurements by McMullen et al. (1961) and other workers. In this method, samples are in the form of borax $(Na_2B_4O_7).10H_2O$ and the peaks are due to $Na_2BO_2^+$ ions. Although memory effects and hydrocarbon backgrounds are eliminated in this way, instrumental discrimination due to other causes is still present. Since it was found that this discrimination remained remarkably constant, provided there were no major changes in alignment of the components of the mass spectrometer, it was possible to calibrate an instrument with a prepared standard of known boron isotope ratio (see Chapter II, Section 4 (9), (v).

With improved chemical preparation of the samples and the application of solid source techniques together with a prepared standard for calibration, more accurate and reliable results for the B^{11}/B^{10} ratio have been obtained by McMullen et al. (1961), Goris et al. (1961), Finley et al. (1962), Shima (1962, 1963), and others. These results indicate practically the same variations in isotopic ratio observed in Thode's (1948) original work, but the absolute ratios, obtained by applying the necessary corrections, are lower by several per cent than those given by early researchers using gaseous samples. Recently, Agyei and McMullen (1968) have obtained a variation of 3 per cent in the absolute B^{11}/B^{10} ratios for boron minerals, confirming the work of Thode, but are about 7 per cent lower than those for gaseous samples agreeing with the results obtained by other workers using solid source techniques.

(c) Importance of B^{11}/B^{10} and Boron Content

Since enriched isotopes of boron are now widely available, variations of boron isotopes in nature have no significance to reactor physics, and earlier work on boron minerals seems quite secure when proper corrections are made for instrumental discrimination. However, the question of an appropriate B^{11}/B^{10} value to use for the earth's crust, the earth as a whole, or the solar system, is unanswered. In order to answer this question analyses have already been performed on boron from sources of primary origin, such as gabbro, basalt and meteorites, Shima (1962), Agyei and McMullen (1968). Some investigations have also been made by Cherepanov (1967) on boron in the kimberlite and meimechite of Siberia, and by Shergina and Kaminskaya (1963) for boron in high temperature silver-antimony deposits and copper-nickel sulphide deposits. The results of the last two groups of workers suggest the possibility of using boron for geological prospecting. The B^{11}/B^{10} ratio from sources of primary origin have not been found to be the same, suggesting that even in the primary materials there is variation of the B^{11}/B^{10} ratio. Just as in the case of minerals, it is essential to analyze many primary substances in order to evaluate the extent of the variation. Analysis of the B^{11}/B^{10} ratio from additional secondary sources, other than boron minerals, will also give further information about the distribution of the boron isotopes in nature.

It is also important to know the boron content for the material analyzed so that the geochemical cycle of boron can be understood. As will be seen in the next section, the average boron content as well as its isotopic ratio is also required for theories on the synthesis of this element.

3. NUCLEOSYNTHESIS

(a) Atomic Abundance

A glance at the atomic abundance curve (Burbidge, Burbidge, Fowler and Hoyle (B^2FH) 1957) in Fig. 1 will indicate that a group of nuclei falls off the main abundance curve and are several orders of magnitude smaller in abundance than their elemental neighbours. These are the isotopes of lithium, beryllium and boron, or (LiBeB) nuclei, which are sometimes referred to as the L-nuclei. Deuterium, too, exhibits similar abundance characteristics to the L-nuclei.

(b) Nuclear Processes

A comprehensive review of the thermonuclear reactions involved

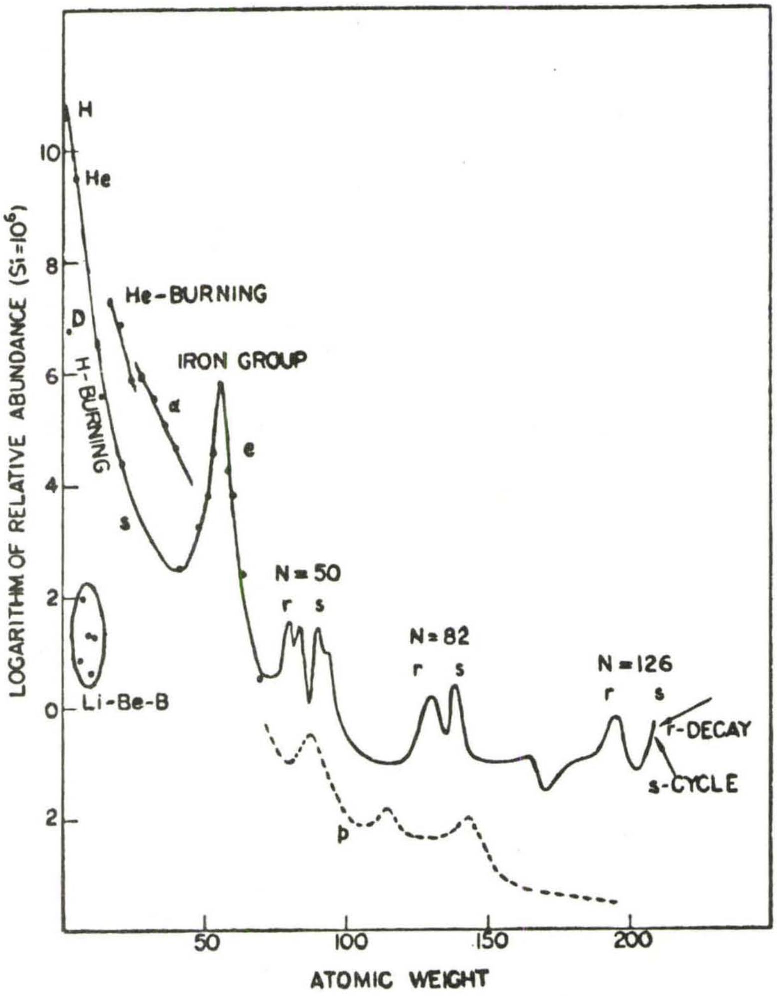

Fig I Atomic abundance curve (B^2FH, 1957) in the building up of the chemical elements in stellar interiors was given by B^2FH (1957). They assumed that all elements were synthesized from hydrogen (proton) by the following processes.

(i) Hydrogen (proton) burning to produce helium, after the initial hydrogen gas has contracted under gravitation to produce a temperature high enough to start fusion of hydrogen (protons).

$$p + p \longrightarrow H^2 + \beta + \nu$$

$$H^2 + p \longrightarrow He^3 + \gamma$$

$$He^3 + He^3 \longrightarrow \underline{\underline{He}}^4 + 2p$$

At a high temperature of say 1.3 x 10^7 $^{\circ}K$, and large He^4 concentration, the pp chain takes the form of:

$$He^3 + He^4 \longrightarrow Be^7 + \gamma$$

$$\left.\begin{array}{l} Be^7 + \beta^- \longrightarrow Li^7 + \nu \\ \\ Li^7 + p \longrightarrow \underline{\underline{2He^4}} \end{array}\right\} \text{ or } \quad \begin{array}{lll} Be^7 + p & \longrightarrow & B^8 + \gamma \\ B^8 & \longrightarrow & Be^{8*} + \beta^+ + \nu \\ Be^{8*} & \longrightarrow & \underline{\underline{2He^4}} \end{array}$$

With the presence of carbon, the well-known C-N cycle takes place, (Von Weizsacker, 1938; Bethe, 1939).

$$\begin{array}{ll} C^{12} + p \longrightarrow N^{13} + \gamma & \qquad N^{14} + p \longrightarrow O^{15} + \gamma \\ N^{13} \longrightarrow C^{13} + \beta^+ + \nu & \qquad O^{15} \longrightarrow N^{15} + \beta^+ + \nu \\ C^{13} + p \longrightarrow N^{14} + \gamma & \qquad N^{15} + p \longrightarrow C^{12} + \underline{\underline{He}}^4 \end{array}$$

This again converts four protons into He^4 and at the same time produces the isotopes: C^{13}, N^{14}, and N^{15}.

If sodium is present we have the neon-sodium cycle in which four protons are converted to He^4 in a similar way as the C-N cycle.

(ii) Helium Burning in which C, O, Ne and perhaps Mg are produced.

When the hydrogen (proton) burning ceases no further nuclear reactions occur until further gravitational contraction raises the temperature high enough to trigger helium burning. Fusion of two He^4 produces Be^{8*} which is very unstable and decays back to two He^4 nuclei (Salpeter, 1952). However, it has been shown that there is a small probability of three He^4 nuclei coming together to form C^{12*} (Hoyle, 1954; Fowler et al., 1956) which provides the means of bridging the gap between helium and carbon in the element synthesis in stellar interiors. Subsequent addition of He^4 to C^{12*} produces O, Ne and probably Mg.

(iii) α - particle processes in which Mg^{24}, Si^{28}, S^{32}, Ar^{36} and Ca^{40} are produced by the addition of α-particles, freed by heavy particle reactions, to produce O^{16} and Ne^{20}.

After all the He^4 produced from the hydrogen burning is consumed, a further increase in temperature by gravitational contraction is needed before further nuclear reactions occur. At temperatures of about 1.3×10^9 °K and over, α-particles are produced by heavy particle reactions such as:

$$Ne^{20} + \gamma \longrightarrow O^{16} + He^{4}$$

At higher temperatures, particles other than α may also be produced.

(iv) The equilibrium process (e-process) by which the elements in the iron peak are synthesized.

In this process, which occurs at temperatures over 3 x 10^9 °K, a statistical equilibrium exists between nuclei, free protons and neutrons. The concentration of the nuclei depends on the binding energies, the number and distribution of excited states, and other nuclear properties.

(v) The s-process in which neutrons are produced and captured at a relatively slow rate in a sequence to form the heavy nuclei.

(vi) The r-process in which neutrons are captured on a fast time scale (.01 - 10 secs).

(vii) The p-process by which proton-rich isotopes of the heavy nuclei are synthesized.

(viii) The x-process to account for the production of deuterium and the L-nuclei.

The particular features corresponding to each of these processes are indicated in Fig. 1.

(c) Nuclear Synthesis of the L-nuclei (the x-process)

We note from the above processes that there is a gap in the sequence of element production between mass 5 and 12 corresponding to the L-nuclei Li^6, Li^7, Be^9, B^{10} and B^{11}. In addition, deuterium was not accounted for. Moreover, even if these elements were produced at all they would be destroyed by such thermonuclear processes as:

$$D\ (d,p)\ H^3\ (\beta^-)\ He^3$$

$$D\ (p,\gamma)\ He^3$$

$$D\ (d,n)\ He^3$$

$$D\ (p,\gamma)\ He^3$$

$$Li^6\ (p,\alpha)\ He^3$$

$$Li^7\ (p,\alpha)\ He^4$$

$$Be^9\ (p,d)\ Be^8 \longrightarrow 2He^4$$

$$Be^9\ (p,\alpha)\ Li^6\ (p,\alpha)\ He^3$$

$$B^{10}\ (p,\alpha)\ Be^7\ (EC)\ Li^7\ (p,\alpha)\ He^4$$

$$B^{11}\ (p,\alpha)\ Be^8 \longrightarrow 2He^4$$

Because of the abundance characteristics of deuterium and the L-nuclei, and the fact that they are not accounted for in the main sequence of element synthesis in the interiors of hot stars, it became evident and first suggested by Fowler, Burbidge and Burbidge (1955) that they are produced in non-thermonuclear reactions at stellar surfaces and not in the interior. B^2FH (1957) considered the possible reactions of this nature which could produce these nuclei, however, it was Fowler, Greenstein and Hoyle (FGH, 1962) who first put this theory in mathematical form. This model was revised by Burnett, Fowler and Hoyle (BFH, 1965) using more recent experimental data.

In the model, deuterium and the L-nuclei in the solar system are obtained by spallation reactions on carbon, oxygen and nitrogen nuclei in metric-sized planetesimals by high energy particles from the sun, during the early history of the solar system. The isotopic ratios of Li and B from spallation are modified by the reactions B^{10} (n,α) Li^7 and Li^6 (n,α) H^3 to give the terrestrial values, the neutrons also having been produced by spallation and thermalized by the icy matrix in the planetesimals. The reaction H^1 (n,γ) D produces more deuterium. Spallation yields from heavy nuclei such as Mg, Si or Fe are also possible and this is discussed by BFH (1965).

In the BFH (1965) paper it is assumed that the high energy particles are mainly protons and the targets 0^{16} nuclei. Differential equations are written for the production of the L-nuclei and deuterium in terms of the number of neutrons, n, as the independent variable, since these are proportional to the number of protons, p. Considerations are given to the long half-life of Be^{10} $(2.7 \times 10^6$ yrs.) which

β-decays into B^{10}, and to the short half-life of Li^6 (0.8 sec). Instead of solving these equations for the isotopic abundances of the L-nuclei, the observed values are used to calculate the spallation yields and the neutron flux required to give these abundances, since it is felt that experimental data on spallation and neutron cross-sections and understanding of secondary processes are not enough for direct calculation of the abundances. For the Li^6/Li, Li^7/Li and B^{10}/B ratios which appear in the equations, the terrestrial values 0.0742, 0.926 and 0.196 respectively are used, whereas for B/Li the meteoritic value of 0.21 is used. It may be asked whether these ratios are constant throughout the solar system, and in particular, whether or not they are the same for meteoritic and terrestrial materials. It therefore becomes necessary to determine the isotopic and elemental abundances in extra terrestrial objects such as meteorites, since any uncertainties in these ratios among others will be reflected in the predicted spallation yields. For example, the calculated spallation yield for B/Li from this theory does not agree very well with laboratory determinations.

A slightly different model for the synthesis of the light elements is given by Bernas et al. (1967). From purely theoretical considerations they compute the spallation cross-sections for the production of (LiBeB) nuclei with high energy protons, and then with cosmic ray protons on (CNONe) targets. They conclude that within the uncertainty of the evaluations, the meteoritic B^{11}/B^{10}

is equal to its formation ratio on (CNONe) nuclei, but the Li^7/Li^6 ratio would have to be modified by (p,α) reactions. This implies that there is no need for slow neutrons, and hence, as discussed below, meteoritic and terrestrial B^{11}/B^{10} should be similar.

(d) Possible Isotopic Abundance Variations

The BFH (1965) theory predicts that if there were any differences in the history of the parent bodies of the earth and meteorites, such as unequal high energy proton irradiations, they should show up as a variation of the isotopic abundance of the L-nuclei and also of the heavy trace elements having high thermal neutron cross-sections, e.g. Gd, Sm and Eu.

Consider the cases of Li and B for example. Since the neutron flux is proportional to the proton flux, for a small neutron flux $Li^6\ (n,\alpha)\ H^3$ is relatively small and so Li^6 and Li^7 will rise linearly with the neutron or the proton flux, with a gradient given by the spallation rates. If the neutron (or proton) flux becomes large, the (n,α) reaction becomes significant and the Li^6 abundance reaches an equilibrium value, whereas Li^7 continues to increase at a greater rate because of the contribution from $B^{10}\ (n,\alpha)\ Li^7$. It can be seen that if the neutron flux varied in the primitive solar matter this could produce differences between the isotopic ratios of meteoritic and terrestrial Li, if, as it is generally believed, the earth and the meteorites were formed from different samples of the solar nebula.

Assuming that the meteorites are representative of the asteroidal belt, it is quite logical to make the assumption that their parent bodies received smaller radiation flux than the region occupied by the earth. In fact, FGH (1965) argue that according to an oversimplified version of Hoyle's (1960) astrophysical model of the solar system, on the basis of which they built their theory, the proton or the neutron flux would vary as 1/r from the inner edge of the solar disc, where r is the distance measured from the centre of the sun. This implies that the meteoritic Li^7/Li^6 should be smaller than the terrestrial value.

First, Shima and Honda (1963) found a 15 per cent variation in this direction, however, Krankowsky and Muller (1964, 1967) could find no variation to within 2 per cent. Ordzhonikidze (1960) also observed no differences. Dews (1966) reported that meteoritic and terrestrial Li^7/Li^6 are identical to within 3.3 per cent at the 95 per cent confidence level. Poschendrieder et al. (1965), using an ion-microprobe spectrometer, reported a variation of up to 200 per cent in Li^7/Li^6 ratio in the same piece of Holbrook meteorite. The variation in terrestrial hornblende does not exceed 8 per cent. These results suggest that terrestrial hornblende is more homogeneous than the Holbrook meteorite as regards the Li^7/Li^6 ratio, but does not provide information about the average value of the ratio in materials. They also found some variations of the boron content in the materials themselves. It, therefore, appears that the overall meteoritic and terrestrial Li^7/Li^6 are the same but this raises further problems, because it suggests that either the radiation was uniform throughout, or both the meteorites and the earth parent bodies once occupied the same position in the solar nebula.

Now consider the case for boron. For small neutron flux, n, both B^{11} and B^{10} will rise linearly with the neutron flux; but for large neutron flux, because of the loss of B^{10} as $B^{10}(n,\alpha)Li^{7}$, B^{10} will reach an equilibrium, while B^{11} will continue to increase. Using the same argument as for Li, this will again result in a smaller B^{11}/B^{10} for meteoritic boron than that of terrestrial boron. Thus far only Shima (1962) has measured the meteoritic B^{11}/B^{10}, and his results indicate that the B^{11}/B^{10} is smaller in meteorites than terrestrial materials by about 5 per cent. Although this agrees with the prediction, it disagrees with the experimental results on lithium, that there is no variation.

The results for the boron elemental abundance in Shima's (1962) work again give rise to another controversy, since they indicate that both stony and iron meteorites have about the same boron content ($\sim$0.5 ppm). This disagrees with the geochemical fact that boron, being a lithophile element would tend to concentrate in the silicate phase of the meteorites (see Appendix III). Because lithium, too, is lithophile, it should also concentrate in the stony meteorites. In support of this view the work of Fireman and Schwarzer (1957) indicates that Li^{6} is a factor of $>3.7 \times 10^{2}$ more abundant in stony meteorites than in the irons. In fact, because of the low abundance of lithium in iron meteorites, almost all the work done on meteoritic lithium has been in the chondrites.

Yiou et al. (1967), from mass spectrometric measurements of spallation yields for the light elements with energetic protons on (CNO) targets give a similar conclusion to that of Bernas et al. (1967). They suggest that there would be no need for a thermal neutron flux to explain the natural isotopic ratios of the light elements observed in the earth and meteorites. These eliminate the expected isotopic variation due to variation in the neutron flux. It is still possible, however, to have some variations due to other causes. As the calculations of Bernas et al. (1967) indicate, the spallation yields depend on the target nucleus, hence if the chemical composition of the solar nebula was not uniform, it might give rise to differences in the formation ratios of the L-nuclei. As mentioned earlier, fractionation of the isotopes could also result from chemical and physical processes and since the meteorites are thought to have been relatively chemically inactive, the primordial isotopic ratios would be better preserved in them than in the earth, especially the crust, which has undergone a great deal of chemical and physical modification. On the other hand, the meteorites could have been subjected to cosmic ray bombardment for some time during their flight through space and further spallation would occur. The B^{11}/B^{10} ratio can thus be altered again, but it is not at all certain in which direction the change will occur. If there is any observable effect at all, it should be a function of depth within the meteorite.

4. SCOPE OF PRESENT WORK

(a) Introduction

From the foregoing summary of the main theories and experimental results on boron, it is quite obvious that the problem of the isotopic composition of boron on the one hand and its elemental abundance on the other hand is far from settled. It is mainly because of this situation that this research was undertaken.

(b) Meteorites and Tektites

It was the prime purpose of this work to determine as accurately as possible both the isotopic and elemental composition of boron in meteorites and tektites, and to make a comparison with terrestrial values.

There is a disagreement about the origin of tektites too; both terrestrial and extra-terrestrial (specifically meteoritic, and even lunar) origins have been proposed. Short notes on these enigmatic objects are given in Appendix III. They appear like coloured glass when broken, but are quite dark and opaque otherwise, and contain between 70 and 80 per cent SiO_2. In one theory tektites are thought to have been formed by the fusion of terrestrial sedimentary rocks, by lightning, comets, or meteoritic impact; while in other theories they are derived from meteorites or the lunar surface by fusion. Hence, comparison of the B^{11}/B^{10} ratio and boron content in meteorites and tektites might give clues about the origin of tektites (Appendix III). It is now accepted that meteorites have an extra-terrestrial origin.

(c) Terrestrial Samples

A number of terrestrial samples were also analyzed. W-1, a diabase geological standard was analyzed carefully in order to test the extraction efficiency of boron for the technique which was developed for this work. In addition, some National Bureau of Standards steel samples were also analyzed. Hawaiian basalt, Finland tourmaline, and South African kimberlite were investigated as well in order to make comparisons of the results of this work with other published results. Other terrestrial samples were included, both to test the merit of the experimental procedure and as a contribution to the collection of pertinent experimental data for boron.

(d) Sea Water and the Clay Experiment

The isotopic ratio of boron for Tokyo Bay water has been reported by Shima (1962), and Agyei and McMullen (1968) to be 4.040 and 4.041 respectively. Shima (1963) has published the result for Pacific Ocean water to be 4.071 but did not indicate the exact source of the sample. These ratios appear to be very close to the average of the measured terrestrial B^{11}/B^{10} ratio and, therefore, seem to be quite reasonable, if one considers that the oceans serve as a large reservoir. However, in an effort to determine whether the B^{11}/B^{10} ratio was the same in different parts of the oceans additional sea water samples were analyzed. In an attempt to find out a possible mechanism giving rise to the results observed for sea water, the clay experiment was performed.

(e) Difficulties

A major problem with this project was to find a suitable extraction procedure for the trace quantities of boron, especially in meteorites. It was known that the boron content in meteorites was about 0.5 ppm. Therefore, it was necessary to reduce natural contamination to a very low level. After careful blank runs, it was found that the conventional chemical technique of methyl borate distillation was unsuitable. Blanks up to 2.5 μg of boron were observed, whilst the expected boron from the samples was about 5 μg. Since an all-quartz apparatus was used for the extraction, the boron in the blank must have come from the analytical grade reagents, all of which were further purified before use, except the sodium hydroxide. This extraction procedure would have been quite workable for boron-bearing minerals, since they contain a great deal of boron (tourmaline: ~3.5 per cent, boracite ~23 per cent). In the ppm range a better technique was necessary. Shima (1962), however, was able to obtain very pure reagents which gave blanks as low as 0.09 µg, as compared to the expected amount of boron of 10 to 15 µg.

Since a considerable part of the time for this work was spent in developing the extraction and detection procedures which are relatively new, they will be described in some detail. It can be seen in the next chapter that the method is applicable to a wide variety of samples. Readers not interested in the details of the detection and extraction may pass over Chapter II, Sections 2 and 3. As mentioned previously, both the extraction and detection were checked by analyzing standards viz. W-1, diabase, geological standard and National Bureau of Standards stainless steel. The curcumin method was compared with the isotope dilution method. Possible isotopic fractionations at various points in the analytical procedure, including the mass spectrometric analyses, were also checked using synthetic standards (see Chapter II, Sections 3 and 4).

After these preliminary calibrations, the samples were analyzed and the results are recorded in Chapter III. In Chapter IV, attempts are made to interpret the experimental results within the framework of the theories on nucleosynthesis and various physicochemical processes. In the appendices, details are given on the synthetic standards, borax A and borax B, the isotope dilution, and all the samples analyzed. Brief notes are also given on meteorites, tektites, the earth, and sea water.

CHAPTER II

EXPERIMENTAL PROCEDURE

1. PURIFICATION AND PREPARATION OF STANDARD SOLUTIONS

The only reagents that were directly involved in the extraction of the boron in this work are water, uranium oxide used as a catalyst, and the ion exchange resins. It will be described in Section 3 (b), (iii) how the catalyst and the resins were purified. All the other reagents to be mentioned in this section were used after the extraction, for either the detection of the boron in an aliquot or for the mass spectrometric determination of the B^{11}/B^{10} ratio. It will be shown in the appropriate sections how the use of these reagents was found to be satisfactory.

Unless otherwise stated, all commercial reagents were analytical grade and all glassware was made of quartz. All standard solutions and reagents prepared for this work were stored in polyethylene bottles, except the curcumin reagent which was stored in a quartz Erlenmeyer flask. There is no particular reason for this latter exception.

(i) 95 per cent Ethanol: This was purified by re-distilling it over sodium hydroxide, discarding the first one-fifth of the distillate and collecting the next three-fifths.

(ii) Distilled Water: The distilled water supplied in the laboratory was re-distilled using a quartz flask or a tin-lined can, discarding the same fractions of the distillate as in (i). By employing the detection method to be described later it was found that the level of boron in the distilled water could be reduced from 0.0008 ppm to 0.0003 ppm. It will be seen that this purification was not absolutely necessary, since the amount of water used was small. However, this re-distillation was always done as a precaution, in the event that the distilled water supplied in the laboratory became contaminated. Alternatively, the level of boron in the original distilled water could be checked and if found suitable, could then be used.

(iii) Curcumin Reagent: 0.01 g of curcumin powder and 1.25 g of oxalic acid crystals were dissolved in a solution containing 20 ml of the purified ethanol and 5 ml of the re-distilled water.

(iv) Sodium hydroxide (1) [NaOH(1)] : About 1.06 g of sodium hydroxide was dissolved in re-distilled water and made up to 1 litre.

(v) Sodium hydroxide (2) [NaOH(2)] : This contained 4.2 μg of sodium hydroxide per ml and was prepared by making up to 1 litre an aliquot of NaOH(1), using re-distilled water.

(vi) Boron Solutions: Standard solutions of borax A, borax B and analytical grade boric acid C were prepared, each containing a known amount of boron per ml. These solutions were to be used for calibration purposes.

2. DETECTION

(a) The Curcumin Method

Although the isotope dilution method of measurement could provide a higher precision than the curcumin method, the latter was used in this work, primarily because of its speed and convenience. It was necessary however to perform some preliminary tests before employing it. The curcumin method which is described below was modified from that of Dible et al. (1954) to suit this particular research. This is a well known technique, the theory of which can be found in many quantitative analytical chemistry books (e.g. Vogel, 1963). However, the experimental procedure used, including the precautions taken and the precision attained will be described.

(i) Calibration Curve:

To determine the boron content a boron-curcumin complex calibration curve was first prepared as follows.

An aliquot of the boric acid C solution was put into a 100 ml platinum evaporating dish and the volume made up to 10 ml with re-distilled water. One ml of the NaOH(1) solution containing 0.00106 g NaOH was then added to the solution in the dish. The resultant solution was slowly evaporated to dryness on a steam bath, inside a fume hood, the dish being covered with a 3 litre pyrex glass beaker. The beaker was heated at the top by a Glas-Col heating mantle to prevent any drops of the condensed water from falling back into the dish. This operation normally took from fifteen to twenty minutes.

Four ml of the curcumin reagent were then added to the contents of the platinum dish, washing down the walls of the dish in the process. The mixture was then evaporated slowly to dryness on a water bath maintained at $55 \pm 2^{\circ}$C for fifteen minutes, using an ordinary kitchen timer for timing. The water bath consisted of a 2.5 litre pyrex beaker and distilled water which were heated gently with a hot plate. The temperature of the bath, measured by a mercury-in-glass thermometer, was controlled manually.

Exactly 10 ml of the purified ethanol was then added and the contents stirred thoroughly with a silver spatula, making certain that all of the boron-curcumin complex was dissolved. The solution was then filtered through a No. 42 Whatman filter paper into a clean Erlenmeyer flask. The transmittance and absorbance of the complex were read on a Beckman DB Spectrophotometer, using 1 cm square absorption cells (cuvettes) at a wave length of 550 mµ where maximum absorption occurs. The reference solution was a sample of the purified ethanol which was used as the solvent for dissolving the boron-curcumin complex. Repeating this operation for different amounts of boron, the calibration curve shown in Fig. 2 was obtained. In this figure, the dots are the original values obtained for the boric acid C standard solution. The three squares correspond to the three means of the absorbance (or transmittance) in Table 1. The results in this table which were taken for aliquots of the standard solution of borax B, about one year later, give an estimate of the precision of the curcumin method. The average precision at the 95 per cent C.L. is 9 per cent, but it is evident that the relative precision is poor for very low values of boron content (<0.05 µg). This was probably due to contaminants in the laboratory. However it can be stated that the detection limit is probably about 0.05 µg.

(ii) Precautions

Results of this kind are possible only if certain precautions are taken. For example, for several months it was not possible to obtain consistent results from which to draw a satisfactory calibration line until it was found that the efficiency of the curcumin reagent was a function of its age. This is shown in Fig. 3.

To obtain Fig. 3, a 100 ml. stock of curcumin reagent was prepared as described earlier. The absorbance (or transmittance) of boron-curcumin complex, for 0.5 µg boron, using curcumin reagent from the same stock solution at different times was measured. It can be

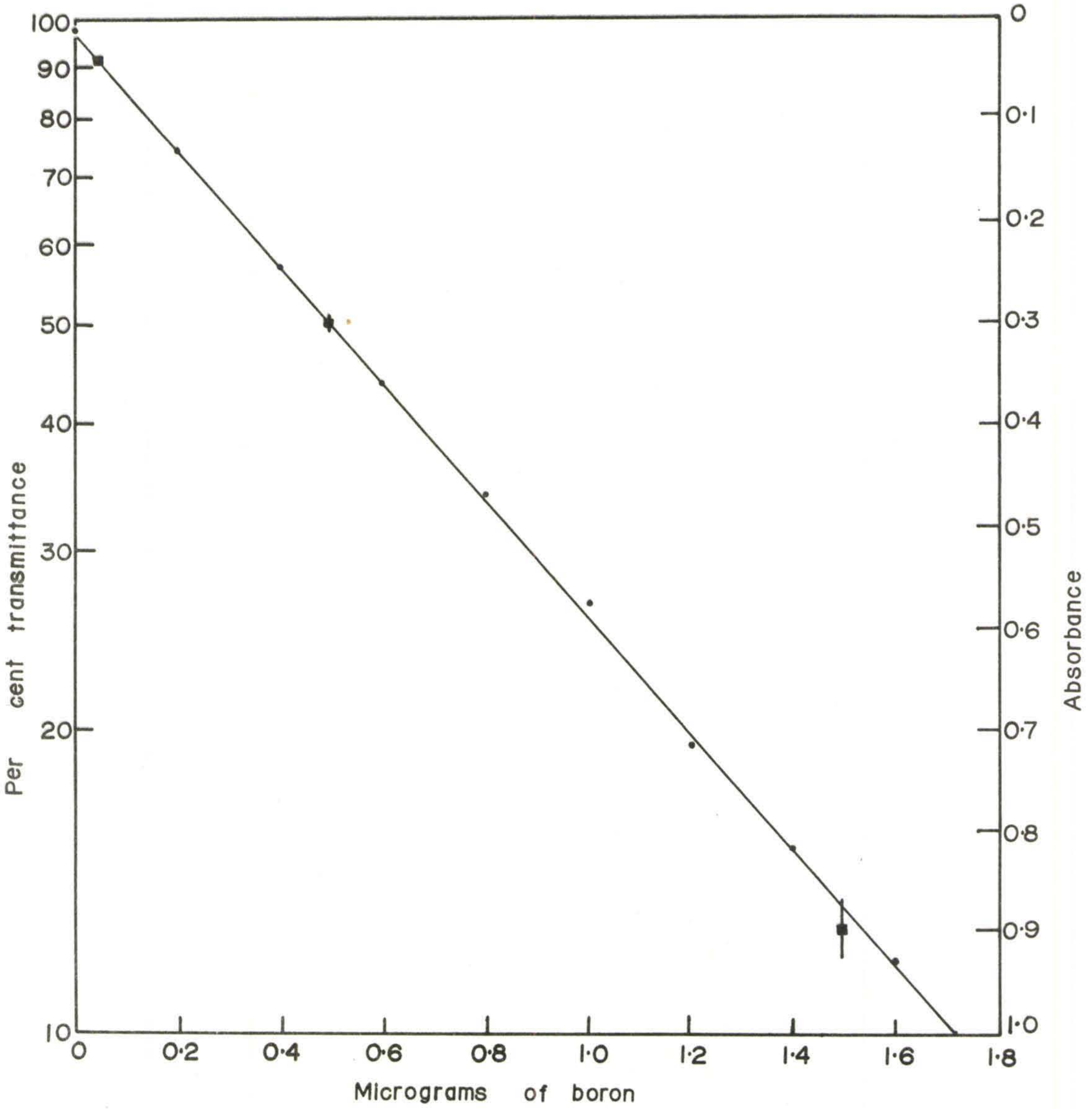

Fig 2 Curcumin calibration curve for determination of boron

TABLE 1

PRECISION OF CURCUMIN METHOD

Amount of Boron (µg)	Absorbance	Mean Absorbance ± std. dev. (95 % C.L.)	Relative Precision (%)
0.05	0.038		
	0.037		
	0.035		
	0.040		
	0.042	0.038 ± 0.006	16.0
0.5	0.304		
	0.294		
	0.306		
	0.297		
	0.290	0.298 ± 0.014	4.6
1.5	0.90		
	0.95		
	0.89		
	0.89		
	0.88	0.90 ± 0.06	6.6

Average relative precision = 9 per cent

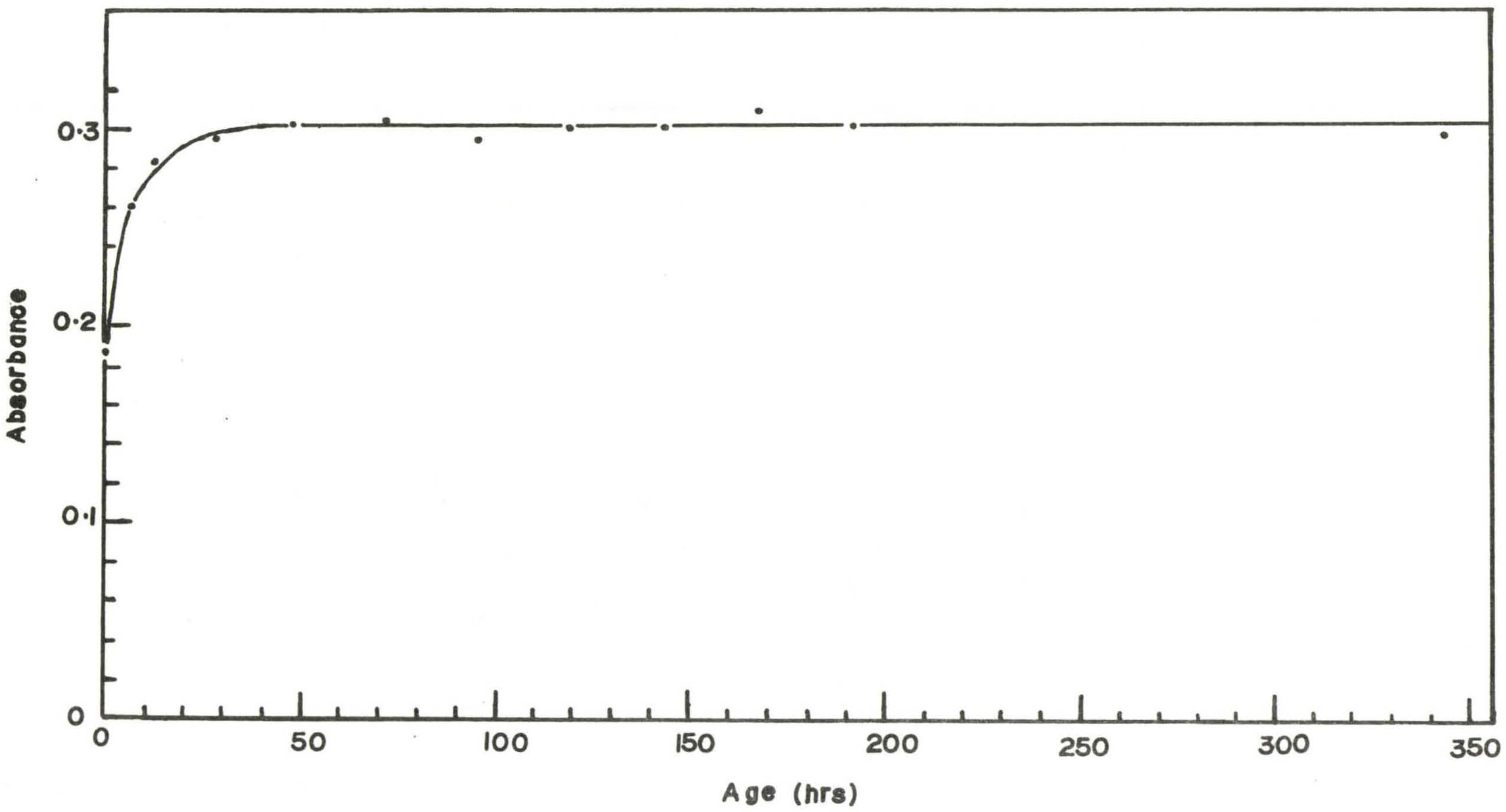

Fig 3 Efficiency of curcumin reagent versus its age

seen in this figure that the absorbance levels off after about 24 hours. Subsequently the reagent was aged for 24 hours before use and discarded after the 7th day, although as the figure shows it is still good after 14 days, and might even be so for a longer period of time. The reagent was kept in a dry cool place away from any direct light.

As has been advised by other workers (e.g. Dible et al., 1954; Spicer and Strickland, 1958a) the spectrophotometric reading was to be taken immediately because of the decay of the colour of the complex. Fig. 3 illustrates how the colour of the boron-curcumin complex decays with time. In this figure, after the formation of the complex the absorbance or transmittance of the same complex was taken at intervals of one hour, keeping the solution in the same cuvette for the whole time. The experiment was done with the cuvette covered and uncovered, and both cases were repeated. It is obvious that the decay depends on various local conditions, such as temperature, illumination etc.; for example, it depends on whether the container is covered or uncovered. In cases where the spectrophotometric reading could not be taken immediately such curves could be used to apply rough corrections to the readings.

Since it was difficult to obtain accurately graduated quartz measuring apparatus, the pipettes used for measuring the curcumin reagent, ethanol, boron standard solutions, and the measuring cylinder for measuring re-distilled water and ethanol were made of pyrex glass. It was quite safe to use these, as indicated by the small absorbance

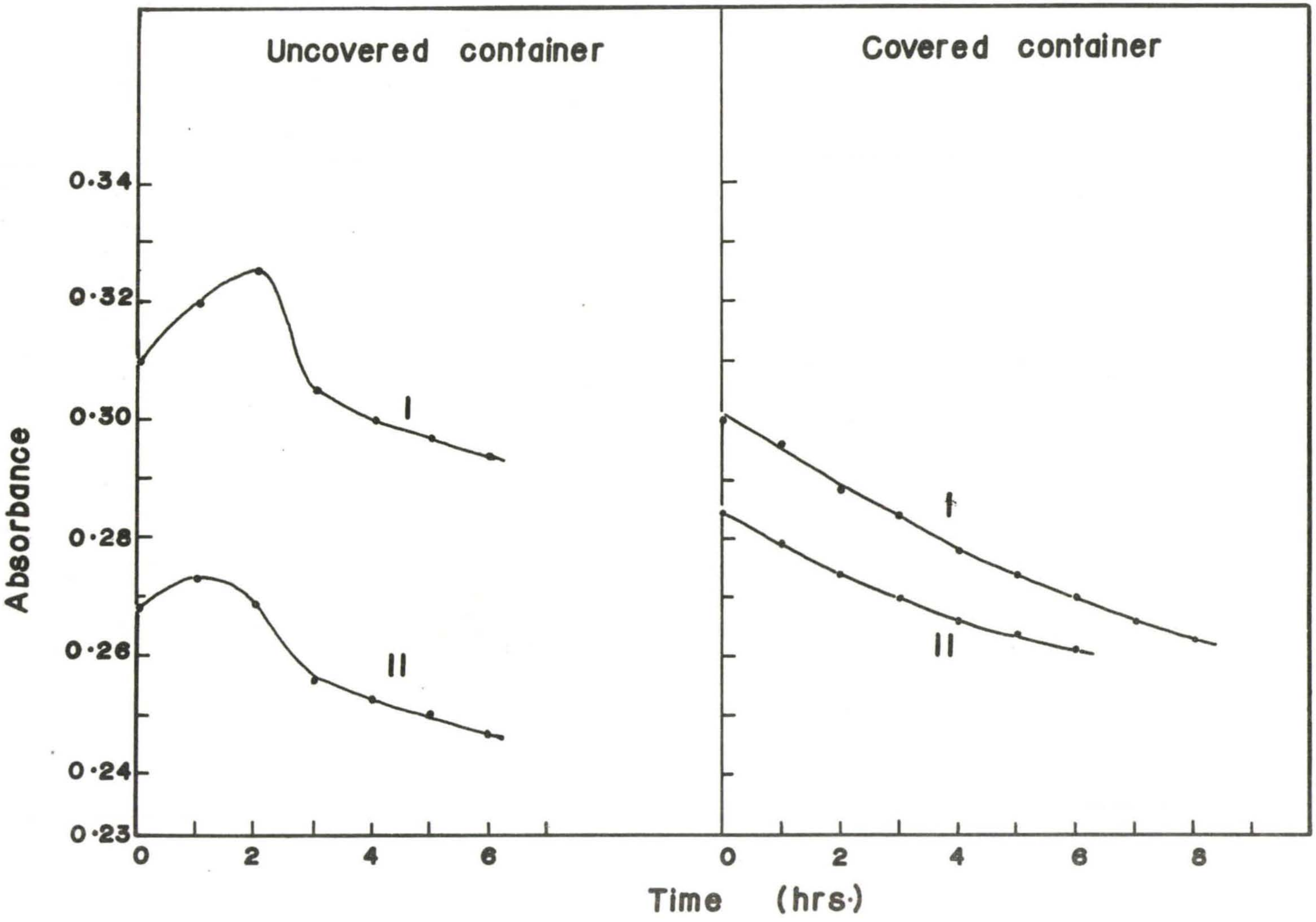

Fig 4 Decay of boron – curcumin complex

(high transmittance) for the blank (0 μg) and the small deviation of the points from the line in Fig. 2. This was possible because the liquids with which the pyrex glass came in contact were neither alkaline nor hot. It is known that alkaline or hot solutions will leach boron from boro-silicate glass. Moreover, they were in contact with the solution for a very short time. As an extra precaution a quartz pipette was used for the sodium hydroxide solutions.

In applying the curcumin method to the determination of boron from the samples care was taken to treat the samples under the same conditions as those for which the calibration curve was prepared. The average time for one measurement was about one hour. With isotope dilution this may take more than two days, since, apart from knowing the isotopic ratio of the standard (spike), the ratios for the target and the blend must be determined. After considerable experience, the worker can estimate with the naked eye to within 20 per cent or better the amount of boron present when the boron-curcumin complex is formed and dissolved in ethanol. Although the isotope dilution technique may give higher precision, when the sample to spike ratio is not correct the error can often be significant. The results can however be improved by repeating the measurement as many times as is necessary, using the previous result as an estimate to choose the sample to spike ratio. In the case of the curcumin method, if it happens that the absorbance of the colour formed is outside the calibrated range, this solution can be diluted to reduce the absorbance and thus make an estimate of the boron content. The process may then be repeated, taking a smaller aliquot of the boron solution.

(b) Comparison of Curcumin and Isotope Dilution Results

Although attempts were made to remove all other ions apart from boron, it is quite conceivable that some foreign ions and particles, such as resin fines, would still be present in the boron solution. The effect of this on the determination was found by comparing the curcumin method results with those of the isotope dilution method. It can be seen that these results agree within experimental errors as indicated in Table 2.

The equation used for the isotope dilution measurement is (De Bièvre and Debus, 1965a).

$$M_T = \frac{R'_S - R'_B}{R'_B - R'_T} \cdot \frac{1 + \gamma K R'_T}{1 + \gamma K R'_S} M_S \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where:

M_T = mass of the target (sample)

M_S = mass of the spike

R'_T = observed B^{11}/B^{10} of the target (sample)

R'_S = observed B^{11}/B^{10} of the spike

R'_B = observed B^{11}/B^{10} of the blend

γ = absolute mass ratio of B^{11} to B^{10}

(= 1.0995; see Everling et al., 1960)

TABLE 2

COMPARISON OF ISOTOPE DILUTION AND CURCUMIN RESULTS

Test boron solution from		Measured amount of boron (μg)		
Sample	Code	Curcumin method (a)	Isotope dilution method (b)	(b)/(a)
W - 1	W12	0.60	0.60	1.00
Dalat	T2	2.02	2.22	1.10
Tourmaline	M11	0.80	0.87	1.09
Abee	C10	0.44	0.50	1.14
Bruderheim (M)	C5	0.66	0.65	0.98
NBS No. 1163	S5	0.76	0.73	0.96
Vulcan	C18	1.03	0.99	0.96
Sea water	E1	0.81	0.68	0.84
		0.81	0.83	1.02
		Mean ± standard deviation (95% C.L.)		1.01 ± 0.18

K = instrumental mass discrimination (correction) factor
(= 0.9961 ± 0.0002, see Table 6)

Since M_T was known from the curcumin method, it was possible to choose M_T/M_S so as to approach the optimal precision. With the exception of the first result in Table 2, for which highly enriched B^{11} ($B^{11}/B^{10} = 99.50$) was used, all the spikes were either standard borax A or borax B ($B^{11}/B^{10} = 4.287$ and 3.971 respectively, see Table 6). No more highly enriched spikes were used because of the possible memory effects and the fact that they were not really necessary in this experiment.

A derivation of equation (1) which applies to a bi-isotopic sample and the attainable precision is reproduced in Appendix I. The case for a poly-isotopic sample and/or spike can be found elsewhere (De Bièvre and Debus, 1965b).

Tables 3 and 11 on standard solutions of borax A and borax B give additional support that foreign elements at the concentration level encountered in this work did not affect the results significantly. In Table 3 the standard borax A and borax B were pyrohydrolyzed in a complete fashion as described in Section 3 (c), (i). On the other hand, in Table 11 the standards were merely passed through the ion exchange column, just as for the sea water samples (Section 3 (c), (iv) and (v).

3. EXTRACTION

(a) Limitations of Conventional Methods

The importance of a complete separation of boron (or any other element) from interfering ions for the chemical determination of its content, and mass spectrometric measurement of its isotopic composition (except perhaps in a spark source mass spectrometer) in a material, is well known. An incomplete separation, not only gives the wrong boron content, but it may also give rise to incorrect isotopic ratios as a result of isotopic fractionation. Foreign ions may also interfere with the chemistry of the boron determination and the mass spectrum for the isotopic measurement, thereby producing incorrect results. When trace quantities of boron, say below the ppm range are involved, this requirement, as well as the precaution against boron contamination in the laboratory, becomes even more important and is usually difficult to achieve. Above the ppm range, existing methods of extraction are quite satisfactory.

For example, consider the application of the conventional methods: (a) methyl borate (Hillebrand and Lundell, 1955; Spicer and Strickland, 1958b; McMullen et al., 1961; Shima, 1962, 1963; Shergina and Kaminskaya, 1963); (b) ion exchange (Martin and Hayes, 1952; Wolszon and Hayes, 1957; Callicoat and Wolszon, 1959; Finley et al., 1962); and (c) pyrohydrolysis (Williams et al., 1959; Wiederkehr and Goward, 1959; Finley et al., 1962) to the separation of boron from meteorites which are known to contain about 0.5 ppm of boron.

Assuming 5 μg of boron will be needed for analysis, 10 g of the meteorite will have to be fused with at least 60 g of sodium hydroxide, dissolved with hydrochloric acid, and then distilled with methanol in the case of (a), or passed through an ion exchange column in the case of (b). Two ion exchange resins are needed for the separation, a cation e.g. Dowex 50 to remove the cations and an anion e.g. Amberlite 1R-45 to romove the anions from the solution. The two resins could be mixed together or used one after the other. The column must be very long because of the large total ion content in the resultant solution. The chances of contamination in both cases will be high because of the many steps and large amount of reagents involved. Good reagent grade sodium hydroxide obtained commercially may contain as much as 0.01 ppm boron or more, as was estimated with the cyclic pyrohydrolysis technique devised for the present work. The boron contamination due to the sodium hydroxide alone will therefore be about 0.6 μg (12 per cent of the expected boron) or more. Contamination due to water, methyl alcohol, hydrochloric acid, etc. will complicate matters even further. As was mentioned in Chapter I, Section 4, (e) a blank run using method (a) gave a value of 2.5 μg of boron, which represents 50 per cent of the total boron expected from a meteorite sample. However, by careful choice or preparation and purification of reagents it may be possible to obtain reasonable results using these methods. For example, Shima (1962) has reported the analysis of meteorites using the methyl borate method.

The conventional pyrohydrolysis method appears to be more suitable, but in this case ions other than boron might distil over and subsequent ion exchange separation becomes necessary. In this method the boron is extracted by passing steam over the sample which is heated at a high temperature (1100°C to 1400°C) in the presence of a catalyst, usually U_3O_8. In all three methods, in order to achieve a complete extraction of the microgram quantities of the boron, approximately 1 litre of distillate or eluant will have to be collected. For subsequent analyses therefore, a great deal of evaporation will have to take place, since in both mass spectrometric and colorimetric measurements the samples have to be in a dry form. Such evaporation is definitely undesirable because of the possible loss of boron and the attendant possibility of isotopic fractionation.

(b) Cyclic Pyrohydrolysis

(i) The Method

Attempts made to satisfy the requirements and solve the problems mentioned above led to an extraction technique which makes use of the following two major modifications to the conventional pyrohydrolysis and ion exchange methods:

(1) A small ion exchange column is placed in series with the pyrohydrolysis apparatus to remove foreign ions after pyrohydrolysis. Finley et al. (1962) passed the pyrohydrolysis distillate through a

cation ion exchange column, but the two apparatuses were not put directly in tandem. Pyrohydrolysis eliminates the need for a long ion exchange column and for reagents except for the possibility of a catalyst, since the ions that eventually go into solution are relatively few in number.

(2) The problem of large quantities of distillate or eluant is solved by a re-cycling process, thus permitting the use of a minimum amount of water. The condensed steam which has gone through the ion exchange column is returned to the steam generating flask, and the process repeated over and over again, leaving the boron behind in the flask.

It is known that boron is volatile in steam and this is probably one of the reasons why pyrohydrolysis is possible. Another reason is the closeness of the pyrohydrolysis temperature to the boiling point of B_2O_3 at $1500^{\circ}C$. However, only a very small fraction of the boron, which depends on the concentration in the flask, should be carried back into the loop as a result of the volatility of boron in steam. This should be negligible in the microgram range and for the long steam column employed here. However, in the case of large boron concentrations where the "carry over" may be considerable, one or both of two precautions could be taken. Sodium hydroxide could be added to the flask to suppress the volatility of the boron in steam and/or the distillate could be taken off at intervals, thereby working towards smaller boron concentrations.

Alternately, the sample size could be reduced so that there will be no need of sodium hydroxide in the flask. This is very convenient for the subsequent mass spectrometric work as the excess sodium hydroxide will have to be separated before a stoichiometric amount of it is added to the boric acid to convert it to borax, which is the final form required for the mass spectrometer.

A simple calculation will demonstrate that the use of sodium hydroxide containing as much as 1 ppm of boron, in the way indicated above and in the chemical (curcumin) determination of boron described in section 2, will introduce negligible contamination. If X μg of boron is expected from the extraction, addition of 10X μg sodium hydroxide is more than sufficient to suppress the steam distillation of the boron from the flask. This gives a boron contamination of just 10^{-5} X μg, i.e. 0.001 per cent. In the conversion of the X μg of boron to borax for the mass spectrometric analysis about 2 X μg sodium hydroxide is required and this gives only 0.0002 per cent contamination (see section 4, (b), (i).

(ii) The Apparatus

After a great deal of experimentation the version of the apparatus shown schematically in Fig. 5 was decided upon for the extraction of boron.

Furnace:

This is a Sentry silicon carbide furnace, Model V, size 2, which has a maximum operating temperature of 1400°C and has a physical

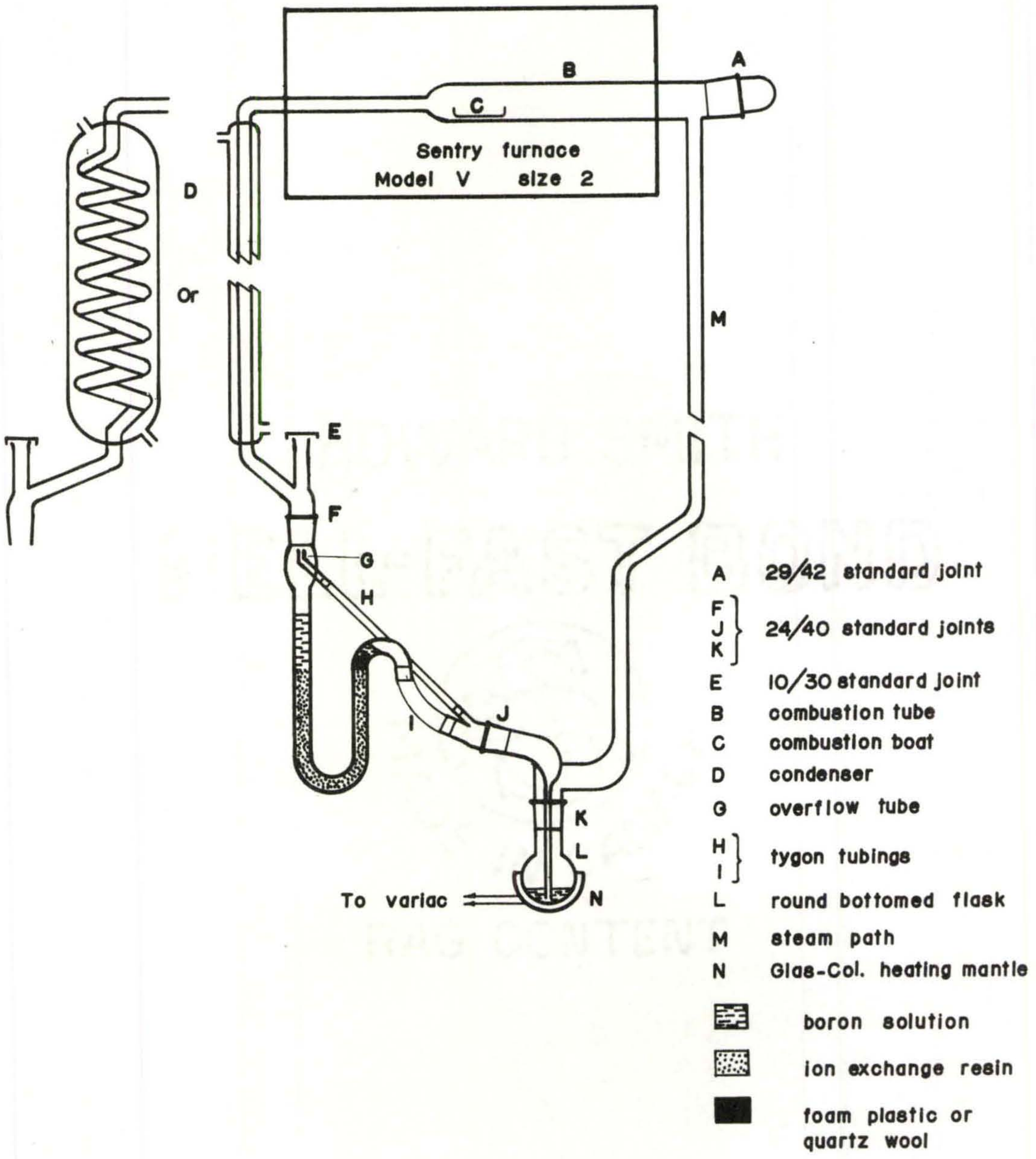

Fig 5 Cyclic pyrohydrolysis apparatus

length of 50.8 cm. The temperature measuring unit consists of a Pt-PtRh thermocouple and a calibrated Hoskin millivoltmeter.

Combustion Tube:

Except for the tygon tubing the whole loop is constructed from quartz. However, a recrystallized alumina tube of 3.2 cm outside diameter, 2.55 cm inside diameter, and 61 cm long, was also used and found to be satisfactory. Its use was discontinued mainly because of the difficulty with the special joints that had to be made to fit it to the rest of the apparatus. The larger portion of the quartz combustion tube has an outside diameter of 2.54 cm and the smaller end 1 cm. Because the quartz combustion tube devitrified each time the furnace was shut off, it had to be replaced a number of times (the lifetime of the heating element of the furnace is about 40 days). The alumina tube could survive more of this abuse, provided the temperature changes were not too rapid.

Condenser:

The Liebig condenser is about 91 cm long, and the inside tube has an inner diameter of about 1.5 cm and the outer jacket 2 cm inside diameter. The condenser is longer than required, but this is an extra precaution taken to ensure that no steam escapes. A Graham condenser of physical length of about 25 cm was also used and found to be adequate. The path length of the condensation coil, which was made of 8 mm inside diameter quartz tubing was about 91 cm, and the diameter of the outer jacket was about 5.5 cm. Actually, only one half or possibly one third of the length of the condensers is sufficient, provided that the flow rate of the steam is not too fast.

Ion Exchange Column:

Following the condenser is a U-tube ion exchange column, also made of a 1 cm ID quartz tubing. By means of this U-tube arrangement it is possible to keep the resin wet at all times, while this cannot be guaranteed with a straight column. The effective size of the column can be made as small as required with a rough knowledge of the major constituents of the sample to be pyrohydrolyzed. For example, in tektites, meteorites and rocks the silicate and the iron-nickel content together are over 90 per cent, but these will not be in solution. Moreover since some of the remaining elements may be soluble in hot water but not necessarily soluble in cold water, the ion content of the distillate may be of the order of only a fraction of a per cent of the total sample. Hence a few grams of the ion exchange resin should be more than sufficient for the separation of a sample of 10 g or less. In this work two ion exchange columns of approximate capacities 10 ml and 30 ml were used. The resin employed in this separation is about 1:1 (dry weight) mixture of Dowex 50 AG, X 8, 50 - 100 mesh cation resin and Amberlite 1R-45 ~20 - 50 mesh anion resin. The Amberlite 1R-45 is of regular analytical grade, while the Dowex 50 AG is the analytical Dowex 50 which had been further purified by the Bio-Rad

Company. Ordinary analytical grade of Dowex 50 was also tried and found to be equally satisfactory. The method of mixed resin bed ion exchange for the separation of boron has already been studied by Wolszon and Hayes (1957), and Callicoat and Wolszon (1959). Quartz wool and foam plastic were both found to serve the purpose for use as a plug in the ion exchange column, but quartz wool was used for most of the extractions.

Between the condenser and the ion exchange column there is an opening, marked E in Fig. 5, through which a thermometer can be inserted to check the temperature at the bottom of the condenser to determine whether or not all of the steam has condensed. Through this opening water can be added to the top of the column, or the resin can be agitated to remove any bubbles.

Connectors:

Two pieces of tygon tubing, one from the top and the other from the bottom of the column, connect the ion exchange column to the steam generating flask through a quartz connector of which the quartz outer joint J forms a part. This connector is cooled by tap water flowing through a rubber coil wound around it, to stop any steam from flowing in that direction. When the connector is long this extra cooling is not required, since the connector will be cooled sufficiently by the air. The tygon tubes provide the only real flexible part of the apparatus. The tube from the bottom of the column is the regular path for the eluant to the flask. The other tube serves two purposes: in case the column plugs up (gas bubbles), or if the rate of steam generation surges up and there is an "overflow", the extra liquid will return to the flask through the small tube that projects inside the top of the column via this tygon tube. It also serves as an exhaust to prevent pressure build-up below the ion exchange resin which tends to push the resin up the column.

The final path of the boric acid solution to the flask is through a small quartz tube of 5 mm ID, the tip of which dips into the solution about one millimeter from the bottom of the flask.

The steam is generated at a constant rate by heating the 100 ml flask with a Glas-Col heating mantle, controlled with a 110 V variac. It rises up to the combustion tube through a 1 cm ID quartz tube (steam path M), which joins the flask to the combustion tube to complete the loop. The steam path is also heated by a 9.1 m insulated nichrome resistance wire (0.054 Ohm per cm) coiled around its entire length. The heating is controlled by a variac which was set at about 75 V.

Joints:

The sample to be analyzed is introduced through the entrance (marked A) which is made of a 29/42 standard joint. This is tilted slightly so that very little condensed steam is trapped in the cap. (The small amount of condensed steam was shown to contain no boron.)

The joints F, J, and K are 24/40 standard joints. Since F and J are cold at all times they are greased lightly with Apiezon grease; however, A and K, which are at steam temperature, are made tight by sealing them with teflon tape. Springs are also put on all four of these joints to ensure a tight fit. When the alumina combustion tube was used the joints between the tube and the rest of the apparatus were made by means of outer quartz cups, which fastened on the ends of the tube, around which teflon tape was wound to make the fittings tight. On top of the joints was wound more teflon tape. No extra precautions are taken for the joints between the tygon and the quartz tubes, since reliable fitting is easily made by careful choice of tube sizes. The opening at E is made of 10/30 inner quartz joint to fit a mercury-in-glass thermometer. Originally it was used to seal the whole system from the atmosphere and thereby prevent loss or contamination of the boron. Since it was experienced that running the system under this condition was very difficult, the thermometer was replaced by a polyethylene cap with a pin hole in it. The pressure build-up due to the evolved gases tends to disrupt the other joints, if the system is made air tight.

Combustion Boat:

A number of different materials were tried. Porcelain was ruled out on account of its high porosity and its high boron content (~ 40 ppm).

Alumina boats had the disadvantage of a poor resistance to heat shock and broke if the boat was introduced or withdrawn from the hot combustion tube quickly. A quartz boat is unsatisfactory for iron samples as it reacts with them, but it is quite good for silicate samples such as tektites, stony meteorites and rocks studied in this research. A 10 ml platinum boat was therefore selected for the remainder of the work as it does not have any of the disadvantages mentioned above, except that it is slightly attacked by iron samples at working temperatures over 1200°C. To overcome this the bottom of the boat is lined with some of the catalyst used, viz. uranium oxide (see section 3, (c) (iii), Steel Samples). It also possesses the advantage that it is not attacked by hydrofluoric acid with which the analyzed sample is removed, thus making it possible to use the same boat over and over again. However, two boats were used alternately since it takes considerable time to dissolve the sample residue in some cases.

The size of the cyclic pyrohydrolysis apparatus described can be considerably reduced since some of the components are much bigger than what is required. In the first place a much smaller wire-wound furnace can be used. The volume of the round bottomed flask can be reduced to 50 mls or even 25 mls. As mentioned above, the length of the Liebig condenser can be reduced to 30 cm and that of the Graham condenser to only 8 cm. The various joints and connectors could also be reduced in size. The size of the combustion tube and boat and the ion exchange column however, will be determined by the kind of samples to be studied. A smaller apparatus may also increase the extraction rate and reduce memory effects.

(iii) Catalyst

The rate of extraction of the boron from a material depends partly on the pyrohydrolysis temperature (Williams et al., 1959) and partly on the kind of matrix containing the boron. For example, it was found that the extraction rate for iron turnings or small chips of steel was higher than that for silicates. The use of a catalyst speeds up the extraction considerably. Williams et al. (1959) after trying a number of catalysts, decided to use a mixture of U_3O_8 and $Na_2SiO_3 \cdot 9H_2O$ for the analysis of boro-silicate glasses. Wiederkehr and Goward (1959), too, were able to analyze successfully uranium alloys. Therefore it was decided to use uranium oxide for the catalyst after trying vanadium pentoxide and tungstic oxide and finding them to be unsuitable. A catalyst was not required for the steel samples. Since the amount of boron to be expected in this work was very small, it was necessary to purify the catalyst before use. The uranium oxide was itself pyrohydrolyzed for some time in the furnace, with the ion-exchange column disconnected from the apparatus, at a temperature slightly higher than that used for the sample. The oxide would no longer be in the form of U_3O_8 but still it accelerated the extraction considerably. Actually the uranium oxide was derived from uranyl nitrate first by heating it in a nickel crucible till it formed a dry yellow cake, which was powdered and then pyrohydrolyzed, turning black in the furnace. This was done partly because uranyl nitrate was more readily available than the oxide, and partly because it was hoped that if it contained any boron, it would be completely removed following this procedure. Since the uranium oxide is a catalyst itself, it is clear to see why it was not difficult to remove the boron from it by pyrohydrolysis. Pyrohydrolysis of the catalyst was normally performed for about one hour. When vanadium pentoxide and tungstic oxide were pyrohydrolyzed in this way, they were completely carried over with the steam, making it impossible to purify them and hence render them useless as a catalyst.

The ion exchange column, filled with water but no resin, was then connected and cyclic pyrohydrolysis continued for at least another hour. Meanwhile, the ion exchange resin was being soaked and washed several times outside the system. After this the column was filled with the resin and pyrohydrolysis carried on further for as long as required to cut down the blank to a satisfactory level. A 24 hour blank run, after flushing in this way for about 12 hours, will yield on the average a value of about 0.05 µg if done carefully. If desired, a blank run can always be done on the same catalyst and resin to be employed before they are used.

(c) Extraction Procedure

(i) Introduction

The cyclic pyrohydrolysis technique described in this work had to be tested for blank and memory effects, loss of boron, isotopic fractionation, extraction efficiency, and reproducibility, before applying it to the samples to be analyzed. The results of the analyses of some of the quartz material used for the apparatus showed no detectable quantity of boron (Table 10). The re-distilled water contained only 0.0003 ppm boron. As discussed in section 3, (b) (iii), most of the blank comes from the catalyst and the ion exchange resin but this can be reduced to about 0.05 μg in 24 hours. It was a practice to always check the blank before a sample was introduced.

There was a small loss of water which could be attributed partly to the dissociation of the water in the furnace and partly to the reaction of the water with the sample. Therefore, the loss depended on a number of factors such as size and nature of the sample. However, more water could be added to the top of the ion exchange column via the point E (Fig. 5) if required. It was also observed that some gases escaped through E. A U-trap containing sodium hydroxide attached at point E indicated no boron in the escaping gases.

Possible loss of boron and incomplete extraction may give rise to isotopic fractionation and also account for poor reproducibility.

To check these a number of standards were analyzed. For the fractionation test, borax A and borax B with known isotopic ratios (see Appendix II) were pyrohydrolyzed.

After flushing the apparatus with the resin and catalyst in place, the boat was taken out and 1 ml of NaOH(1) containing 0.00106 g sodium hydroxide added. Since the catalyst was normally hot at this time it dried very quickly. Then an aliquot of standard solution of borax A or borax B was added and the boat replaced very quickly in the furnace, and the cap of the combustion tube replaced immediately. Without taking these precautions some boron might be lost before the cap was put on. W-1 was analyzed several times on different dates in the same way as stony meteorites, tektites and other silicate samples. The three NBS steel standards (NBS No. 1165 and 465 are supposed to be identical as far as the chemical composition is concerned) were also studied since this research involved extraction of boron from iron meteorites. In the analysis the sample size was chosen in such a way that the total extracted boron did not exceed about 30 μg. Some of the samples were analyzed several times and these are indicated in the tables of results. The rate of passage of the steam during the pyrohydrolysis of the samples was on the average about 1.5 ml/min.

(ii) Silicate Samples

The sample was first broken into very small pieces in an iron mortar, then the pieces were washed in a mixture of re-distilled water, hydrochloric acid and methanol, to etch away any fingerprints and tiny pieces of iron from the mortar that may have been added to the sample. The pieces were then dried in an oven and powdered in a Diamond mortar, if the sample was not too hard to run the risk of adding contamination from the mortar. If the sample was too hard, such as Abee, it was left in small pieces. (W-1 was received in powder form). This made very little difference to the extraction rate, since most of the samples melted at the extraction temperature.

A weighed amount of the sample thus prepared was then mixed thoroughly with up to 25 g of the catalyst which had been pyrohydrolyzed and purified. Meanwhile, about 10 ml of re-distilled water was being heated in the flask and the furnace termperature was set at about 1330°C. As soon as the steam started to arrive at the combustion tube the platinum boat was pushed into place with a quartz pusher, the cap put on, tied up with teflon tape and the spring clamp applied. The same procedure was used to join the flask to the bottom of the apparatus. For the majority of the samples the boric acid collected in the flask was removed at intervals of about three, six and twelve hours. The idea was to prevent loss of boron which could result in fractionation, since on the average over 80 per cent of the total yield of boron would have been in the flask after the first three hours. The extraction was performed for about 24 hours to ensure approximately 100 per cent yield. The three extracts together were made up to a known volume in a quartz volumetric flask (pyrex glass flask was also found to be suitable and used for some of the samples since re-distilled water stored in it for one day indicated no detectable boron). An aliquot of this was pipetted and the amount determined by the curcumin method. In the preliminary analysis, each extract was determined separately to determine the rate of extraction. In this way it was possible to observe the effect of the catalyst on the extraction rate. Figure 6 shows the yield curve as a function of time for boron from 0.75 g of W-1 using no catalyst, 0.89 g of W-1 using a catalyst, and 0.365 g of NBS No. 1164 steel.

As discussed in section 2 (b), the boron content in a number of samples determined by the curcumin method was cross-checked by the isotope dilution method. To another aliquot of the sample the content of which had already been determined by the curcumin method was added a spike, normally borax A or borax B and the boron content determined as discussed elsewhere (section 2 (b), and Appendix I).

(iii) Steel and Iron Samples

Since very small amounts of the NBS No. 1163 and 1164 samples were required, they were analyzed as turnings, whereas because a large amount of NBS No. 1165 or 465 was required they were analyzed

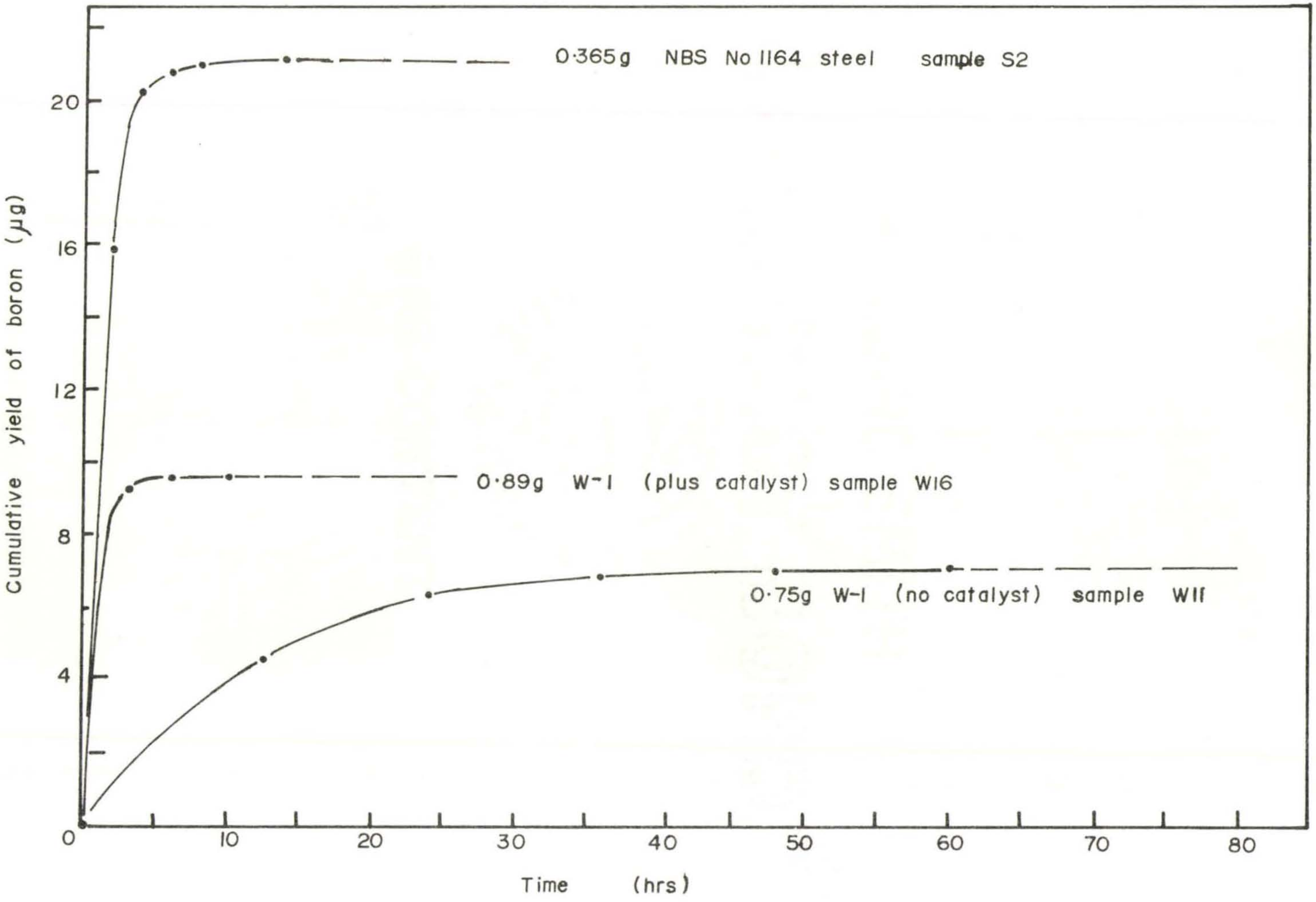

Fig 6 Cyclic pyrohydrolysis extraction rate of boron from W-1 and NBS steel

as pieces as were the iron meteorites. If the starting meteorite specimen was small it was possible to saw it into smaller pieces using an ordinary hack saw. To break big specimens into small pieces, they were frozen in liquid air and immediately broken with a steel hammer when removed from the coolant. The prepared samples were cleaned in the same way as the silicate samples, except that in this instance the cleaning was done more quickly so as not to dissolve away the sample. Although no catalyst was necessary here the bottom of the platinum boat was lined with the uranium oxide to prevent reaction of the steel sample with the platinum. Moreover, the pyrohydrolysis was performed at about $1200^{\circ}C$ instead of about $1330^{\circ}C$. In preparing the iron meteorite sample, care was taken not to include any of the outside rust which had been in contact with the soil.

(iv) Sea Water Samples

For these samples it was assumed that all of the boron was in solution so that each sample was put on top of the ion exchange resin directly and the elution carried out by re-cycling of steam as in the case of cyclic pyrohydrolysis. Each of the sea water samples was made up to 10 ml before extraction. To verify that the extraction of boron by this method did not cause any fractionation, the boron in borax A and borax B were extracted in exactly the same way as was the boron from the sea water.

(v) Clay Experiment

To a mock sea water sample, obtained commercially under the name "Instant Ocean", was added 100 ppm of boron as boric acid. The boric acid was obtained commercially from the McArthur Chemical Co. Ltd., Montreal (Shawinigan Lot No. F7 4766G2). The original boron content in the Instant Ocean was about 1 ppm. To 17 ml of the resulting boron-sea water solution was added 30 g of API (American Petroleum Institute) project illite No. 35 clay which had been leached by 0.1 N HCl to remove most of the boron which might have been absorbed by the clay. The original boron content of the clay was about 200 ppm. The clay to hydrochloric acid ratio was about 1:5000. The clay and the sea water were thoroughly mixed and centrifuged for many hours and the supernatant sea water collected. The process was repeated for 32.3 g of clay and 21.5 ml of sea water. The boron in the three artificial sea water samples were extracted and its amount and isotopic ratio measured as in the case of natural sea water.

4. MASS SPECTROMETRY

(a) The Instrument

The mass spectrometer used in this research work is a first order direction focusing, single stage instrument with a homogeneous magnetic field of $\pi/2$ sector shape and radius of magnetic deflection of 10 inches. The source of positive ions, which are $Na_2BO_2^+$, was a rhenium triple filament. The detection was made by means of a 14-stage electron multiplier having a gain of about 6 x 10^4, and a vibrating reed electrometer coupled to a recorder. There was no shunt selector used in connection with the recorder, however the two boron peaks were measured on different voltage ranges of the vibrating reed electrometer. The scanning of the peaks was performed by varying the magnetic field. This instrument is exactly the same as used and described by Agyei (1965), except that almost all the electronic units had been replaced and also some drastic shifting of the magnets had been done to improve the peak shape. Slight modifications were also made in the source and collector.

(b) Analytical Procedure

(i) Sample Loading

A portion of the extracted boron solution was transferred into a flat teflon evaporating dish. This was normally between 1 and 2 μg of boron in 20 ml or less of water. To every 1 μg of boron in the dish was added 2.5 μg NaOH of the sodium NaOH(2) and the resultant solution evaporated slowly to a tiny drop under an infrared lamp. The teflon dish was covered with a pyrex glass beaker to keep out dust.

Actually, only 2 µg of NaOH was required to convert 1 µg of boron to borax, but the extra 0.5 µg was added in case there were other ions present in solution. Tests with borax A and borax B showed that excess sodium hydroxide of this order did not affect the isotopic ratio. Usually the evaporation took about three hours if the starting solution was 20 ml. Preliminary tests showed that the isotopic ratio of the boron did not depend on the amount of the starting solution in this range of volume.

Using a tygon-tipped syringe, the last drop was transferred onto the two side filaments which had been pre-treated (see section 4 (b), (ii)). The sample was slowly dried by passing current through the filaments. Then the current was increased slowly until the resin fines in the sample became charred. The temperature was raised still further to a very dull red for a few seconds to burn off some of the carbon. This step seemed rather drastic and could suggest that isotopic fractionation would occur. However, comparison of results showed that if there is any fractionation at all it is negligible. If the resin is not burned off in this way the hydrocarbons would interfere with the peaks and make it difficult to take any measurements.

One hour after putting the sample into the spectrometer the source end was baked for about 15 minutes at about 60°C. Then the liquid air dewars were removed to allow the traps to warm up to about 0°C while the pumps were still functioning. Baking of the source end was started again when the liquid air traps were replaced, increasing the temperature to about 100°C. At this time the pressure in the instrument was about 1×10^{-5} mm Hg. The current supply for the ionization filament of the source was turned on and the current increased gradually to about 5 A. Initially the pressure surged up but soon started decreasing again. After about another hour the current through the filament was decreased to about 4 A and the baking temperature reduced to about 60°C again. Usually, after about an additional two hours the pressure was down to about 2×10^{-6} mm Hg. Then the ionization filament current was increased to 5 A again, and the current through the two side filaments in parallel turned on to about 1 A. Meanwhile, the remainder of the electronics had been turned on and the baking system shut off. The sample current was increased to 2 A slowly, at which value the peaks corresponding to the $Na_2BO_2^+$ ions started to appear on the 1 V and 300 mV scales of the vibrating reed electrometer with a grid leak resistor of 10^9 Ohm.

(ii) Hydrocarbon and Strontium Interference

Although all new filaments were pretreated, some hydrocarbon and other peaks appeared when the $Na_2BO_2^+$ peaks from the sample were first observed. These interfering peaks probably came from the sample filament which had been relatively cool. However, these peaks

quickly disappeared except that occasionally the peak at mass 86 which suggests another peak at 88 and corresponding to Sr persisted for longer periods. It was observed that baking the source end again at times increased this peak at mass 86, but with time it disappeared. Hence it was made a practice to do this final baking and checking of the peak at mass 86 before measurements were begun.

(iii) Pretreatment of New Filaments

Before a new filament button was used it was pretreated in the mass spectrometer with the ionization current set at 5 A and the sample filament at 8 A for about one day, applying a high voltage of 5 kV for about one quarter of the time. When the filament currents were first turned on peaks were observed at every mass in the region of masses 88 and 89 which correspond to the $Na_2B^{11}0_2^+$ and $Na_2B^{10}0_2^+$ ions. Most of these which were probably due to hydrocarbons disappeared quickly, but the Rb peaks at mass 85 and 87 and the Sr peaks at 86 and 88 persisted for a long time. After some time however, the Sr peaks were not observable, even with the sample filament current set at about 4 A and ionization current at 5 A. When the sample current was increased above 4 A the Sr peaks re-appeared.

(iv) Operating Conditions

The operating pressure was about 2 x 10^{-7} mm Hg. The ionization filament current was set at 5 A (corresponding to about 2000°C) and the current through the two sample filaments in parallel 2.5 - 3.5 A (corresponding to about 120°C - 240°C). Any analysis requiring sample current of more than 4 A was rejected as interference from Sr^{88} peak was very likely.

The accelerating voltage and the electron multiplier voltages were +5 kV and -2.5 kV respectively. With a grid leak resistor of 10^9 Ohm the $Na_2B^{11}O_2^+$ peaks were measured on the 1V scale and the $Na_2B^{10}O_2^+$ on the 300 mV scale on the vibrating reed electrometer.

With the instrument thus set the isotopic ratio was measured by scanning up and down the two masses. The four peaks of one complete cycle of a scan gave one ratio. About 35 such ratios were obtained for each sample loaded and the mean computed. The experimental error was calculated as the standard error by considering the whole 35 ratios as a sample population. Fig. 7 shows an example of the peaks obtained for Pacific Ocean water boron, sample E6 in Table 12. This is typical of the peaks obtained in this work. In this work there was no observable fractionation of the isotopes during the mass spectrometric analysis (Agyei, 1965) as a result of the evaporation of the sample from the filament, since for several hours the isotopic ratio did not change with time. It must be mentioned that when the analysis was

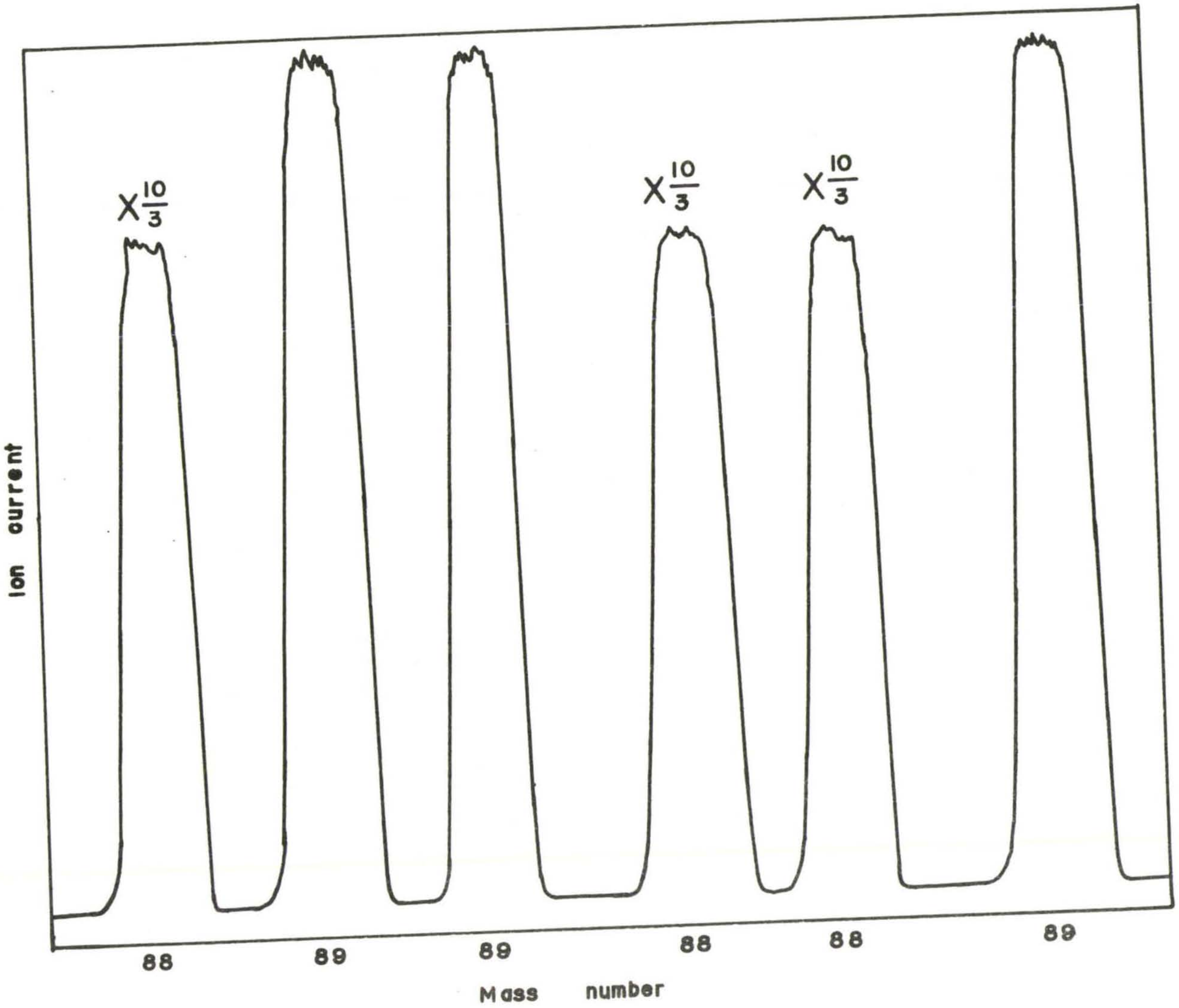

Fig 7 Mass spectrogram of $Na_2BO_2^+$ for sea water sample E6

first started the ratio could be very low or high, and very erratic because of the hydrocarbon or Sr interference. However, when conditions were stabilized the ratio remained constant during the analysis.

Although much of the sample remained upon completion of most runs it was not possible to analyze the small samples from the iron meteorites. This was because the ratio of the amount of resin to the boron content was too high to be able to burn the resin off as described in Section 4 (a), (i). In these samples, not only would one require a tremendous amount of burning but also the sample tended to flake off the filaments and be lost. This unfortunate situation occurred for a number of other samples too, which also happened to have too much resin fines in them. In the tables of results these are indicated as having been lost. At times the boron isotopic measurement was repeated for the same extracted boron solution and these are indicated as such in the results. Such results demonstrate the reproducibility of the mass spectrometric analyses.

(v) Calibration

To calibrate the instrument borax A and borax B with known isotopic composition were analyzed from time to time during this work. The instrumental discrimination correction factor K defined in Chapter 3, Section 2 (a) (iv), was computed from the observed and calculated ratios. All the observed isotopic ratios were therefore corrected by multiplying them by K to give the absolute ratios.

(vi) Baking and Cleaning

On completion of a run the rest of the sample was burnt off by increasing the sample filament current to 8 A, still applying the high voltage. After three hours the high voltage was turned off and the burning continued for three or more hours, after which the instrument would be ready for the next sample.

After ten to twenty analyses, the source became very dirty and the peaks were no longer stable. Usually high voltage breakdowns occurred. The entire source was then dismantled and cleaned as follows. Most of the dirt which included soot from the resin was removed by brushing. The metallic components of the source were soaked in a solution containing about 100 ml of water and 74 ml nitric acid (sp. gr. 1.420) at a temperature of $21^{\circ}C$ to $38^{\circ}C$ for about one hour. More of the dirt was removed by rubbing with tissue paper when the metallic parts were removed from the solution. The source plates were then put back into the solution and cleaned in an ultrasonic bath for about five minutes, after which they were washed with distilled water. They were then dried in an oven.

The quartz spacers were cleaned in a similar fashion using cleaning solution (a mixture of 70 gm sodium dichromate and 1 litre of concentrated sulphuric acid).

CHAPTER III

EXPERIMENTAL RESULTS

1. INTRODUCTION

Unless otherwise stated, all errors included in the experimental results are expressed as the standard error at the 95 per cent confidence level, considering all the individual measurements together as a sample population. The standard error is given by:

$$\sigma_{m} = \sqrt{\frac{\sum (X_m - X_i)^2}{N\ (N - 1)}}$$

where X_m and X_i are the mean and individual values respectively of the quantity measured. N is the number of analyses. The errors indicated in the results are therefore 2 σ_m. In the Tables, the dashed lines indicate that either the sample was lost as pointed out in Chapter II, Section 4, (b) (iv), or were not considered suitable and therefore meaningless to analyze using the method developed in this work.

The precision and accuracy of results were not high enough to make corrections due to O^{17} necessary at mass 89. As described in Chapter II, Sections 4 (b) (ii) and 4 (b) (iii), efforts were made to reduce the contribution due to background peaks, such as Sr^{88}, to a negligible level so that corrections for these peaks were unnecessary.

The absolute isotopic ratios indicated in Tables 4, 5, 7, 8, 9, 10, 12 and 13 were obtained by multiplying the corresponding observed ratios by K = 0.9961 ± 0.0002. K is the correction factor for the instrumental discrimination and this data is presented in Table 6.

The δ-values in the tables mentioned above are defined as follows:

$$\delta \,{}^{o}/oo = \left[\frac{(B^{11}/B^{10})_{sample}}{4} - 1 \right] \times 1000$$

where $(B^{11}/B^{10})_{sample}$ is the absolute ratio.

The value 4 was chosen as the reference because it is very close to the mean value of the B^{11}/B^{10} ratio for tektites, meteorites and terrestrial rocks. Otherwise the choice is quite arbitrary, unlike the case of sulphur isotopes, where the meteoritic sulphur ratio, which is constant from one meteorite to the other, is taken as the standard.

Except in Table 6, where the samples can easily be identified by the date on which they were analyzed, all samples are given code numbers.

2. THE RESULTS

(a) Calibrations

(i) Borax A and borax B

Table 3 shows the results of the yield of boron and boron isotopic ratio of the two standards, borax A and borax B which were pyrohydrolyzed. The yield of sample A1 may be low because excess NaOH was not added when it was placed in the platinum boat. This could have resulted in loss of boron outside the apparatus. Despite the loss of boron, isotopic fractionation was negligible.

(ii) W-1

In Table 4 are shown the results of the analysis of the W-1 diabase standard. The average boron content obtained in this work is 10.6 ± 0.6 ppm and the absolute isotopic ratio is 4.074 ± 0.002. The δ-value is 18.4 ± 0.4. The spread of the experimental results in this table also demonstrates the reproducibility of the analytical procedure.

(iii) NBS Steel

Table 5 records the results of the analyses of the National Bureau of Standards stainless steel. The NBS No. 1165 and No. 465 results are put together because they were reported to be identical in chemical composition (see Appendix IV).

(iv) Instrumental Discrimination

The observed isotopic ratios of the borax A and borax B standards determined concurrently with the analyses of the unknown samples are exhibited in Table 6. These also include the ratios of borax A and borax B which had been pyrohydrolyzed (Table 3), and those which were passed through the ion exchange column (Table 11). From these values the instrumental discrimination for the B^{11}/B^{10} ratio and the discrimination correction factor K are calculated.

The relative instrumental discrimination error for the B^{11}/B^{10} ratio is defined here as:

$$\left[\frac{(B^{11}/B^{10})_{\text{observed}} - (B^{11}/B^{10})_{\text{calculated}}}{(B^{11}/B^{10})_{\text{calculated}}}\right]_{\text{standard}}$$

$$= \left[\frac{(B^{11}/B^{10})_{\text{observed}}}{(B^{11}/B^{10})_{\text{calculated}}} - 1\right]_{\text{standard}} = (1 - K)/K$$

The discrimination correction factor K is the factor by which the observed values of the ratio for the unknown should be multiplied to give the absolute isotopic ratio:

$$\text{i.e.} \quad \left[\frac{(B^{11}/B^{10})_{\text{absolute}}}{(B^{11}/B^{10})_{\text{observed}}}\right]_{\text{unknown}} = K$$

TABLE 3

BORON IN STANDARD BORAX (pyrohydrolysis)

Boron Tested				
Standard	Code	(μg)	Yield* (%)	Observed B^{11}/B^{10}
A	A1	3.36	85	4.283 ± 0.006
	A2	3.36	100	- - - - - - - -
	A3	3.36	98	4.287 ± 0.006
B	B1	3.5	109	3.967 ± 0.006
	B2	3.5	105	3.970 ± 0.006
	B3	3.5	100	3.977 ± 0.006
	B4	3.5	100	3.973 ± 0.006

* The average precision (standard deviation at the 95 per cent confidence level) of curcumin determination of boron content is 9 per cent, (Chapter 11, Table 1).

TABLE 4

Boron in W-1

Code	Sample Weight (g)	Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
W11	0.75	9.5	4.085 ± 0.014	4.069 ± 0.014	+17.3
W12	0.90	10.2	4.090 ± 0.014	4.074 ± 0.014	+18.5
W13	0.90	10.7	4.093 ± 0.014	4.077 ± 0.014	+19.3
W14	0.90	9.5	4.091 ± 0.014	4.075 ± 0.014	+18.8
W15	0.90	12.3	- - - - - - -	- - - - - - -	- - -
W16	0.90	10.9	4.090 ± 0.006	4.074 ± 0.006	+18.5
W17	0.89	11.3	4.090 + 0.006	4.074 ± 0.006	+18.5
W18	0.89	10.6	4.087 ± 0.006	4.071 ± 0.006	+17.8
W19	0.89	10.4	4.090 ± 0.006	4.074 ± 0.006	+18.5
Mean		10.6 ± 0.6	4.090 ± 0.002	4.074 ± 0.002	+18.4 ± 0.4

TABLE 5

Boron in Steel Standards

NBS No.	Code	Sample Weight (g)	Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
1164	S1	0.33	56	4.057 ± 0.006	4.041 ± 0.006	+10.3
	S2	0.37	58	4.060 ± 0.006	4.044 ± 0.006	+11.0
1163	S3	0.77	9.3	4.090 ± 0.006	4.074 ± 0.006	+18.5
	S4	1.12	11.2	4.070 ± 0.006	4.054 ± 0.006	+13.5
	S5	0.82	10.6	4.080 ± 0.006	4.064 ± 0.006	+16.0
1165	S6	6.7	0.83	4.170 ± 0.006	4.154 ± 0.006	+38.5
	S7	8.5	0.72	4.173 ± 0.002	4.157 ± 0.002	+39.3
465	S8	6.8	0.91	4.117 ± 0.002	4.101 ± 0.002	+25.3
				4.113 ± 0.002	4.097 ± 0.002	+24.3
	S9	6.9	0.82	4.173 ± 0.002	4.157 ± 0.002	+39.3
				4.177 ± 0.006	4.161 ± 0.006	+40.3

TABLE 6

Instrumental Discrimination

Sample	Calculated B^{11}/B^{10}	Date	Observed B^{11}/B^{10}	Relative Discrimination error	Discrimination correction factor (K)
Standard A	4.270	Oct. 16/66	4.283 ± 0.002	+0.0040	0.9960
		Oct. 23/66	4.287 ± 0.008		
		Dec. 23/66	4.290 ± 0.006		
		Feb. 3/67	4.287 ± 0.008		
		Apr. 13/67	4.287 ± 0.012		
		May 18/67	4.285 ± 0.006		
		Dec. 21/67	4.290 ± 0.006		
		Jan. 6/68	4.283 ± 0.006*		
		Jan. 12/68	4.287 ± 0.006*		
		Feb. 23/68	4.290 ± 0.002		
		Apr. 10/68	4.290 ± 0.006		
			4.287 ± 0.002		

continued...

TABLE 6 (continued)

Instrumental Discrimination

Sample	Calculated B^{11}/B^{10}	Date	Observed B^{11}/B^{10}	Relative Discrimination error	Discrimination correction factor (K)
Standard B	3.956	Oct. 13/66	3.973 ± 0.018	+0.0038	0.9962
		Oct. 14/66	3.970 ± 0.016		
		Dec. 20/66	3.970 ± 0.010		
		Mar. 18/67	3.970 ± 0.010		
		May 11/67	3.960 ± 0.006		
		Sept. 21/67	3.977 ± 0.008		
		Nov. 8/67	3.963 ± 0.006		
		Feb. 7/68	3.967 ± 0.006*		
		Feb. 8/68	3.970 ± 0.006*		
		Feb. 25/68	3.970 ± 0.006		
		Apr. 8/68	3.977 ± 0.007		
		Apr. 28/68	3.977 ± 0.006*		
		May 2/68	3.973 ± 0.006*		
			3.971 ± 0.002		
Mean				K	0.9961 ± 0.0002

* Boron sample prepared by pyrohydrolysis

(b) Meteorites

(i) Chondrites

Table 7 gives the results for boron in chondritic meteorites. Square brackets are used to indicate samples which originated from the same parent sample powder or pieces. The parentheses indicate boron samples for which duplicate mass spectrometric analyses were performed. These indicate the reproducibility of the mass spectrometric measurements.

(ii) Irons and Stony-Irons

It was possible to obtain values for only the elemental composition of boron in the five iron meteorites analyzed. These are recorded in Table 8. As described in the text, mass spectrometric measurements of the isotopic ratios were not possible. However, it was possible to analyze completely the silicate phase of Canyon Diablo, the results of which are also included in Table 8, along with the results of the two stony-iron meteorites which were analyzed.

(c) Tektites

In Table 9 are given the elemental and isotopic composition of boron in the four tektites analyzed. Duplicate analyses were made for each tektite. The square brackets again indicate samples from the same powdered material.

TABLE 7

Boron in Chondritic Meteorites

Meteorites	Code	Sample Weight (g)	Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
Bruderheim (M)	C1	10.4	0.55	4.111 ± 0.014	4.095 ± 0.014	+23.8
	C2	9.3	0.97	4.107 ± 0.014	4.091 ± 0.014	+22.8
	C3	5.4	0.80	- - - - - - - -	- - - - - - - -	- - -
	C4	6.0	0.70	4.087 ± 0.006 4.087 ± 0.006	4.071 ± 0.006 4.071 ± 0.006	+17.8 +17.8
	C5	7.1	0.76	4.087 ± 0.006	4.071 ± 0.006	+17.8
Bruderheim (O)	C6	5.0	0.73	4.030 ± 0.006 4.023 ± 0.006	4.014 ± 0.006 4.007 ± 0.006	+ 3.5 + 1.8
	C7	4.6	0.70	4.020 ± 0.006	4.004 ± 0.006	+ 1.0
Abee	C8	5.1	0.80	4.047 ± 0.006 4.047 ± 0.006	4.031 ± 0.006 4.031 ± 0.006	+ 7.8 + 7.8
	C9	5.6	0.88	4.040 ± 0.006	4.024 ± 0.006	+ 6.0
	C10	5.4	0.92	4.047 ± 0.002	4.031 ± 0.002	+ 7.8

continued

TABLE 7 (continued)

Boron in Chondritic Meteorites

Meteorites	Code	Sample Weight (g)	Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
Peace River	C11	5.1	0.77	4.047 ± 0.006	4.031 ± 0.006	+ 7.8
	C12	5.6	0.51	4.047 ± 0.006	4.031 ± 0.006	+ 7.8
	C13	5.4	0.57	4.040 ± 0.002	4.024 ± 0.002	+ 6.0
Vulcan	C14	5.1	0.52	4.060 ± 0.006	4.044 ± 0.006	+11.0
	C15	7.8	0.48	4.040 ± 0.006	4.024 ± 0.006	+ 6.0
	C16	7.1	0.48	4.040 ± 0.006	4.024 ± 0.006	+ 6.0
Gladstone	C17	6.4	0.47	4.027 ± 0.006	4.011 ± 0.006	+ 2.8
Dimmitt	C18	7.6	0.57	4.040 ± 0.006	4.024 ± 0.006	+ 6.0

TABLE 8

Boron in Iron and Stony-iron Meteorites

Meteorite			Sample Weight (g)	Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
Name	Class	Code					
Madoc	Iron	F1	7.3	0.03	- - - - - - - -	- - - - - - - -	- - -
Skookum	Iron	F2	7.7	0.02	- - - - - - - -	- - - - - - - -	- - -
Toluca (Xiquipilco)	Iron	F3	7.5	0.02	- - - - - - - -	- - - - - - - -	- - -
Odessa	Iron	F4	9.6	0.07	- - - - - - - -	- - - - - - - -	- - -
Canyon Diablo	Iron	F5	9.9	0.03	- - - - - - - -	- - - - - - - -	- - -
Canyon Diablo	Silicate phase	F6	8.0	0.82	4.083 ± 0.006	4.067 ± 0.006	+16.8
		F7	7.2	0.43	4.077 ± 0.006	4.061 ± 0.006	+15.3
Bondoc	Stony-iron	F8	7.2	0.09	4.090 ± 0.006	4.074 ± 0.006	+18.5
		F9	14.7	0.13	- - - - - - - -	- - - - - - - -	- - -
Dalgaranga	Stony-iron	F10	7.6	0.57	4.170 ± 0.002	4.154 ± 0.002	+38.5
		F11	3.8	1.22	4.177 ± 0.002	4.161 ± 0.002	+40.3

TABLE 9

Boron in Tektites

Tektite	Code	Sample Weight (g)	Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ‰
Indochinite (Dalat, South Vietnam)	T1	1.05	20.0	4.043 ± 0.014	4.027 ± 0.014	+6.8
	T2	0.52	19.0	4.037 ± 0.006	4.021 ± 0.006	+5.3
Indochinite (Northeast Thailand)	T3	0.44	25.0	4.037 ± 0.006	4.021 ± 0.006	+5.3
	T4	0.55	27.4	4.033 ± 0.006	4.017 ± 0.006	+4.3
Bediasite (Sommerville, Texas)	T5	0.95	10.0	4.041 ± 0.006	4.025 ± 0.006	+6.3
	T6	0.60	10.0	4.040 ± 0.006	4.024 ± 0.006	+6.0
Rizalite (Bugad, Luzon)	T7	0.49	33.6	4.037 ± 0.006	4.021 ± 0.006	+5.3
	T8	0.43	38.0	4.043 ± 0.006	4.027 ± 0.006	+6.8

(d) Terrestrial Materials

(i) Rocks and Minerals

Table 10 contains the results obtained from miscellaneous terrestrial samples. The porcelain and G.E. quartz cannot be considered as natural samples since they were produced artificially. Two samples were prepared from the same piece of G.E. quartz.

(ii) Sea Water

The results in Table 11 are for borax A and borax B which have been passed through the ion exchange column.

The results for sea water are grouped separately in Table 12 because of their peculiar B^{11}/B^{10} ratios. Again, the square brackets have the same meaning as in the preceding tables. The average density of all the sea waters was determined to be 1.03 g/ml.

(e) Clay Experiment

In Table 13 are shown the results of the clay experiment. The density of the synthetic sea water was assumed to be unity in this experiment, since there were not enough samples of P2 and P3 available for an accurate determination of the density.

TABLE 10

Boron in Terrestrial Rocks and Minerals

Sample			Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
Name	Code	Weight (g)				
Beryl	M 1	2.0	7.3	4.053 ± 0.014	4.037 ± 0.014	+ 9.3
	M 2	1.2	6.6	4.040 ± 0.006	4.024 ± 0.006	+ 6.0
Hawaiian Basalt	M 3	2.5	1.8			
	M 4	3.2	1.5	4.047 ± 0.002	4.031 ± 0.002	+ 7.8
	M 5	3.6	2.0	4.047 ± 0.014	4.031 ± 0.014	+ 7.8
G.E. Quartz	M 6	7.2	0	- - - - - - - -	- - - - - - - -	- - -
	M 7	9.1	0	- - - - - - - -	- - - - - - - -	- - -
Porcelain	M 8	0.35	40.0	4.050 ± 0.006	4.034 ± 0.006	+ 8.5
Slate (shale)	M 9	0.1	105	4.060 ± 0.006	4.044 ± 0.006	+11.0

continued

TABLE 10 (continued

Boron in Terrestrial Rocks and Minerals

Sample			Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
Name	Code	Weight (g)				
Kimberlite	M10	2.4	4.0	4.057 ± 0.014	4.041 ± 0.014	+10.3
				4.057 ± 0.014	4.041 ± 0.014	+10.3
Finland Tourmaline						
1	M11	5.1×10^{-3}	3.5×10^{4}	4.013 ± 0.006	3.997 ± 0.006	- 0.8
				4.013 ± 0.006	3.997 ± 0.006	- 0.8
2	M12	2.1×10^{-3}	3.3×10^{4}	4.023 ± 0.006	4.009 ± 0.006	+ 2.3
3	M13	2.3×10^{-3}	3.0×10^{4}	3.993 ± 0.006	3.977 ± 0.006	- 5.8

TABLE 11

Boron in Standard Borax (ion exchange)

Boron Tested			Yield (%)	Observed B^{11}/B^{10}
Standard	Code	(μg)		
A	A4	14.9	95	4.290 ± 0.006
B	B5	11.1	93	3.977 ± 0.006

TABLE 12

Boron in Sea Water

Sample			Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
Name	Code	Weight (g)				
Pacific Ocean (1) (Mexico)	E1	4.5	4.13	4.243 ± 0.006	4.226 ± 0.006	+56.5
				4.240 ± 0.006	4.223 ± 0.006	+55.8
	E2	4.5	4.42	4.233 ± 0.006	4.216 ± 0.006	+54.0
	E3	1.24	4.30	4.237 ± 0.006	4.220 ± 0.006	+55.0
Arctic Ocean (Resolute Bay)	E4	2.27	4.10	4.253 ± 0.006	4.236 ± 0.006	+59.0
Pacific Ocean (2) (Peru)	E5	2.27	4.40	4.240 ± 0.006	4.223 ± 0.006	+55.8
Pacific Ocean (3)	E6	4.54	4.30	4.233 ± 0.006	4.216 ± 0.006	+54.0
Atlantic Ocean	E7	4.54	4.10	4.230 ± 0.006	4.214 ± 0.006	+53.5
				4.230 ± 0.006	4.214 ± 0.006	+53.5

TABLE 13

CLAY EXPERIMENT

Sample Name	Code	Weight (g)	Observed Boron Content (ppm)	Observed B^{11}/B^{10}	Absolute B^{11}/B^{10}	δ ‰
Synthetic Sea Water + 100 ppm B	P1	0.22	102	4.060 ± 0.006	4.044 ± 0.006	+11.0
Supernatant of Clay - Sea Water Mixture (1)	P2	0.44	53.2	4.137 ± 0.014	4.121 ± 0.014	+30.3
Supernatant of Clay - Sea Water Mixture (2)	P3	0.44	54.5	4.130 ± 0.006	4.114 ± 4.006	+28.5

(f) Distribution of the Boron Isotope Ratio in Nature

Figure 8 shows the distribution of the B^{11}/B^{10} in nature. All artificial samples such as the NBS steel standards (Table 5), G. E. quartz (sample No. MG and M7, Table 10) and porcelain (sample No. M8, Table 10) are not included in the histogram. On the abscissa are plotted the B^{11}/B^{10} ratios or the δ-values, and on the ordinate the number of independent analyses. Considering the possibility that the isotopic ratio can vary within the same material, all samples taken from different locations of the same material before preparing them for analysis are considered as independent. Samples from the same powdered specimen are not independent since their B^{11}/B^{10} ratios should be the same. Hence, in the tables the means of the ratios for samples enclosed by square brackets are counted as individual analyses. The same convention also applies to the sea water samples.

The boxes containing a question mark correspond to the three values from the stony-iron samples F8, F10 and F11 in Table 8. It is uncertain whether or not these values are representative of the stony-iron meteorites, Bondoc and Dalgaranga, because they were badly weathered and oxidized. These meteorites, being small and having been in contact with the soil for such long periods, may have been contaminated even in their interiors. However, the ratios have been included in the histogram, but the reason for the anomalous ratio is unknown.

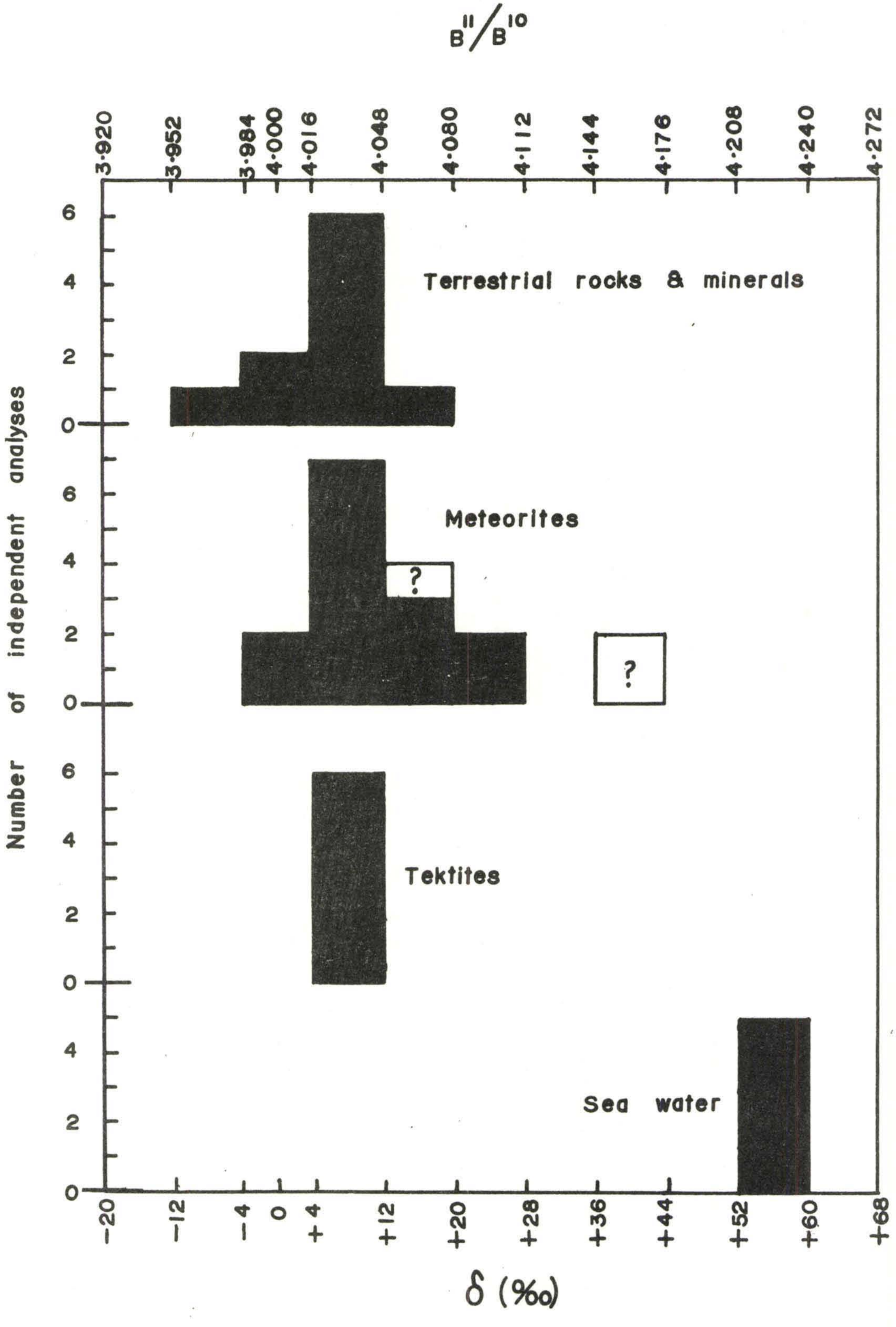

Fig 8 Distribution of the boron isotopes in nature

CHAPTER IV

DISCUSSION

1. ERRORS

(a) Boron Content [B]

From Table 1, the statistical error or precision associated with the curcumin method of determination of boron is, on the average, 9 per cent (standard deviation at the 95 per cent confidence level). The reproducibility (half-range) for the complete cyclic pyrohydrolysis extraction and determination of boron, can be estimated from the results of W-1 (Table 4), borax A and borax B (Table 3, excluding sample A1), the steel standards (Table 5, omitting sample S8) and from those samples enclosed in square brackets in Table 7 and 9, to be 5.1 per cent. The reproducibility for the ion exchange extraction calculated from the results of borax A and borax B in Table 11, and the sea water samples E1, E2 and E3 in square brackets (Table 12), is 2.3 per cent.

An estimate of the accuracy of the boron determination using curcumin can be obtained by comparing the curcumin results with those of the isotope dilution in Table 2. The mean value deviates by 1 per cent from the mean of the isotope dilution results. Using equation 14 or Fig. 9 in Appendix I and re-defining σ as the standard error and ϵ (= $\sigma (R^{/})/R^{/}$ = 0.17 per cent, see Section 1 (b)) as the relative standard error or relative precision, all at the 95 per cent confidence level, the attainable optimum precision $\sigma (q)/q$ (standard error at the 95 per cent confidence) of the isotope dilution method itself is calculated to be about 0.08 per cent. The value for q, the sample to spike ratio of the number of atoms, is taken to be unity and the ratio $R_S^{/} = (B^{10}/B^{11})_S^{/}$ and $R_T^{/} = (B^{10}/B^{11})_T^{/}$ to be both about 0.25.

(b) Boron Isotope Ratio B^{11}/B^{10}

The average precision for one complete mass spectrometric determination of the isotope ratio of an aliquot of the extracted boron is 0.17 per cent (standard error at the 95 per cent confidence level). This is computed by taking the average of the precisions for all individual complete mass spectrometric measurements made in this work. The mean reproducibility of the mass spectrometric determination of the absolute ratio 0.08 per cent (defined as the half-range) is obtained from the data in Table 6 for samples which were not pyrohydrolyzed and the data from samples S8, S9 (Table 5), C4, C6, C8 (Table 7), M10, M11 (Table 10), E1 and E7 (Table 12). The isotope measurement was repeated for different aliquots of the same extracted boron for each of these samples.

The reproducibility for the whole pyrohydrolysis extraction, together with the mass spectrometric measurements, is computed to be 0.08 per cent and is determined from the results of W-1 (Table 4), the steel standards (Table 5, excluding samples S8 and S9), borax A and borax B (Table 3) and those samples enclosed in square brackets in Tables 7 and 9. The corresponding value 0.12 per cent for the ion exchange extractions and the subsequent mass spectrometric measurements is obtained from the results for the sea water samples E1, E2 and E3 in Table 12.

In addition to the statistical error in the absolute B^{11}/B^{10} ratios there is also a systematic error of about 0.05 per cent due to the instrumental mass discrimination (see Appendix II, Section 2).

2. COMPARISON OF RESULTS

Some of the samples analyzed in this research have already been studied by other workers and their results are quoted in Appendices III and IV.

Within experimental errors, the boron content 10.6 ± 0.6 ppm of W-1 obtained in this work agrees with the values 11.1 ppm, 12 ppm and 10 ppm reported by Mills (1966), Lerman (1966), Clark and Swaine (1962) respectively and others listed in Appendix IV, however, it disagrees with the value 17 ppm apparently accepted by Fleischer (1965). The isotopic ratio 4.074 ± 0.002 (δ ‰ = 18.4 ± 0.4) is only

0.7 per cent higher than that reported by Shima (Appendix IV).

The mean values of the boron content 57 ± 2 ppm, 10.4 ± 1.0 ppm and 0.8 ± 0.08 ppm for the NBS steel standards Nos. 1164, 1163 and 1165 or 465 (excluding sample S8) respectively are 14 per cent, 13 per cent and 20 per cent lower than the NBS values (see Appendix IV). There are no known published values for the boron isotope ratios for these steel standards.

The results of sample S8 were excluded in taking the mean of the boron content [B] for NBS No. 1165 or 465, because although the duplicate isotopic ratios are quite consistent with each other, they are not at all in agreement with the data for samples S6, S7 and S9 which are reported to be identical materials. Moreover, the [B] in S8 appears higher than the rest, which suggests that this sample may have been contaminated during the sample preparation.

The results obtained for the Hawaiian basalt can be compared with those reported for Hawaiian and Mohole basalt by Shima (Appendix IV). The B^{11}/B^{10} ratio obtained in this work for Finland tourmaline samples are also in agreement with the value 4.007 ± 0.002 reported by Agyei and McMullen (1968). The mean [B] for tourmaline, 3.3 per cent (3.0 per cent - 3.5 per cent) agrees with the average value of 3.34 per cent calculated from the formula, $(H, Li, Na)_9\ Al_3\ [BOH]_2\ Si_4\ O_{19}\ (+\ Fe_2O_3, FeO, MgO, MnO)$ for tourmaline. It is again remarkable that the [B], 105 ppm obtained for slate (shale) agrees exactly with that reported by Shaw and

Bugry for the same sample (Appendix IV). The results mentioned in this section, together with those on borax A and borax B in Table 3 indicate that the extraction yield of boron is about 100 per cent.

No enrichment in the heavy isotope was detected in kimberlite samples as observed by Cherepanov in Siberian kimberlite (Appendix IV). The $[B]$ of 4 ppm is about two orders of magnitude smaller than that obtained by Cherepanov. The value 4 ppm seems more probable since kimberlite is igneous as are basalt (1.8 ppm), gabbro (10 ppm, Agyei and McMullen, 1968; Shima, 1963) and W-1 (10.6 ppm).

3. METEORITES

The B^{11}/B^{10} ratios for all the chondrites analyzed in this work fall within limits having a range of 22 $^{o}/oo$ (Table 7). The results show that in the same chondritic meteorite, the isotope ratio may vary. This can clearly be seen in the isotope ratios for Bruderheim. The Bruderheim (0) obtained from Ottawa has a lower B^{11}/B^{10} ratio than the Bruderheim obtained from McMaster University. Since the piece of Bruderheim (M) from which the sample was taken included a fusion crust, this piece must be part of the outer portion of the Bruderheim meteorite. If it is assumed that Bruderheim (0) comes from the inner portion of the meteorite, one possible cause of the change in isotopic ratio is cosmic-ray radiation during the flight of the meteorite through space.

According to the theory of BFH (1965) the spallation yield of B^{11}/B^{10} is about 0.4 and this would tend to decrease the B^{11}/B^{10} ratio in the outer portion of the meteorite. This is contrary to what is observed. However, according to the theory of Bernas et al. (1967) the B^{11}/B^{10} from spallation can either be greater or less than the average natural B^{11}/B^{10} ratio depending on the target nucleus. Hence the overall spallation yield of B^{11}/B^{10} will depend on the chemical composition of the irradiated material. Assuming that the outer sample (Bruderheim (M)) initially had a $[B]$ of say 0.5 ppm (compare with values for other meteorites in Table 7), it would require about 0.3 ppm more boron to give the observed concentration of about 0.8 ppm. This will require that the B^{11}/B^{10} produced by spallation due to cosmic rays be 4.226, providing that the inside sample (Bruderheim (O)) did not receive any irradiation. This ratio agrees with the value 5 ± 3 given by Bernas et al. (1967). By comparison with the yield of cosmic-ray produced Li^6 of 1.1×10^{16} atoms/g to 6.2×10^{16} atoms/g in stony meteorites (Fireman and Schwarzer, 1957), the extra 0.3 ppm boron expected from spallation due to cosmic rays is a real possibility.

The average B^{11}/B^{10} ratio 4.045 (4.008 - 4.095) for the chondrites is only 0.45 per cent different from the average value 4.027 (3.977 - 4.074) for terrestrial rocks and minerals, and only 0.1 per cent different from the value 4.023 (4.019 - 4.027) for tektites. These results are in disagreement with those reported by Shima for boron

(Appendix III), but agree with the results of Krankowsky and Müller (1964, 1967) and others that the terrestrial lithium isotope ratio is essentially the same as the meteoritic lithium isotope ratio.

The average [B] for all the chondrites is 0.67 ppm (0.47 ppm - 0.97 ppm), whereas for iron meteorites the average [B] is 0.03 ppm (0.02 ppm - 0.07 ppm) in agreement with the geochemical fact that boron is lithophile and hence will tend to concentrate in the stony meteorites. This also disagrees with Shima's results (Appendix III). As explained in Chapter II it was impossible to measure the isotopic ratio of boron in these irons. However, the silicate nodule of Canyon Diablo was found to possess a [B] and B^{11}/B^{10} ratio similar to that of stony meteorites. The observed variation of the [B] in the same nodule is probably due, in part, to the fact that sample F7 contained some of the iron phase which contributes a negligible amount of boron, thus giving rise to an apparent low [B] . The results for the two stony-iron meteorites analyzed cannot be given much credence, because of their possible contamination from terrestrial boron during their contact with the earth's surface. Such a contamination of the order of 10 ppm is observed for the rusty coating of Canyon Diablo, whereas the fresh interior has a [B] of only 0.03 ppm.

4. TEKTITES

The four tektites studied have a very narrow range of boron isotopic ratio (B^{11}/B^{10} = 4.019 - 4.025) the mean being 4.021, supporting one view that although they are found in different geographical locations, they may have originated from a common source. The [B] which ranges from 10 ppm to 35.8 ppm suggests that they probably have sedimentary rock origin (e.g. [B] for slate = 105 ppm, Table 10) rather than igneous rock (e.g. [B] for W-1 = 10.6 ppm, Hawaiian basalt = 1.8 ppm and kimberlite = 4 ppm, Tables 4 and 10), or chondritic origin (average [B] = 0.67 ppm, Table 7). The fact that some boron may have been lost with the loss of water during the fusion of the rocks to form the tektites cannot be discounted.

5. SEA WATER AND THE CLAY EXPERIMENT

In sea water, the boron isotope ratios B^{11}/B^{10} lie in the narrow range 4.214 to 4.236. The average value, 4.222 is 4.8 per cent greater than the value for terrestrial rocks and minerals (4.030). The isotope ratio for sea water disagrees with the results obtained by Shima (1963). Parwel et al. (1956) have also measured the isotopic ratio of boron in Pacific Ocean water and many other terrestrial minerals. Although they did not observe any variations in the B^{11}/B^{10} ratios of the minerals, they observed that sea water was about two parts per mil enriched in B^{11}. The average [B] of sea water is 4.22 ppm (4.10 ppm - 4.40 ppm).

The results of the clay experiment indicate that absorption of marine boron by certain types of clay is one of the principal processes which cause the observed large isotopic fractionation in sea water. In this experiment absorption of about 50 per cent of the boron gives rise to a 1.8 per cent enrichment of B^{11} in the residual boron. If it is assumed that the present day oceans are capable of holding in solution as much boron ($\sim$100 ppm) as is found in sedimentary rocks (Appendix IV), it is possible that the absorption of about 96 per cent boron could give rise to the observed 4.8 per cent isotopic fractionation.

As will be noted in Appendix III, it is logical to expect the absorption and hence the fractionation to depend to some degree on other factors such as the pH, temperature and salinity of the water. The fact that both isotopic composition and elemental abundance of boron in sea water are constant might mean that the oceans are thoroughly mixed and that the differences between the factors mentioned above are not large enough to have any appreciable effect.

It has already been suggested that the boron content in sedimentary rocks may be used as a paleosalinity indicator (e.g. Fleet, 1965). The results therefore suggest that the isotopic ratio of boron may be used to supplement the $[B]$ as a paleosalinity indicator.

6. MEAN VALUES OF [B] AND B^{11}/B^{10}

Since most of the earth's crust is made up of igneous rocks (Fig. 11, Appendix III) and sedimentary rocks are derived from them, a rather crude average of the [B] for the earth's crust may be taken as the mean value of the boron concentration in the igneous rocks, W-1, Hawaiian basalt and kimberlite (Tables 4 and 10) i.e. 5.5 ppm. It is difficult to see how the [B] in the ocean, minerals and sediments could make any significant change in this mean value. The value 0.67 ppm determined for chondrites may be considered as representative of the mantle and the average value of iron meteorites, 0.03 ppm of the core.

It is assumed at this point that meteorites are fragments of a single disrupted planet which once existed in the asteroidal belt. This is one of the three main theories proposed for the origin of meteorites. In general, one of the remaining two is quite similar except that the meteorites are pieces of smaller parent bodies. The third theory supposes two successive generations of parent bodies, primary and secondary objects. The primary objects were broken up into fragments by collision between themselves and the secondary objects accumulated from the primary debris. A brief outline of these theories is given by Mason (1962, Chapter 12). It is further assumed that the meteorite parent body underwent melting and subsequent cooling and geochemical stratification just as it is supposed for the earth.

By using Figure 10 in Appendix III and assuming a uniform density for the earth, the mean value of the [B] for the earth can be estimated to be 0.65 ppm. If similar structural and geochemical composition is assumed for the meteoritic parent body, its average [B] will also be very probably close to 0.65 ppm, whereas the average [B] for chondrites is 0.67 ppm and for irons 0.03 ppm. Using the same argument, it appears that the average B^{11}/B^{10} ratio for both the earth and the meteorites will not be too different from the average of the B^{11}/B^{10} ratio for chondrites, and terrestrial rocks and minerals viz. 4.036. Probably the mean [B] and B^{11}/B^{10} ratio of other planets too is not very different from these estimated values. It should be emphasized that the mean values are only approximate because of the many assumptions made. For instance, if the density of the earth is taken into account the mean values may change somewhat. Also, consideration will have to be given to the other types of meteorites such as stony-irons, achondrites and carbonaceous chondrites.

7. CONCLUSION

This research concludes that there are no differences to within 0.45 per cent between the average terrestrial and meteoritic (parent body) isotopic and elemental composition of boron as a consequence of nuclear synthesis of the element. As discussed in Chapter I, Section 3 (c) and (d), this implies that no slow neutrons are required to give the terrestrial and meteoritic B^{11}/B^{10} ratios. However, there may be local isotopic and elemental anomalies due to other chemical and physical phenomena such as those accounting for the results of the sea water and Bruderheim (M) anomalies.

Tektites could not have been produced by fusion of chondritic meteorites or igneous rock because of the large $[B]$ of tektites. It is possible they are derived from sedimentary rocks.

The estimated $[B]$ and B^{11}/B^{10} ratio for the planets and meteorites to be employed in such theories as the synthesis of the L-nuclei are 0.65 ppm and 4.036 respectively.

APPENDIX I

PRECISION MASS SPECTROMETRIC ISOTOPE DILUTION ANALYSIS

1. INTRODUCTION

It is known that the use of mass spectrometry in isotope dilution measurements is one of the powerful analytical tools for determining minute quantities of elements. By careful choice of the parameters involved, high precision can be attained in this method of analysis.

The technique consists of blending an unknown amount of the element to be determined (target) with a known amount of the same element, having a different isotopic ratio (spike). The amount of element in the target can be calculated by using the appropriate formula (derived below), if the isotopic ratios of the target, spike and blend, are measured mass spectrometrically. If the target is too small to allow direct determination of its amount and of its isotopic ratio, two different quantities of highly enriched spike can be used in order to determine both the isotopic ratio and the amount of the target. Several aspects of the isotope dilution method have been treated in the literature and are referred to by de Bièvre and Debus (1965a).

The formulas used in isotope dilution determinations, involving a bi-isotopic sample and spike, are derived by de Bièvre and Debus (1965a) and are reproduced here. The general relations for a poly-isotopic sample and/or spike are given by the same authors elsewhere (de Bièvre and Debus, 1965b).

2. SYMBOLS AND BASIC RELATIONS USED

A = absolute mass of an isotope

M = total mass of the element considered

N = number of atoms of element or isotope

B, T, S = subscripts referring respectively to the Blend, to the sample (Target), and to the Spike.

R = N_2/N_1 = true ratio of second to first isotope

R' = measured isotope ratio

NOTE that the symbols R and R' have been interchanged to make them consistent with those used in Appendix II.

K = R/R' = mass discrimination factor

This linear relationship between R, R' and K is assumed to be sufficiently accurate for the purpose of this derivation.

γ = A_2/A_1 = absolute mass ratio of second to first isotope

p = M_T/M_S = sample to spike mass ratio

q = N_T/N_S = sample to spike number of atoms ratio

σ = standard deviation

ϵ = $\sigma(R')/R'$ = the relative standard deviation or relative precision of an isotope ratio measurement. ϵ is assumed to be constant.

The following basic relations apply:

$$\left[\frac{N_2}{N_1}\right]_T = KR'_T \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\left[\frac{N_2}{N_1}\right]_S = KR'_S \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$\left[\frac{N_2}{N_1}\right]_B = \frac{\left[N_2\right]_S + \left[N_2\right]_T}{\left[N_1\right]_S + \left[N_1\right]_T} = KR'_B \quad \ldots\ldots\ldots\ldots \quad (3)$$

By definition, the total amount of sample expressed in number of atoms is:

$$N_T = q\, N_S \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

and expressed as total mass:

$$M_T = p\, M_S \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Hence knowledge of the spike and p or q defines the unknown sample size.

3. CALCULATION OF p and q

$$q = \frac{N_T}{N_S} = \frac{\left[N_1 + N_2\right]_T}{\left[N_1 + N_2\right]_S} = \frac{\left[N_1\right]_T}{\left[N_1\right]_S} \cdot \frac{1 + KR'_T}{1 + KR'_S} \quad \ldots\ldots\ldots \quad (6)$$

for $N_1 \neq 0$ in both sample and spike

$\dfrac{\left[N_1\right]_T}{\left[N_1\right]_S}$ is calculated from (1), (2) and (3)

$$\frac{\left[N_1\right]_T KR'_T + \left[N_1\right]_S KR'_S}{\left[N_1\right]_T + \left[N_1\right]_S} = KR'_B$$

and $\dfrac{\left[N_1\right]_T}{\left[N_1\right]_S} = \dfrac{R'_S - R'_B}{R'_B - R'_T}$ $\quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$

Using equations (6) and (7)

$$q = \frac{R'_S - R'_B}{R'_B - R'_T} \cdot \frac{1 + KR'_T}{1 + KR'_S} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

which is only a function of the measured isotope ratio in blend, sample, and spike, and of the mass discrimination factor.

p is calculated from:

$$M_T = [N_1]_T \; A_1 + [N_2]_T \; A_2 = [N_1]_T \; A_1 \; (1 + \gamma \, R'_T)$$

$$M_S = [N_1]_S \; A_1 \; (1 + \gamma \, KR'_S)$$

$$p = \frac{M_T}{M_S} = \frac{[N_1]_T}{[N_1]_S} \cdot \frac{1 + \gamma \, KR'_T}{1 + \gamma \, KR'_S} \quad \ldots\ldots\ldots\ldots\ldots \tag{9}$$

Using equation (7)

$$p = \frac{R'_S - R'_B}{R'_B - R'_T} \cdot \frac{1 + \gamma \, KR'_T}{1 + \gamma \, KR'_S} \quad \ldots\ldots\ldots\ldots\ldots \tag{10}$$

q can be derived from p by putting $\gamma = 1$.

4. ATTAINABLE PRECISION

For $M_T = pM_S$ and assuming the determination of M_S to be independent of p, the statistical error is:

$$\sigma^2(M_T) = p^2 \, \sigma^2(M_S) + M_S^2 \, \sigma^2(p) \quad \ldots\ldots\ldots\ldots \tag{11}$$

or

$$\left[\frac{\sigma(M_T)}{M_T}\right]^2 = \left[\frac{\sigma(p)}{p}\right]^2 + \left[\frac{\sigma(M_S)}{M_S}\right]^2 \quad \ldots\ldots\ldots \tag{12}$$

Similarly, for a spike given in number of atoms:

$$N_T = q\ N_S$$

$$\left[\frac{\sigma(N_T)}{N_T}\right]^2 = \left[\frac{\sigma(q)}{q}\right]^2 + \left[\frac{\sigma(N_S)}{N_S}\right]^2 \quad \ldots\ldots \quad (13)$$

The relative errors $\left[\sigma(p)/p\right]^2$ and $\left[\sigma(q)/q\right]^2$ can be calculated from equations (8) and (10) according to the normal law of propagation of statistical errors.

After elimination of R'_B with the aid of equation (8), and taking into account the constant relative precision on an isotope ratio measurement $\left[\sigma(R) = \epsilon R\right]$, the following result is obtained:

$$\left[\frac{\sigma(p)}{p}\right]^2 = \frac{1}{p^2} \cdot \frac{(1+p)^2\ (1+\gamma\ KR'_T)^2}{(R'_S - R'_T)^2\ (1+\gamma\ KR'_S)^2}\ \epsilon^2\ (R'_S)^2 +$$

$$+ \frac{(1+p^2)\ (1+\gamma\ KR'_S)^2}{(R'_S - R'_T)^2\ (1+\gamma\ KR'_T)^2} \cdot \epsilon^2\ (R'_T)^2 +$$

$$+ \frac{1}{p^2} \cdot \frac{\left[pR_T(1+\gamma KR'_S) + R_S(1+\gamma KR'_T)\right]^2 \cdot \left[p(1+\gamma KR'_S) + (1+\gamma KR'_T)\right]^2}{(R'_S - R'_T)^2 (1+\gamma KR'_T)^2 (1+\gamma KR'_S)^2}\ \epsilon^2 +$$

$$+ \frac{\gamma^2 (R'_T - R'_S)^2}{(1 + \gamma K R'_T)^2 \ (1 + \gamma K R'_S)^2} \epsilon^2 \quad \ldots\ldots\ldots\ldots \quad (14)$$

Equation (14) expresses the expected dependence of the relative precision on p from all isotope dilution parameters, of which one has an approximate knowledge before starting an isotope dilution measurement.

The relative precision on q is obtained by replacing p by q in equation (14) and putting $\gamma = 1$. It is graphically presented in Fig. 9 for $R'_T = 20/80$ (approximate case for boron if R is defined as B^{10}/B^{11}), and K = 1. $\left[\sigma(q)/q\right]^2$ is given in units of ϵ^2 as a function of q for different values of R'_S. $\left[\sigma(q)/q\right]^2$ for other values of R'_T can be found in the original report (de Bièvre and Debus, 1965a).

<u>NOTE</u>: If R is defined as B^{11}/B^{10} the same figure is applicable provided the values of R'_S on the graph are changed to their reciprocals.

The precision on the spike and that indicated by the graphs give a knowledge of the expected precision by the isotope dilution technique. To attain high precision, a proper choice of the sample to spike ratio has to be made. This means that the sample size has to be estimated before the isotope dilution procedure is begun.

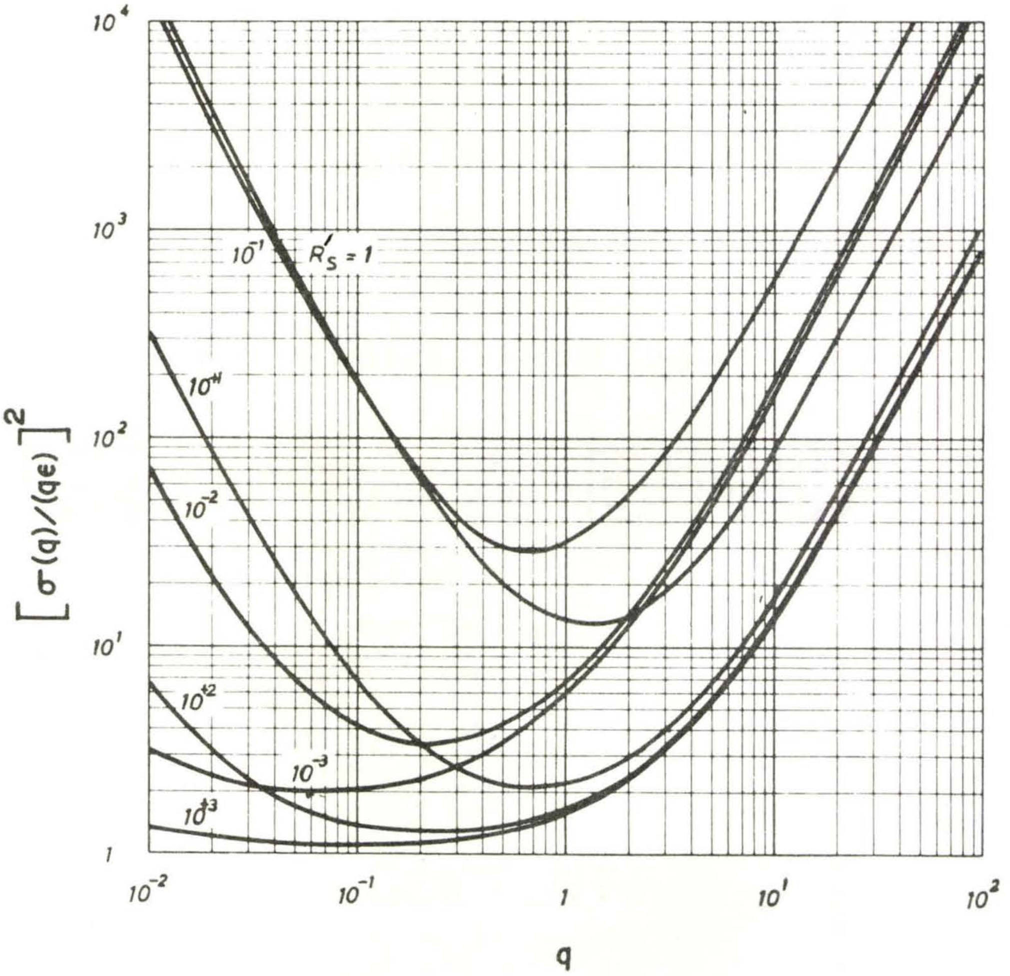

Fig 9 Precision of Isotope dilution measurement

(De Bièvre and Debus, 1965a)

APPENDIX II

SYNTHETIC BORON STANDARDS

1. INTRODUCTION

For the purpose of reference, the theory and preparation of the two boron standards of known isotopic composition borax A ($B^{11}/B^{10} = 4.270$) and borax B ($B^{11}/B^{10} = 3.956$), used to calibrate the mass spectrometer used in this research are reproduced here. This has been reported by Agyei (1965).

The preparation of the synthetic boron standards provided by McMullen et al. (1961) was made in this laboratory using the following three steps:

(a) The isotopic composition of boron samples enriched in B^{11} and B^{10}, which were obtained from the Oak Ridge National Laboratory in the form of boric acid, was determined.

(b) The enriched samples were converted into a suitable chemical form (borax) for quantitative combination.

(c) Accurately known amounts of the B^{10} and B^{11} were then blended to obtain the synthetic mixtures of borax A and borax B.

2. THEORY

Using the notation of Bentley and Hamer (1958), the B^{10}

concentration of the mixture will be given by:

$$C_m = fC_d + (1 - f)C_e \quad . . . . \quad (1)$$

where

C_m is the B^{10} concentration of the mixture,

C_d is the B^{10} concentration of the B^{10} depleted (or B^{11} enriched) blending material;

C_e is the B^{10} concentration of the B^{10} enriched (or B^{11} depleted) blending material;

f is the molar fraction of the depleted material used in the mixture.

The quantities C_d and C_e are determined approximately on the mass spectrometer to be calibrated. The calculated B^{10} concentration in the prepared standard will be in error depending on the errors associated with the measurement of C_d and C_e. From equation (1) the error ΔC_m is given by:

$$\Delta C_m = f \Delta C_d + (1 - f) \Delta C_e \quad . . . . \quad (2)$$

It should be noted that, usually in mass spectrometric measurements the quantity that is determined is the isotopic abundance ratio. Errors arising from instrumental mass discrimination will affect this ratio which will be assumed to be related to the absolute ratio by the expression:

$$R = KR'$$

where,

R is the absolute B^{11}/B^{10} ratio

R' is the observed ratio

K is a constant for all values of R

The error due to the instrumental discrimination:

$\frac{\Delta R}{R'}$ is given by:

$$\frac{\Delta R}{R'} = \frac{R' - R}{R'} = 1 - K \qquad \ldots\ldots\ldots\ldots \qquad (3)$$

The concentration of an isotope can be written as:

$$C = \frac{1}{1 + R'} \qquad \ldots\ldots\ldots\ldots \qquad (4)$$

The error in C arising from the use of R' in place of the true value, R will be:

$$\Delta C = -\frac{\Delta R}{(1 + R')^2} \qquad \ldots\ldots\ldots\ldots \qquad (5)$$

and from equation (3)

$$\Delta C = -\frac{(1 - K)R'}{(1 + R')^2} \qquad \ldots\ldots\ldots\ldots \qquad (6)$$

From equations (1) and (6) the error ΔC_m can be computed. This corresponds to an error ΔR_m in the calculated isotopic ratio R_m. It will now be shown that the error in the calculated value of the constituents of the standard mixture, $\frac{\Delta R_m}{R_m}$ is always smaller than the corresponding $\frac{\Delta R}{R'}$ (= (1-K)) which arises from the mass discrimination in a direct measurement on the constituent materials or the isotopic ratio of the standard is calculated to a greater accuracy than that of the blending materials.

<u>Accuracy of the preparation of the boron standards</u>

From equation (6)

$$\Delta C_d = - \frac{(1 - K)R'_d}{(1 + R'_d)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

can be written for the depleted blending material, and

$$\Delta C_e = - \frac{(1 - K)R'_e}{(1 + R'_e)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

for the enriched blending material.

In the preparation of the standards used in this work,

$R'_d \approx 28$ and $R'_e \approx 0.01$.

Substituting these in equations (7) and (8),

$$\Delta C_d \approx -0.033 \ (1 - K) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

and $$\Delta C_e \approx -0.01 \ (1 - K) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

Substituting ΔC_d and ΔC_e in equation (2)

$$\Delta C_m = - f \times 0.033 \ (1 - K) - (1 - f) \times 0.01 \ (1 - K)$$

$$= -0.023 f (1 - K) + 0.01 (1 - K)$$

$$= -(1 - K) (0.023 f + 0.01) \quad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

From equation (6), the associated error R_m is given by:

$$\Delta R_m = - C_m (1 + R_m)^2 = (1 + R_m)^2 (1 - K)(0.023 f + 0.01)$$

$$\therefore \frac{\Delta R_m}{R_m} = \frac{(1 + R_m)^2}{R_m} (1 - K)(0.023 f + 0.01)$$

For the blend where f is chosen to be ≈ 0.2 to give $R_m \approx 4$ we can write:

$$\frac{\Delta R_m}{R_m} = \frac{25}{4} \times 0.0146 (1 - K)$$

$$\frac{\Delta R_m}{R_m} = 0.091 (1 - K) \quad \ldots\ldots\ldots\ldots\ldots \quad (12)$$

Comparison of equation (12) with equation (3) indicates that the error in the calculated isotopic ratio of the standard mixture is about ten per cent of the instrumental discrimination error in the approximate determination of the quantities C_d and C_e.

The next step is to analyze the prepared standards on the mass spectrometer to be calibrated and from the measured isotopic ratios R'_m an estimate of the constant K is made. This is used to adjust the values of R'_d and R'_e needed in the calculation of C_d and C_e so that C_m is determined with a greater accuracy. This procedure can be repeated as many times as required by the accuracy needed for the standards.

For the particular standards used in this experiment (McMullen et al., 1961), it appears that the process was done only once. To estimate $\frac{\Delta R_m}{R_m}$ we assume the value of K obtained by the authors viz. 1.005. Substituting in equation (2):

$$\frac{\Delta R_m}{R_m} = 0.091 \times (1 - 1.005)$$

$$= - 0.091 \times 0.005$$

$\therefore$ per cent error in R_m

$$= 0.091 \times 0.005 \times 100$$

$$\approx 0.05 \text{ per cent}$$

It can also be shown that the difference between the concentrations of either of the isotopes in standards A and B as determined by measurement should be equal to the difference obtained by calculation. This will serve as a further check on the calculations and measurements on the prepared standards.

Consider the B^{10} concentration in the two boron standards A and B.

$$C_A = \frac{1}{1 + R_A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

$$C_B = \frac{1}{1 + R_B} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

$$C_A^{/} = \frac{1}{1 + R_A^{/}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

$$C'_B = \frac{1}{1 + R'_B} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

All the symbols have the same meaning as before. The subscripts A and B refer to the standards A and B. Using $R = KR'$, equations (13) and (14) can be written as:

$$C_A = \frac{1}{1 + KR'_A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13a)$$

$$C_B = \frac{1}{1 + KR'_B} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14a)$$

The difference in the B^{10} concentration in the two standards is given by the difference between equations (15) and (16).

$$C'_A - C'_B = \Delta C_{\text{measured}}$$

$$\Delta C_{\text{measured}} = \frac{1}{1 + R'_A} - \frac{1}{1 + R'_B} \quad \ldots\ldots\ldots\ldots \quad (17)$$

$$\Delta C_{\text{calculated}} = (13a) - (14a)$$

$$= \frac{1}{1 + KR'_A} - \frac{1}{1 + KB'} \quad \ldots\ldots\ldots \quad (18)$$

K is generally ≈ 1. Therefore, put $K = 1 + \epsilon$ where $\epsilon \ll 1$ and in this work particularly $R'_A \approx R'_B \approx 4$.

$$\therefore \Delta C_{\text{calculated}} = \frac{1}{1 + (1 + \epsilon)R'_A} - \frac{1}{1 + (1 + \epsilon)R'_B}$$

$$\approx \frac{1}{1 + R'_A}(1 - \frac{\epsilon R'_A}{1 + R'_A}) - \frac{1}{1 + R'_B}(1 - \frac{\epsilon R'_B}{1 + R'_B}) \approx \frac{1}{1 + R'_A} - \frac{1}{1 + R'_B}$$

Therefore, $\Delta C_{\text{calculated}} \approx \Delta C_{\text{measured}}$.

3. CHEMICAL PREPARATION

The boric acid was converted to methyl borate (Archibald, 1932) by heating the acid with methanol and taking off the methyl borate-methanol azeotrope through a glass-helix-packed fractionating column. The azeotrope boils at 55°C and the reaction was considered complete when the temperature at the top of the column reached 64°C. Titrations of the distillate, in test runs, with sodium hydroxide indicated that the yield of this step was greater than 95 per cent.

The methyl borate-methanol solution was then mixed with a stoichiometric amount of 1 N sodium hydroxide solution. When this solution was seeded with a small crystal of borax and stirred, crystals of borax were precipitated.

The methanol was expelled with a minimum loss of boron as methyl borate by allowing the solution to evaporate to dryness at room temperature. The borax was purified by two re-crystallizations, using distilled water, after which the borax crystals were washed with ethanol and ether, and stored in a dessicator over a saturated agueous solution of sucrose and sodium chloride.

Samples of the pure borax produced from B^{10}-enriched boric acid and B^{11}-enriched boric acid were weighed on an analytical balance and combined to form the synthetic standards borax A and borax B.

Small amounts of the pure borax from the enriched samples were set aside for mass spectrometric analysis. To ensure uniform isotopic mixing in the synthetic standards the borax was dissolved in a minimum amount of hot water, held in solution and stirred for about half an hour, then chilled and allowed to evaporate to dryness at room temperature.

APPENDIX III

GEOLOGICAL NOTES

There is extensive literature on meteorites, tektites and the earth, including sea water. Below are some important definitions and notes, some of which are mentioned in the body of the thesis. These are mostly taken from Mason (1962), who has given a comprehensive introduction to the study of meteorites and tektites, and to Ahrens (1965) who has given an introduction to geochemistry. They also record an extensive list of references.

1. METEORITES

A meteorite is a meteoroid which has survived the passage through the earth's atmosphere and arrived on the earth as a solid body.

A meteoroid is an extra-terrestrial solid body passing through the earth's atmosphere, which produces a luminous streak in the sky, called a meteor. A meteoroid may or may not reach the earth's surface.

Since meteorites are the only tangible objects reaching us from outer space, they are of special interest to scientists, e.g. astronomers, astrophysicists, geochemists, geophysicists, nuclear physicists and biologists. The study of their external and internal structure has given useful information regarding astronautical problems such as the design of space ships and the problems of re-entry into the earth's atmosphere.

A fall is a meteorite which was picked up after it was seen to fall.

A find is a meteorite which was not seen to fall but was recognized as having the chemical, minerological and structural properties of meteorites. Normally falls are more reliable for meteoritic studies than finds, since they are less likely to have been contaminated by terrestrial material.

Classification of Meteorites:

Meteorites can be divided into three main groups:

1. Aerolites or stones, which are made up of silicate minerals, mainly olivine $\left[(Mg,Fe)_2SiO_4\right]$ and orthopyroxene $\left[(Mg,Fe)SiO_3\right]$ or a mixture of these. They also contain some nickel-iron. The stones which have chondrules or chondri in them are called chondrites; those without chondri are called achondrites. These chondri are spheroidal inclusions of olivine or pyroxene, usually 1 mm in diameter.
2. Siderites or irons which are made up of about 90 per cent Fe and 10 per cent Ni, with a small amount of other minerals.
3. Siderolites or stony-irons which consist of about 50 per cent of nickel-iron and 50 per cent silicates.

These three groups are further subdivided according to their mineralogical content. Such a division is shown in Table 14.

Published Isotopic and Elemental Composition of Meteoritic Boron

(a) Irons 0.9 ppm)
) Goldschmidt and Peters (1932)
Stones 1.6 ppm)

Breitscheid (chondrite) 5 ppm, Vilcsek (1959)

(b) The isotopic and elemental composition of boron in meteorites reported by Shima (1962) are quoted in Table 15.

2. TEKTITES

Tektites consist of a silica-rich (70 - 80 per cent SiO_2) glass which on the outside resembles obsidian glass, but quite distinct from any terrestrial obsidian. They differ from one another in shape, size and colour, yet tektites from different localities resemble each other in internal structure and chemical composition. They have small (up to 200 - 300 g) rounded to elongated form and are found in different geographical localities, which tend to preclude volcanic origin. When broken, the small flakes are translucent like coloured glass but they look dark and opaque when unbroken. Usually the tektites are named after the geographical locations in which they are found. Unlike meteorites, tektites have not actually been seen to fall, yet some of the theories about their origin suggest an extra-terrestrial source.

TABLE 14

CLASSIFICATION OF THE METEORITES

(Figures in parentheses are the numbers in each class)

(Mason, 1962)

Group	Class	Principal Minerals
Chondrites	Enstatite (11)	Enstatite, nickel-iron
	Olivine-bronzite) (900)	Olivine, bronzite, nickel-iron
	Olivine-hypersthene)	Olivine, hypersthene, nickel-iron
	Olivine-pigeonite (12)	Olivine, pigeonite
	Carbonaceous (17)	Serpentine
Achondrites	Aubrites (9)	Enstatite
	Diogenites (8)	Hypersthene
	Chassignite (1)	Olivine
	Ureilites (3)	Olivine, pigeonite, nickel-iron
	Angrite (1)	Augite
	Nakhlites (2)	Diopside, olivine
	Eucrites and howardites (39)	Pyroxene, plagioclase

... continued

TABLE 14 (continued)

CLASSIFICATION OF THE METEORITES

(Figures in parentheses are the numbers in each class)

(Mason, 1962)

Group	Class	Principal Minerals
Stony-irons	Pallasites (40)	Olivine, nickel-iron
	Siderophyre (1)	Orthopyroxene, nickel-iron
	Lodranite (1)	Orthopyroxene, olivine, nickel-iron
	Mesosiderites (22)	Pyroxene, plagioclase, nickel-iron
Irons	Hexahedrites (55)	Kamacite
	Octahedrites (487)	Kamacite, taenite
	Ni-rich ataxites (36)	Taenite

TABLE 15

BORON IN METEORITES (Shima, 1962)

Sample	B (ppm)	B^{11}/B^{10}
Toluca, iron	0.45	3.850 ± 0.03
Richardton, chondrite	0.38	3.815 ± 0.05
Ehole, chondrite	0.41	3.820 ± 0.03
Achilles, chondrite	0.50	3.902 ± 0.02
Shallow water, achondrite	0.42	- - - - - -
Pasamonte, achondrite	1.25	3.960 ± 0.02

Below are listed the recognized true tektites:

Australites
Bediasites (Texas)
Billitonites
Indochinites
Ivory Coast tektites
Javaites
Moldavites
Philippinites (or rizalites)

Origin of Tektites

A state of controversy exists regarding the origin of tektites. There are two main groups of theories on the origin of tektites: terrestrial and extra-terrestrial. These can be sub-divided as shown below. For the discussion on these the reader is referred to Mason (1962) and to additional references given by him.

A. Tektites have been formed from terrestrial materials by:

1. Impact (a) of meteorites; (b) of comets.
2. Lightning (a) fusing soil; (b) fusing dust particles in the atmosphere.
3. Natural fires: burning straw, forest fires, coal seams, etc.
4. Volcanic activity.
5. Human activity: furnace slags, artificial glasses, etc.

B. Tektites are of extra-terrestrial origin; they came from:

1. The moon: from (a) lunar volcanoes; (b) splashes from meteorite impact.
2. Comets.

3. A disrupted planetary body having a glassy surface layer.
4. Meteorites consisting of free Si, Al, Mg, etc.
5. Stony meteorites, by fusion in the earth's atmosphere.

There is also a controversy between proponents of an igneous or a sedimentary rock origin for tektites. The study of boron in tektites, which is known to be enriched in certain marine sediments might help to resolve this controversy.

Reported Boron Contents of Tektites:

3 - 22 ppm, Preuss (1935)

$<$ 10 ppm (in 14 australites), Taylor and Sachs (1960)

3. GEOCHEMISTRY

The earth is thought to have solidified from a parent body which was at one time molten. On solidifying, the earth became stratified as shown in Figure 10 according to the geochemical properties of the elements and their compounds.

The Core consists of a metallic mass, mainly iron, plus some of the rarer metals which are not chemically very active: gold, platinum and nickel for example. The inner section of the core is probably solid, surrounded by a metallic fluid forming the outer section.

The Mantle, which is the major component of the earth, is made up of dense silicates of Mg and Fe mainly. The division into different sections is due to the different chemical and physical properties of the silicates in these layers, such as the melting points and densities. One interesting indicator of the composition of the upper mantle is from cognate xenoliths, which are found in basalts and in kimberlite pipes.

The Crust Some of the main features of the crust are shown in Fig. 11. The crust is mainly made up of igneous rocks, basalt, diorite and granite, plus grandiorite.

The following geochemical properties control the distribution of the elements in the different layers.

Term	Tendency
siderophile (iron phase)	tendency to be associated with metallic iron
chalcophile (sulfide phase-troilite)	tendency to be bound to sulfur (affinity to sulfur)
lithophile (silicate phase)	tendency to be bound to oxygen (affinity for oxygen)
atmophile	tendency to occur as a gaseous component of the atmosphere

Sea Water Sea water forms only a small part of the crust. The major proportion of the several constituents of sea water, including sodium chloride, the principal salt, has originated from the slow weathering of rocks and also from volcanic activity.

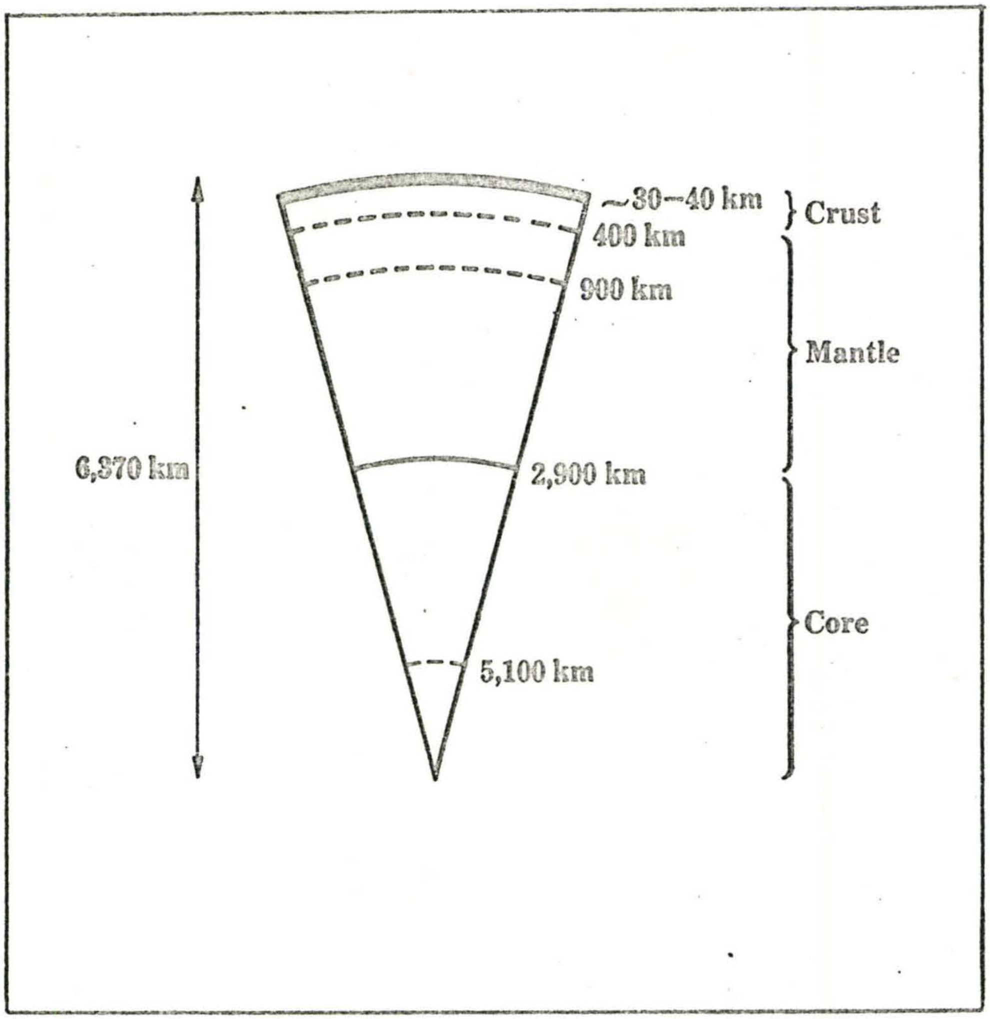

Fig 10 Structural components of the earth (Ahrens 1965)

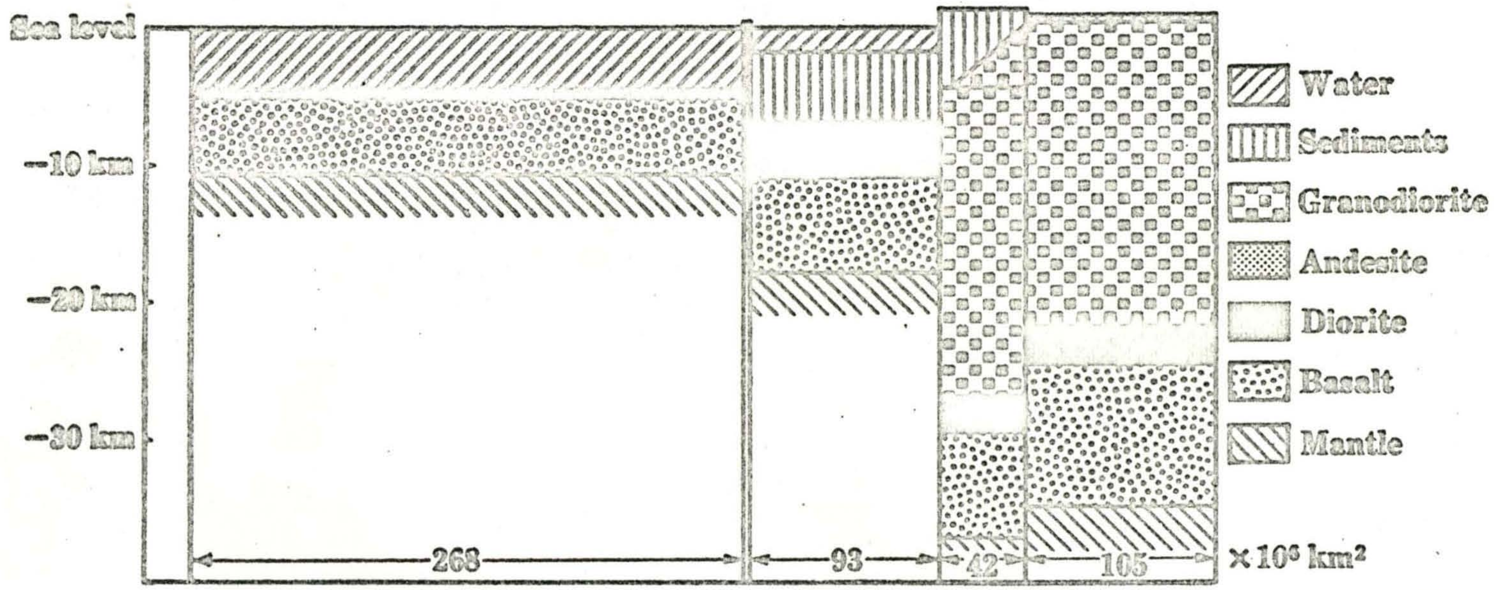

Fig II Schematic section of the earth's crust (Ahrens1965)

Urey (1953) has shown that boron in the earth's crust is concentrated in the sedimentary rocks, but it can be shown that the oceans are capable of dissolving an amount of boron equivalent to that in sedimentary rocks. It is believed that the boron in the oceans must have been removed by absorption of the boron by certain types of clays, e.g. illite. The amount of absorption depends on several factors, e.g. salinity, temperature and pH, (e.g. see Harder, 1961; Fleet, 1965; and Lerman, 1966). This can be seen by comparing the boron content in the ocean to that in clays.

ocean $\sim$ 4.5 ppm
illite $\sim$ 200 ppm

APPENDIX IV

DESCRIPTION OF SAMPLES

In this appendix are given all of the available pertinent details about the samples which have been given code numbers in the text. They are presented in the same order in which they appear in the results except for samples A4 and B5.

Photographs in this appendix were taken with a Pentar S.P. Macro Takumar lens camera, using a Kodachrome II, type A, 3400°K film and two No. 2 photoflood (3400°K) lights.

1. STANDARDS

A1 to A4 (borax A)

Synthetic boron standard in the form of borax. See Appendix II for its preparation. Calculated $B^{11}/B^{10} = 4.270$. Stock standard solution contains 0.67 μg of boron per ml (see Chapter 2, section 1).

B1 to B5 (borax B)

Synthetic boron standard in the form of borax. See Appendix II for its preparation. Calculated $B^{11}/B^{10} = 3.956$. Stock standard solution contains 0.5 μg of boron per ml (see Chapter 2, section 1).

W11 to W19 (W-1)

Geological rock standard, obtained from the United States Geological Survey in the form of a powder. W-1 is a diabase containing about 53 per cent of SiO_2. In Tables 16, 17 and 18 are some of the values determined for the boron content in W-1. The values of the boron content in G-1 (diabase, 73 per cent SiO_2), also a geolgical rock standard, are also recorded.

S1, S2

U. S. National Bureau of Standards No. 1164 steel standard. Supplied as a disk 3.18 cm in diameter and 1.9 cm thick. Boron content certified by NBS: 50 ppm, probably determined by spectrochemical analysis.

S3 to S5

U. S. National Bureau of Standards No. 1163 steel standard, supplied as a disk 3.18 cm in diameter and 1.9 cm thick. Boron content certified by NBS: 12 ppm, probably determined by spectrochemical analysis.

S6, S7

U. S. National Bureau of Standards No. 1165 steel standard supplied as a disk 3.18 cm in diameter and 1.9 cm thick. Certified boron content: 1 ppm, probably determined by spectrochemical analysis.

S8, S9

U. S. National Bureau of Standards No. 465 steel standard, identical with NBS No. 1165 in chemical composition but supplied as a rod 0.56 cm in diameter and 10.2 cm long. Certified boron content: 1 ppm, probably determined by spectrochemical analysis.

TABLE 16

BORON CONTENT OF W-1 and G-1 (ppm) (Ahrens and Fleischer, 1960)

W-1	G-1	Method	Reference
17	1.5	chem. color	Haln-Weinheimer (1959)
2.6	1	spectrochemical	Eugster (1954)
20	30	"	McBurney (1956)
10	20	"	Chodos (1957)
10	- -	"	Murata (1951)
- -	7	"	Hall (1958)
<12	- -	"	Shaw, Filby, Siroonian and Yip (1958)
12	1.2	"	Harder (1959)

TABLE 17

BORON CONTENT OF W-1 and G-1 (ppm) (Fleischer, 1965)

W-1	G-1	Method	Reference
17?	1.5?	colorimetry	Ahrens and Fleischer (1960), Fleischer and Stevens (1962)
17 av. of 20	- -	spectrochemical	Taylor and Koble (1964)
17	trace	"	Pavlenko and Popova (1964)
18*	2.8*	spark source mass spectrometer	Brown and Wolstenholme (1964)

* In the authors' own words, "Results can be in error by as much as a factor of 3. Experience has shown that the majority of the elements do not have the same sensitivity."

Silicon is used as the internal standard.

? The magnitudes were taken by Ahrens and Fleischer (1960) from the only colorimetric result (see Table 16).

TABLE 18

BORON CONTENT AND ISOTOPIC RATIO OF W-1
(published)

Content (ppm)	B^{11}/B^{10}	Method	Reference
9 (av. of 22)	- - -	spectrographic	Govindaraju (1961)
10 (av. of 4)	- - -	spectrographic	Clark and Swaine (1962)
20.3	4.046	methyl borate dist. and colorimetry	Shima (1963)
12	- - -	methyl borate dist. and colorimetry	Lerman (1966)
11.1	- - -	methyl borate dist. and colorimetry	Mills (1966)
10.6 (av. of 9)	4.074	cyclic-pyrohydrolysis and colorimetry	This work.

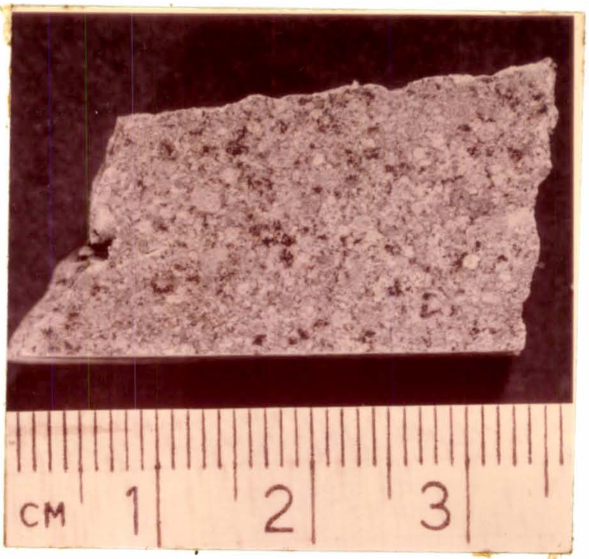

Plate 1. Polished surface of Bruderheim

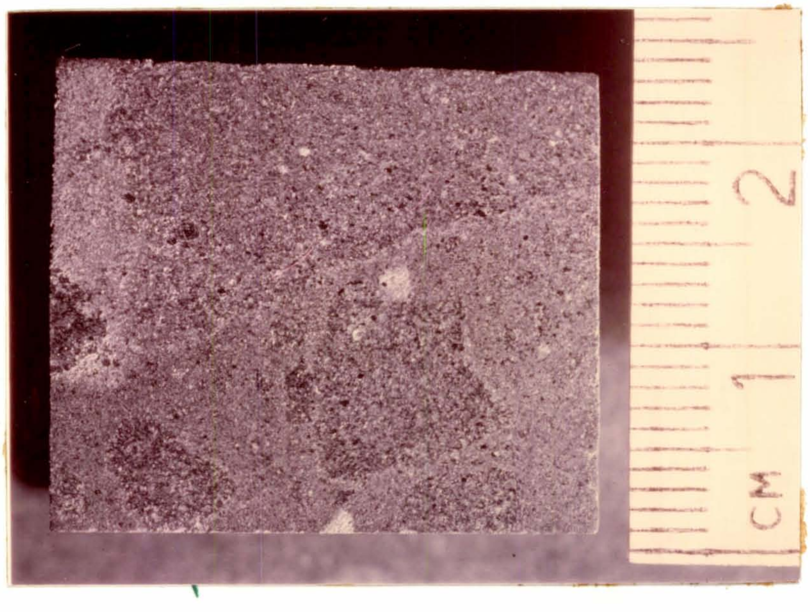

Plate 2. Polished surface of Abee

2. CHONDRITES

C1 to C5

Bruderheim (M): grey olivine-hypersthene chondrite, fall, 1960. About 200 g piece obtained from W. B. Clarke, McMaster University. This sample included the black fusion crust.

C6, C7

Bruderheim (O): grey olivine-hypersthene chondrite, fall, 1960, Alberta, Canada. 20 - 30 g piece obtained from J. A. V. Douglas, Geological Survey of Canada, Ottawa, Ontario. A polished surface of this piece from which samples C6 and C7 were taken is shown in Plate 1.

C8 to C10

Abee: black polymict brecciated, enstatite chondrite, fall, 1952, Alberta, Canada. 20 - 30 g piece obtained from J. A. V. Douglas, Geological Survey of Canada, Ottawa, Ontario. A polished surface of this piece is shown in Plate 2.

C11 to C13

Peace River: olivine-hypersthene chondrite, fall, 1963, Canada. 20 - 30 g piece obtained from J. A. V. Douglas, Geological Survey of Canada, Ottawa, Ontario. See Plate 3 for a picture of a polished surface of the piece.

Plate 3. Polished surface of Peace River

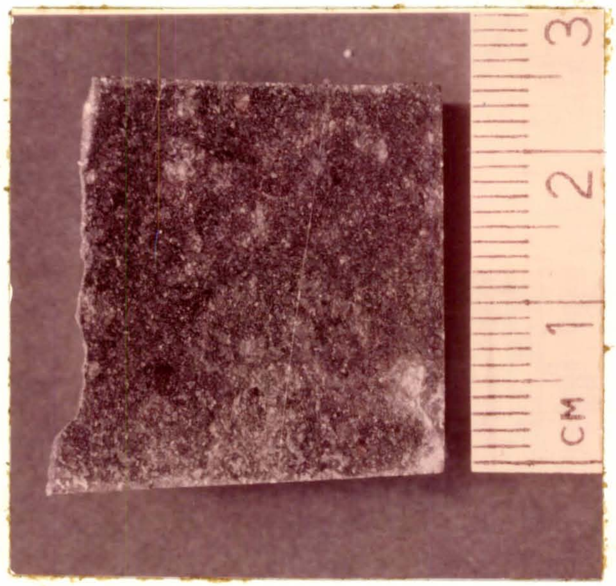

Plate 4. Polished surface of Vulcan

C14 to C17

Vulcan: olivine-hypersthene chondrite, fall, 1962, Canada. 20 - 30 g piece obtained from J. A. V. Douglas, Geological Survey of Canada, Ottawa, Ontario. Plate 4 is a picture of a polished surface of this piece.

C17

Gladstone: Black veined crystalline sphereical olivine-bronzite chondrite, find, 1936. Slightly oxidized. Although a find, the piece which was obtained from Jan Monster, McMaster University, looked fairly well preserved. The slice probably came from the interior of a big meteeorite. A polished surface of this slab is shown in Plate 5.

C18

Dimmitt: olivine-bronzite chondrite. Recognized as a distinct fall, 1950, Texas, U.S.A. Very slightly oxidized. 38.5 g slice obtained from the American Meteorite Laboratory. Plate 6 shows a picture of its polished surface.

Plate 5. Polished surface of Gladstone

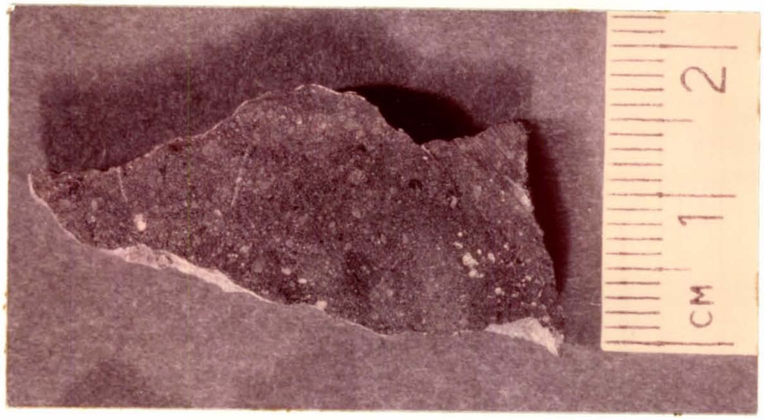

Plate 6. Polished surface of Dimmitt

3. IRON AND STONY-IRON METEORITES

F1

Madoc: fine-octahedrite iron, find, 1854, Hastings County, Ontario. A 20 - 30 g piece obtained from J. A. V. Douglas, Geological Survey of Canada. A picture of its polished and etched surface is shown in Plate 7.

F2

Skookum: Ni-rich ataxite iron meteorite, find, 1905, Canada. 20 - 30 g obtained from J. A. V. Douglas, Geological Survey of Canada, Ottawa, Ontario. A polished and etched surface is shown in Plate 8.

F3

Toluca (Xiquipilco): medium octahedrite iron meteorite, find, 1776, Mexico. Obtained from Jan Monster, McMaster University. Plate 9 shows a polished and etched surface of the specimen weighing about 15 g.

F4

Odessa: coarse octahedrite iron meteorite, find, before 1922, Ector County, Texas, U.S.A. A 40 g rough specimen obtained from the American Meteorite Laboratory.

F5

Canyon Diablo: coarse octahedrite iron meteorite, find, 1891, Arizona, U.S.A. A large piece weighing about 500 g was obtained

Plate 7. Polished and etched surface of Madoc

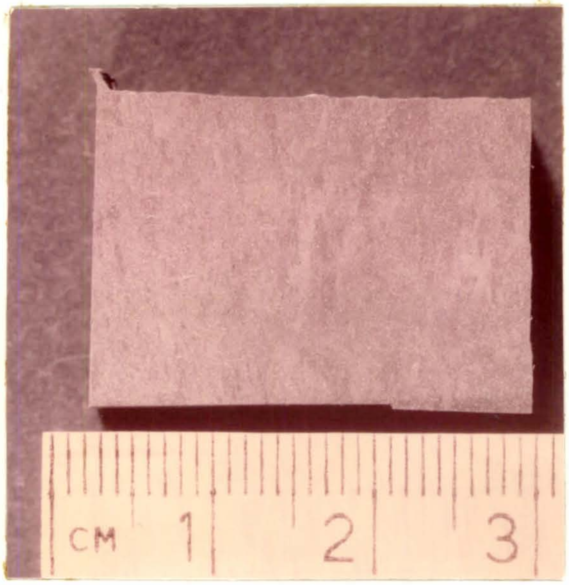

Plate 8. Polished and etched surface of Skookum

Plate 9. Polished and etched surface of Toluca (Xiquipilco)

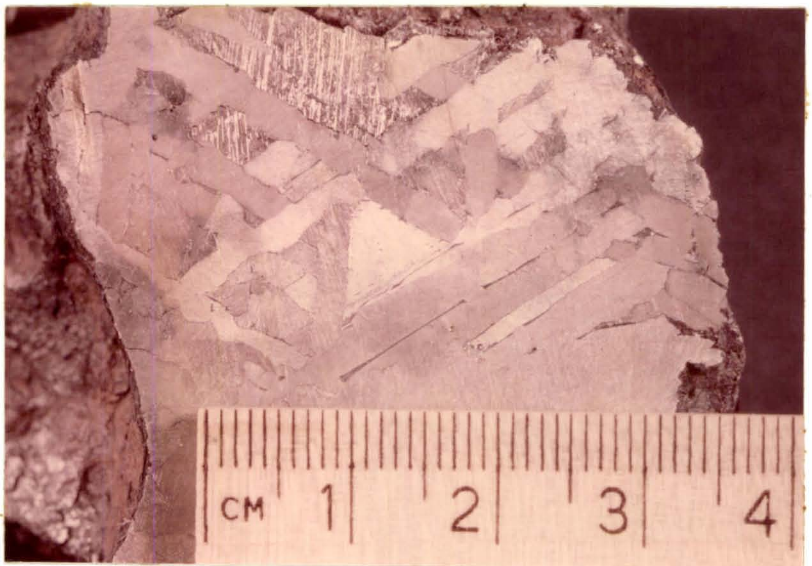

Plate 10. Polished and etched surface of Canyon Diablo

from Jan Monster, McMaster University. It was procured from the American Meteorite Laboratory. The polished and etched surface shown in Plate 10 does not include the portion analyzed since the sample was selected before the picture was taken.

F6, F7

Canyon Diablo: Silicate phase. Nodule containing a great deal of FeS and some of the iron phase. The specimen which was unoxidized was obtained from W. B. Clarke, McMaster University, Canada.

F8, F9

Bondoc: mesosiderite, stony-iron meteorite, find, 1959, Philippine Islands. A 34.1 g fragment, which was slightly oxidized, was obtained from the American Meteorite Laboratory.

F10, F11

Dalgaranga: rough pit specimen, find, 1923, Western Australia. A 36 g of badly oxidized and weathered specimen was obtained from the American Meteorite Laboratory.

4. TEKTITES

T1, T2

Indochinite tektite (Dalat, South Vietnam): Original weight 44 g. Part of the specimen which was obtained from the American Meteorite Laboratory is shown in Plate 11. On the right and at the bottom of the picture it can be seen that pieces have been broken off.

T3, T4

Indochinite Tektite (Northeast Thailand): A 20.5 g specimen obtained from the American Meteorite Laboratory is shown in Plate 12.

T5, T6

Bediasite Tektite (Sommerville, Texas): A 25 g specimen obtained from the American Meteorite Laboratory is shown in Plate 13.

T7, T8

Rizalite tektite (Bugad, Luzon): In Plate 14 is shown the 14.9 g specimen obtained from the American Meteorite Laboratory.

Plate 11. Piece of Indochinite (Dalat, South Vietnam)

Plate 12. Indochinite (Northeast Thailand)

Plate 13. Bediasite (Sommerville, Texas)

Plate 14. Rizalite (Bugad, Luzon)

5. TERRESTRIAL ROCKS AND MINERALS

M1, M2

Beryl: Obtained from the Department of Geology, McMaster University. Origin unknown.

M3 to M5

Hawaiian Basalt (Oahu Island): Obtained from the Department of Geology, McMaster University. Reported boron content is 3.26 ppm (Table 19).

M6, M7

Quartz: Ordinary quartz tubing obtained from the General Electric Company, U.S.A. According to General Electric the boron content is 0.6 ppm.

M8

Porcelain: From ordinary porcelain pestle procured from Fisher Scientific, Canada.

M9

Slate (Shale) Littleton Quadrangle, New Hampshire: Obtained from the Department of Geology, McMaster University. Published boron content: 105 ppm, by emission spectroscopy (Shaw and Bugry 1966, Sample L10, Table III).

M10

Calcareous kimberlite. Swartruggens fissure Nooitgedacht 381 Swartruggens District, Transvaal, South Africa.

Obtained from the Department of Geology, McMaster University. The results of the boron content and isotopic ratio should be compared with those of Siberian kimberlite.

M11

Finland Tourmaline 1. Ylöjärvi, Finland. Raw material. Made available by Olavi Kouvo, Outokumpu, Finland.

M12

Finland Tourmaline 2. Ylöjärvi, Finland. Purified tourmaline. Made available by Olavi Kouvo, Outokumpu, Finland.

M13

Finland Tourmaline 3. Tourmaline granite. Kiihtelysvaara, Finland. Raw material made available by Olavi Kouvo, Outokumpu, Finland.

6. SEA WATER

E1 to E3

Pacific Ocean sea water (1). Surface water 100 miles off the coast of Central Mexico, between San Diego and the Panama Canal. Collected on October 27, 1960 by R. N. Spencer and V. Baird. It contained a little mercury bromide which had been added for sulphur work. Made available for this work by Jan Monster, McMaster University.

TABLE 19

BORON IN BASALT (Shima, 1963)

Sample	B (ppm)	B^{11}/B^{10}
Hawaiian	3.26	4.051 ± 0.02
Mohole	4.22	4.042 ± 0.06

TABLE 20

BORON IN SIBERIAN KIMBERLITE (Cherepanov, 1966)

Sample	B content (ppm)	B^{11}/B^{10}
$A_2B_2C_2$	31	4.119
$A_1B_1C_1$	125	4.107
$A_1B_2C_1$	595	4.120

E4

Arctic Ocean (Resolute Bay). Sample diluted very slightly by ice. Obtained from Jan Monster, McMaster University.

E5

Pacific Ocean sea water (2). A sample collected off the coast of Peru.

E6

Pacific Ocean sea water (3). Surface unfiltered sample - latitude 43°, 16'S; longitude 113°, 48°W. Sample provided by Prof. Karl Turekian, Department of Geology, Yale University, New Hampshire.

E7

Atlantic Ocean sea water: depth 70 m, unfiltered, latitude 60°, 8'S; longitude 14° 49'W. Sample made available by Prof. Karl Turekian, Department of Geology, Yale University, New Hampshire.

7. CLAY EXPERIMENT SAMPLES

P1

Synthetic sea water plus 100 ppm of boron. Boric acid obtained from the McArthur Chemical Co. Ltd., Montreal (Shawinigan Lot No. F7 4766G2). The synthetic sea water originally contained about 1 ppm boron. See Chapter 2, Section 3 (e), (v).

P2

Synthetic sea water: supernatant of clay-sea water mixture. Original boron content of illite clay 200 ± 10 ppm. See Chapter 2, Section 3 (c), (v).

P3

Same as P2, except that the clay to sea water ratio is slightly different. See Chapter 2, Section 3 (c), (v).

BIBLIOGRAPHY

Agyei, E. K. (1965) A study of the isotopic abundance of boron in minerals. M.Sc. Thesis (Physics), McMaster University, Hamilton, Ontario.

Agyei, E. K. and McMullen, C. C. (1968) A study of the isotopic abundance of boron from various sources. Can. J. Earth Sci., 5, pp 921-927.

Ahrens, L. H. and Fleischer, M. (1960) Report on trace constituents in granite G-1 and diabase W-1. U. S. Geol. Surv. Bull, 1113, pp 83-111.

Ahrens, L. H. (1965) Distribution of the elements in our planet. McGraw-Hill Book Company, 110 pp.

Archibald, E. H. (1932) Preparation of pure inorganic substances. John Wiley and Sons Inc., N.Y., Chapman and Hall Ltd., Lond., pp 155-157.

Aston, F. W. (1920) The mass spectra of chemical elements, (part II). Phil. Mag., 40, pp 628-643.

Aston, F. W. (1931) The isotopic constitution and atomic weights of selenium, bromine, boron, tungsten, antimony, osmium, ruthenium, tellerium, germanium, rhenium and chlorine. Proc. Roy. Soc., Ser. A., 132, pp 487-498.

Bentley, P. G. (1960) Isotopic analysis of boron in BF_3 by mass spectrometry and measurement of natural B^{10} concentration. J. Sci. Instrum., 37, No. 9 pp 323-328.

Bentley, P. G. and Hamer, A. N. (1958) The preparation of boron isotopic standards. UKAEA Industrial Group Technical Note No. IGR-TN/CA-850, 13pp.

Bernas, R., Gradsztajn, E., Reeves, H. and Schatzman, E. (1967) On the nucleosynthesis of lithium, beryllium and boron. Ann. Phys., 44, pp 426-478.

Bethe, H. A. (1939) Energy production in stars. Phys. Rev. 55, pp 103, 434-456.

Brown, R. and Wolstenholme, W. A. (1964) Analysis of geological samples by spark source mass spectrometer. Nature (London) 201, p 598.

Burbidge, E. M., Burbidge, G. R., Fowler, W. A., and Hoyle, F. (1957) Synthesis of the elements in stars. Rev. Mod. Phys. 29, No. 4, pp 547-650.

Burnett, D. S., Fowler, W. A. and Hoyle, F. (1965) Nucleosynthesis in the early history of the solar system. Geochim. Cosmochim. Acta 29, pp 1200-1241.

Callicoat, D. L. and Wolszon, J. D. (1959) Separation of microgram quantities of boron by mixed resin bed ion exchange. Anal. Chem. 31, No. 8, pp 1437-1439.

Clark, M. C. and Swaine, D. J. (1962) The contents of several trace elements in the standard rocks G-1 and W-1. Geochim. Cosmochim. Acta 26, pp 511-517.

Cherepanov, V. A. (1967) Boron in the kimberlite and meimechite of Siberia. Dokl. Acad. Nauk SSR 172, No. 3, pp 696-699.

Chodos, A. A. (1957) Cal. Inst. Tech. written communication with Ahren and Fleischer (1960).

De Bièvre, P. J. and Debus, G. H. (1965a) Precision mass spectrometric isotope dilution analysis. Nucl. Instrum. Methods 32, pp 224-228.

De Bièvre, P. J. and Debus G. H. (1965b) Optimal conditions for mass spectrometric quantitative determinations by isotope dilution. EAEC Report EUR 2219.e, 42pp.

Dews, J. R. (1966) The isotopic composition of lithium in chondrules. J. Geophy. Res. 71, No. 16, pp 4011-4020.

Dible, W. T., Truog, Emil and Berger, K. C. (1954) Boron determination in soils and plants. Simplified procedure. Anal. Chem. 26, No. 2, pp 418-421.

Dole, M. (1936) The relative atomic weight of oxygen in water and in air. II. A note on the relative atomic weight of oxygen in fresh water, salt water and atmospheric water vapor. J. Chem. Phys. 4, pp 778-780.

Dole, M. and Jenks, G. (1944) Isotopic composition of photosynthetic oxygen. Science 100, p 409.

Dole, M. and Slobod, R. L. (1940) Isotopic composition of oxygen in carbonate rocks and iron ores. J. Amer. Chem. Soc. 62, pp 470-479.

Elliott, A. (1930) Determination of the abundance ratio of isotopes from band spectra. Nature 126, pp 845-846.

Elliott, A. (1931) Determination of the isotope ratio from intensity measurements of boron monoxide spectrum. Z. Phys. 67, pp 75-88.

Eugster, H. P. (1954) Quoted by Ahrens, L. H. (1954) Quantitative spectrochemical analysis of silicates. Pergamon Press (London), pp 20-38.

Everling, F., König, L. A., Mattauch, J. H. E. and Wapstra, A. H. (1960) Relative nuclidic masses. Nucl. Phys. 18, No. 4, pp 529-569.

Finley, H. O., Eberle, A. R. and Rodden C. J. (1962) Isotopic boron composition of certain boron minerals. Geochim. Cosmochim. Acta 26, pp 911-914.

Fireman, E. L. and Schwarzer, D. (1957) Measurement of Li^6, He^3 and H^3 in meteorites in relation to cosmic radiation. Geochim. Cosmochim. Acta 11, pp 252-262.

Fleet, M. E. L. (1965) Preliminary investigations into the sorption of boron by clay minerals. Clay Minerals 6, pp 3-16.

Fleischer, M. (1965) Summary of new data on rock samples G-1 and W-1, 1962-1965. Geochim. Cosmochim. Acta 29, pp 1263-1283.

Fleischer, M. and Stevens, R. E. (1962) Summary of new data on rock samples G-1 and W-1. Geochim. Cosmochim. Acta 26, pp 525-543.

Fowler, W. A., Burbidge, G. R. and Burbidge, E. M. (1955) Nuclear reactions and element synthesis in the surface of stars. Ap. J. Suppl. 2, pp 167-194.

Fowler, W. A., Cook, C. W., Lauritsen, C. C., Lauritsen, T. and Mozer, F. (1956) Alpha radioactivity of C^{12} and the stellar process $3He^4 \longrightarrow C^{12*}$. Bull. Amer. Phys. Soc. 1, pp 191-192.

Fowler, W. A., Greenstein, J. L. and Hoyle, F. (1962) Nucleosynthesis during the early history of the solar system. Geophys. J. 6, pp 148-220.

Goldschmidt, V. M. and Peters, C (1932) Zur Geochemie des Bors. Nachr. Ges Wiss. Göttingen Math.-Physik Kl., pp 377-401.

Goris, P., Morgan, T. D. and Nielson, R. A. (1961) Comparative boron isotopic analysis. USAEC Report IDO-145-49, 9 pp.

Govindaraju, K. (1961) Emploi de l'excitation en atmosphere controlec (CO_2) pur le dosage spectrographique des elements des traces dans les silicates et carbonates naturels. Presented in C. R. 9th Colloq. Spectrosc. Int., Lyon, 10 June, 1961.

Hahn-Weiheimer, P. (1959) Univ. at Frankfurt, Germany. Written communication with Ahrens and Fleischer (1960).

Hall, W. L. (1958) The Texas Co., Bellaire, Texas, written communication with Ahrens and Fleischer (1960).

Harder, H. (1959) Univ. Göttingen, Germany. Geochemistry of boron. 1. Boron in minerals and igneous rocks. 11. Boron in sediments. Nachr. Akad. Wiss Göttingen 11. Math.-Physik Kl. No. 5, pp 67-122, No. 6, pp 123-183.

Harder, H. (1961) Eibau von Bor in detritische tonminerale. Geochim. Cosmochim. Acta 21, pp 284-294.

Hillebrand, W. R. and Lundell, G. E. F. (1955) Applied inorganic analysis. 2nd Ed. 2nd printing, John Wiley and Sons Inc., N.Y., pp 749-761.

Hoyle, F. (1954) On nuclear reactions occurring in very hot stars. 1. The synthesis of elements from carbon to nickel. Ap. J., Supp. 1, pp 121-146.

Hoyle, F. (1960) On the origin of the solar nebula. Quart. J. R. Astron. Soc. 1, pp 28-55.

Inghram, M. G. (1946) Isotopic constitution of tungsten, silicon and boron. Phys. Rev. 70, pp 653-660.

Krankowsky, D. and Müller, O. (1964) Isotopenhäufigkeit und Konzentration des Lithium in Steinmeteoriten. Geochim. Cosmochim. Acta 28, pp 1625-1630.

Krankowsky, D. and Müller, O. (1967) Isotopic composition and abundance of lithium in meteoritic matter. Geochim. Cosmochim. Acta 31, pp 1833-1842.

Lerman, A. (1966) Boron in clays and estimation of paleosalinities. Sedimentology 6, pp 267-286.

Martin, J. R. and Hayes, J. R. (1952) Application of ion exchange to determination of boron. Anal. Chem. 24, No. 1, pp 182-185.

Mason, B. (1962) Meteorites. John Wiley and Sons Inc., N.Y., 274pp.

McBurney, T. C. (1956) Smith-Emery Co., Los Angeles, California. Written communication with Ahrens and Fleischer (1960).

McMullen, C. C., Cragg, C. B. and Thode, H. G. (1961) Absolute ratio of B^{11}/B^{10} in Searles Lake borax. Geochim. Cosmochim. Acta 23, pp 147-149.

Mills, A. A. (1966) The separation and determination of boron in meteorites and tektites. Proc. Soc. Anal. Chem. 3, pp 161-162.

Murata, K. J. (1951) U.S. Geol. Survey. Quoted by Ahrens (1951) Spectrochemical analysis of some of the rarer elements in granite and diabase samples. U.S. Geol. Survey Bull. 980, part 4, pp 53-57.

Nier, A. O. and Gulbransen, E. A. (1939) Variations in the relative abundance of the carbon isotopes. J. Amer. Chem. Soc. 61, pp 697-698.

Nier, A. O. and Murphy, B. F. (1941) Variations in the relative abundance of the carbon isotopes. Phys. Rev. 59, pp 771-772.

Ordzhonikidze, K. (1960) Relative abundance of lithium isotopes in uranium minerals and meteorites. Geokhimiya No. 1, pp 37-44 (in Russian).

Parwel, A., Ubisch, H. V. and Wickman, F. E. (1956) On the variations in the relative abundance of boron isotopes in nature. Geochim. Cosmochim. Acta 10, pp 185-190.

Paton, R. F. and Almy, G. M. (1931) Boron hydride bands. Phys. Rev. 37, p 1710.

Pavlenko, L. I. and Popova, V. S. (1964) Spectrographic determination of tin, lead and boron in silicate rocks and minerals. Zavodskaya Lab. 30, pp 669-702 (in Russian).

Preuss, E. (1935) Specktralanalytische Untersuchung der Tektite. Chem. Erde 9, pp 365-418.

Poschenrieder, W. P., Herzog, R. F. and Barrington, A. E. (1965) The relative abundance of the lithium isotopes in the Holbrook meteorite. Geochim. Cosmochim. Acta 29, pp 1193-1195.

Salpeter, E. E. (1956) Nuclear reactions in stars without hydrogen. Ap. J. 115, pp 326-328.

Shaw, D. M., Filby, R. H., Siroonian, H. and Yip, C. (1958) McMaster University, Hamilton, Ontario. Written communication with Ahrens and Fleischer (1960).

Shaw, D. M. and Bugry, R. A. (1966) A review of boron sedimentary geochemistry in relation to new analyses of some North American shales. Can. J. Earth Sci. 3, pp 49-63.

Shergina, Yu. P. and Kaminskaya, A. B. (1963) Isotope composition of boron in nature. (All-Union Sci.-Res., Inst. Geological Prospecting, Leningrad). Geokhimiya No. 8, pp 725-731.

Shima, M. (1962) Boron in meteorites. J. of Geophy. Res. 67, No. 11, pp 4521-4523.

Shima, M. (1963) Geochemical study of boron isotopes. Geochim. Cosmochim. Acta 27, pp 911-913.

Shima, M. and Honda, M. (1963) Isotopic abudance of meteoritic lithium. J. Geophys. Res. 68, No.9 , pp 2849-2854.

Spicer, G. S. and Strickland, J. D. H. (1958a) The determination of microgram and sub-microgram amounts of boron. Part 1. Absorptiometric determination using curcumin. Anal. Chim. Acta 18, pp 231-239.

Spicer, G. S. and Strickland, J. D. H. (1958b) The determination of microgram and sub-microgram amounts of boron. Part 11. The separation of boron by distillation and the evaporation of distillates. Anal. Chim. Acta 18, pp 523-533.

Taylor, S. R. and Sachs, M. (1960) Trace elements in australites. Nature 188, pp 387-388.

Taylor, S. R. and Koble, P. (1964) Geochemical standards. Geochim. Cosmochim. Acta 28, pp 447-457.

Thode, H. G., Macnamara, J., Lossing, F. P. and Collins, C. B. (1948) Natural variations in isotopic content of boron and its chemical atomic weight. J. Amer. Chem. Soc. 70, pp 3008-3011.

Thode, H. G., Macnamara, J. and Collins, C. B. (1949) Natural variations in the isotopic content of sulfur and their significance. Can. J. Res. 27B, pp 361-373.

Urey, H. C. and Rittenberg, D. (1933) Some thermodynamic properties of H^1H^2 and H^2H^2 molecules and compounds containing the H^2 atom. J. Chem. Phys. 1, pp 137-143.

Urey, H. C. and Greiff, L. J. (1935) Isotope exchange equilibria. Amer. Chem. Soc. 57, pp 321-327.

Urey, H. C. (1953) The concentration of certain elements at the earth's surface. Proc. Roy. Soc., Ser. A (London) 219, pp 281-292.

Vilscek, E. (1959) Der Meteorit von Breitscheid. 11. Chemische Analyse. Geochim. Cosmochim. Acta 17, pp 320-322.

Vogel, I. A. (1963) A text book of quantitative inorganic analysis, including elementary instrumental analysis. J. Wiley and Sons Inc., Third Ed. (new impression), pp 738-837.

Von Weizsäcker, C. F. (1938) Transformation of elements in the interior of stars. II. Z. Physik 39, pp 633-645.

Weber, L. A., Wahl, M. H. and Urey, H. C. (1935) The fractionation of oxygen isotopes in an exchange reaction. J. Chem. Phys. 3, p 129.

Whitehouse, W. J. and Pontecorvo, B. (1948) Private communication with Thode (1948).

Wiederkehr, V. R. and Goward, G. W. (1959) Separation of boron from alloys and other materials by pyrohydrolysis. Anal. Chem. 31, No. 12, pp 2102-2103.

Williams, J. P., Campbell, E.E. and Magliocca, T. S. (1959) Determination of boric acid in glass by pyrohydrolysis separation. Anal. Chem. 31, No. 9, pp 1560-1563.

Wolszon, J. D. and Hayes, J. R. (1957) Application of anion exchange resins to determination of boron. Anal. Chem. 29, No. 5, pp 829-832.

Yiou, F., Baril, M. Dufaure des Citre, J., Fontes, P., Gradsztajn, E. and Bernas, R. (1968) Mass spectrometric measurement of lithium, beryllium and boron isotopes produced in ^{16}O by high-energy protons and some astrophysical implications. Phys. Rev. 166, No. 4, pp 968-974.