BORON COSMOCHEMISTRY

by

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BORON COSMOCHEMISTRY

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ABSTRACT

The efforts I made for the analysis of boron isotope composition in meteorites are first discussed. Alkali fusion followed by boron-selective anion exchange resin purification is not suitable for the analysis of silicate rocks because of precipitation in the sample solution and consequent loss of boron. An HF dissolution followed by cation exchange resin and anion exchange resin purification needs improvement to remove some interference elements. Mass spectrometry of boron converted to potassium borate has a standard deviation of 0.08% (2σ) which is acceptable for boron isotope analyses.

Thirty six fragments of meteorite falls, never touched by water or other possible sources of boron contamination were analyzed for B by prompt gamma-ray neutron activation analysis at McMaster University and at the U.S. National Institute of Standards and Technology. Boron concentrations are close to the sensitivity limit in both laboratories. Results between the two laboratories agree well, but with slight systematic differences attributable to blank and background correction factors.

The mean B concentrations in different meteorites are similar, from 0.5 to 0.9 ppm, and the ranges in different carbonaceous chondrite (CC), ordinary chondrite (OC) and achondrite (ACH) classes overlap, mostly from 0.3 to 1.4 ppm. similar to previous measurements on falls. H, L and LL ordinary chondrites overlap in B content with Antarctic chondrites.

The solar system abundance, taken as the mean B content of the matrix in all carbonaceous chondrites was calculated from seven samples and is 0.69 ± 0.09 ppm. When normalized, this abundance is 16.9 ± 2.2 (atoms/10^6Si). Normalized B and S concentrations show a linear relationship in the CC; the average OC lies on the same line, but individual OCs are dispersed.

This solar system abundance supports a nucleosynthesis model, in which boron was formed by continual bombardment of interstellar medium (ISM) by the galactic cosmic rays (GCRs), to which a very intense low energy is added.

The Si and CI meteorite normalized abundances of moderately volatile and low-refractory elements in carbonaceous chondrites show a linear correlation with their condensation temperatures. Compared with other elements, the normalized boron abundances in CM, CO, and CV meteorites indicate that the boron condensation temperature is about 910 °K, similar to gallium.

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CHAPTER 1. INTRODUCTION

Boron is one of the light elements which are destroyed in the stellar hydrogen-burning reactions. Its abundance in primitive meteorite types is therefore of particular interest. In addition, boron is a moderately volatile element, whose cosmochemical behavior in condensation processes of the nebula is important.

The study of boron isotope ratios in meteorites is of interest to geochemists for a number of reasons. Boron, being a light element, has a proportionately high mass difference between its two naturally occurring isotopes at masses 10 and 11. Boron is known as a moderately volatile element in the condensation process, thus isotopic fractionation may occur in meteorites. Little is known, however, about boron isotope ratios in extraterrestrial samples. The only two analyses of boron isotope ratios in meteorites by thermal ionization mass-spectrometry gave different results. Shima (1962, 1963) found that chondrites are rich in ^{10}B and δ^{11}B ranges from -36 to -58. Agyei and McMullen (1978) found that δ^{11}B for chondrites ranges from -8.2 to +2.2.

There were few reliable data on the concentration of B in meteorites before the work of D. Curtis (see later), primarily due to the analytical difficulties and terrestrial contamination. Matrix effects and difficulties with line resolution hampered optical emission spectrographic (OES) analysis, and the element does not lend itself to instrumental neutron-activation analysis (INAA) because of the short half-life. Several analyses using different methods were published, but the results now appear high. For example, Harder (1961) observed 5.0, 5.0 and 3.5 ppm (OES) in CI, H, L, chondrites respectively. Mills (1968) employed a colorimetric method and reported 5.7 ppm in CI meteorites. Quijano-Rio and Wänke (1969) used a fluorimetric technique and found 9.4 ppm for CM and 7.2 ppm for CO and CV meteorites. In the 1980s, a more sensitive method, prompt gamma-ray neutron activation analysis (PGNAA), was applied, the terrestrial contaminations were taken seriously and the first reliable results were obtained by D. Curtis and collaborators (Curtis et al., 1980). After that, Curtis and Gladney (1985) and Shaw et al. (1988 a, 1988 b) studied boron in meteorites using PGNAA, ion probe and alpha-track images (ATI), published boron contents in clean samples of nineteen falls and thirteen Antarctic meteorites, calculated the boron solar system abundance, and discussed boron condensation temperatures.

It has been recognized since the mid-1950's that light elements are characterized by fairly weak nuclear stability and that during the normal course of thermonucleosynthesis they are not formed (Burbidge et al. 1957). Fowler et al. (1955) first suggested non-thermonuclear spallation reactions as the mechanism of nucleosynthesis for light elements. This suggestion was followed by a number of papers in which the possible reactions were considered in detail with a reliance on experimental data. However the establishment of detailed procedure and mathematical model needs reliable solar system abundances of light elements. The big difference of boron solar system abundances calculated from meteorites by different authors and the difference between the boron abundances measured from solar photosphere and meteorites made astrophysicists hesitate (Reeves 1971, Walker at al. 1985).

Condensation temperature is an important parameter for solar system cosmochemistry. Boron condensation is not well understood because of the lack of accurate thermodynamic data and knowledge of boron behavior. Cameron et al. (1973) estimated a condensation temperature T_c=750°K for boron at a nebular pressure of 10^{-3}atm. Curtis and Gladney (1985) calculated depletion factors for different types of chondrites (the degree of depletion of the silicon-normalized abundances of elements relative to CI carbonaceous chondrites, called Si and CI normalized abundance in this work); they concluded that the depletion factors for boron in chondritic subgroups correlate with sulphur, and this correlation indicates that boron, like sulfur, is a moderately volatile element with a condensation temperature between 400 and 900°K.

This dissertation introduces the effort I made to analyze boron isotopes in meteorites, presents thirty six new analyses for boron concentrations in interior fragments of meteoritical falls, of which seven are achondrites, few of which have previously been analyzed. This work also presents a revised boron solar system abundance, investigates further the relationship of boron and sulphur, discusses its nucleosynthesis and estimates its condensation temperature.

CHAPTER 2. SAMPLE PREPARATION

We requested from participating museum curators interior parts of chosen falls, never touched by water or any other possible sources of boron contamination. Thirty six were obtained from six museums (Table 1). This work would not have been possible without the kindness of the following Curators: R.S. Clarke Jr. and G. MacPherson, National Museum Smithsonian Institution, Washington D.C.; R.K. Herd, Geological Survey of Canada, Ottawa; C.B. Moore, Center for Meteorite Studies, Arizona State University, Tempe; E.J. Olsen, Field Museum of Natural History, Chicago; P. Pellas and B. Zanda, Muséum national d'histoire naturelle, Paris and X. Hua, China University of Geoscience, Wuhan.

In terms of sample appearance, the meteorites can be grouped in three categories:

1. fusion crust over the entire specimen;
2. interior part with crushed surface;
3. interior part with sawn surface.

All samples were trimmed in a clean room by a steel

chisel on a small steel anvil. The thickness trimmed was at least 1.0 mm for melted surfaces or 0.5 mm for other surfaces. Then, the interior parts were crushed in a small steel mortar and pestle until the diameter of the largest parts was smaller than 3 mm. Finally, samples were sealed in bags made of thin Teflon sheet and stored in polypropylene tubes.

Table 1. Meteorite falls

No.	Sample Name	Source	Source Number	Type	Sample Categ.#
1	IVUNA	USNM	USNM6631	CI1	2
2	ORGUEIL		No. 234,251	CI1	2
3	COLD BOKKEVELD	MNHN	290	CM2	3
4	MURCHISON*	FMNH	Me 2752	CM2	1
5	ALLENDE	USNM	USNM 3638	CV3	1
6	MOKOIA	ASU	75.1	CV3	2
7	WESTON	ASU	238sb	H4	2
8	PANTAR	ASU	503.3	H5	2
9	RICHARDTON	ASU	100h	H5	2
10	DRESDEN	GSC	0408-1	H6	3
11	NULLES	ASU	783	H6	2
12	BJURBOLE	FMNH		L4	2
13	SARATOV	ASU	740	L4	2
14	FARMINGTON	FMNH	Me 346	L5	3
15	KNYAHINYA*	FMNH	Me 1823	L5	2
16	BRUDERHEIM	GSC	0220-8	L6	1
17	HOLBROOK	FMNH	Me 801	L6	1
18	L'AIGLE	MNHN	15	L6	3
19	LEEDEY	ASU	489.1	L6	2
20	MOCS	FMNH	Me1447	L6	1
21	MODOC	FMNH	Me744	L6	2
22	PEACE RIVER	GSC	1611-2	L6	2
23	SUIZHOU	CUG		L6	3
24	PARNALLEE	ASU	93sb	LL3	2
25	INNIS FREE	GSC	0906-6	LL5	2
26	ST. SEVERIN	MNHN	2879D	LL6	3
27	ABEE	GSC	0117-9	E4	2
28	INDARCH	FMNH	Me 1404	E4	3
29	HVITTIS	FMNH	Me 578	E6	3
30	BISHOPVILLE	ASU	212s	AUB	2
31	NORTON COUNTY	ASU	523.3x	AUB	2
32	TATAHOUINE	FMNH	Me 2651	DIOG	2
33	JUVINAS*	FMNH		EUC	2
	JUVINAS*	MNHN			3
34	SERRA DE MAGE	MNHN	1606	EUC	3
35	SIOUX COUNTY	ASU	198.3	EUC	2
36	STANNERN*	FMNH		EUC	2
	STANNERN*	MNHN			3

ASU: Arizona State University.
CUG: China University of Geoscience.
FMNH: Field Museum of Natural History, Chicago.
GSC: Geological Survey of Canada
MNHN: Museum National d'Histoire Naturelle.
USNM: US National Museum, Smithsonian Instirutian.
\# Sample category:
1: Fusion crust over entire specimen.
2: Interior part with crushed surface.
3: Interior part with sawn surface.
* Two pieces of one meteorite from two sources

CHAPTER 3. ANALYSIS OF BORON ISOTOPES IN METEORITES

3.1. Introduction

Study of boron isotope geochemistry in meteorites has been severely limited by the difficulty of analysis. Compared with most terrestrial rocks, meteorites contain less boron: the average is about 0.7 ppm (calculated from table 7), but in the continental crust is about 10 ppm (Taylor 1964). Therefore it is necessary to have a high-precision analytical method, which is highly sensitive, needs only a small amount of sample and has a low blank. I have tried to determine the boron isotope composition in meteorites, but I did not get enough reliable data. The following sections of this chapter describe the effort I have made to find a method to analyze boron isotopes in meteorites, and the problems encountered.

The analysis procedure is composed of two parts: first, to dissolve the meteorite sample, to recover boron from that solution and to purify it; second, to determine the isotope ratio by the thermal ionization mass spectrometer.

Two methods have been tried to dissolve rock samples and to purify boron: the first is alkali fusion, followed by boron-selective anion exchange resin purification; the second is HF dissolution, followed by cation exchange and anion exchange resins purification.

In order to reduce the contamination in the chemical procedure, some reagents were cleaned before analysis. The preparation of these reagents is set out in Appendix 1.

3.2. Alkali fusion with boron-selective anion exchange resin purification

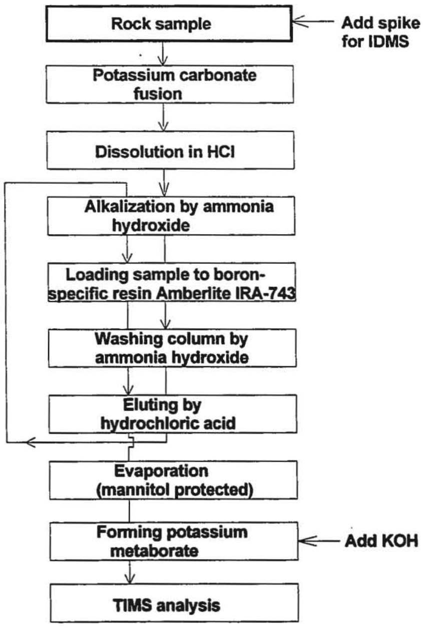
This method was modified from Kiss (1988). The rock samples and spike for isotope dilution mass spectrometry (IDMS) were mixed with potassium carbonate and fused in a platinum crucible. In the beginning of these experiments, pure nickel crucible and super pure K_2CO_3 (Johnson & Matthew and Aldrich) were used for the alkali fusion, but later, it was found that these two materials cause serious boron contamination. The use of a platinum crucible and analytical grade K_2CO_3 (B.D.H.) give less contamination. Isotope dilution mass speccrometer analyses show that the super pure K_2CO_3 of Johnson & Matthew Comp. contains 0.4 ppm boron, the super pure K_2CO_3 of Aldrich Comp. contains 0.6 ppm boron, but the analytical grade K_2CO_3 of B.D.H. Comp. has no detectible boron.

The fusion cake was dissolved in 2M HCl, and alkalized to pH=10 by NH_4OH. This solution was put through the boron-selective ion exchange resin twice. Then mannitol was added to the final eluate and dried. The purpose of mannitol is to protect boron, because in water or acid solution, boron may be lost when the solution is heated to dryness. KOH solution was added to form dipotassium metaborate for analysis by mass spectrometry. The simplified procedure is showed in a flow diagram in Fig. 1. and the detailed procedure is given in Appendix 2.

The major problem for this method is that after the dissolution of the fusion cake in the HCl, when the solution is changed from acid to alkali, some precipitation occurs, and more than 50% of the boron is coprecipitated and lost.

In the original method of Kiss (1988), the fusion cake was not dissolved in HCl, but in hot water. However it was found that the fusion cake does not all dissolve in the hot water; usually at least 20 per cent remains undissolved and about half of the boron stays in the solid phases. Also, the hot water solution is viscous and is rich in CO_3^{2-}, thus

Fig. 1. Flow diagram of alkali fusion with boron-selective anion exchange resin purification.



the ion exchange is difficult: some precipitation occurs and blocks the column when the solution is loaded, and CO_2 gas is generated and blocks the column when the column is leached by HCl.

However, if the boron in a sample can be transferred into an alkali solution (pH>9) without significant loss, and if this solution does not contain any CO_3^{-2} anions, the boron can be purified by a second boron-selective anion exchange resin. Boric acid solutions containing 0.5 to 2 μg of boron were treated with ammonia hydroxide and passed through the resin twice. Their isotope compositions were readily analyzed. The boron content in chemical K_2CO_3 was analyzed successfully in this manner.

The aforementioned experimental results show that although this method is not suitable for the boron isotope analysis in silicate rocks, it might be used to analyze boron isotopes in calcite, and the purification procedure using boron selective-resin can be adopted for the analysis of boron in water samples if there is no precipitate when NH_4OH is added.

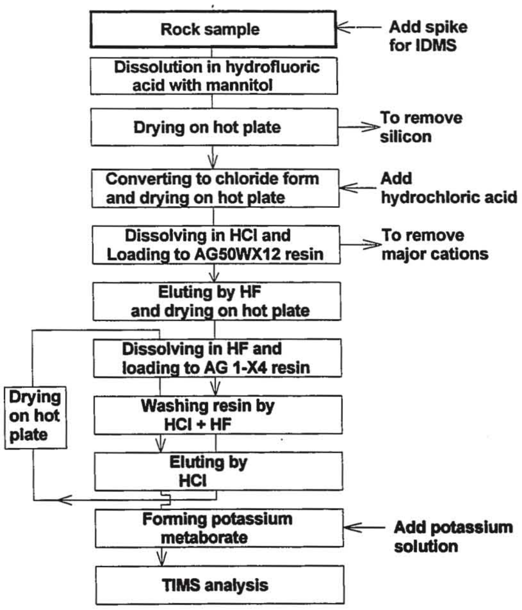
3.3. HF dissolution with cation exchange and anion exchange resins extraction

The second method was adopted from Nakamura et al. (1992), and is based on the fact that mannitol can totally suppress boron evaporation in water and acids (Ishikawa and Nakamura 1990). In this method, rock samples and the spike for IDMS are dissolved in HF and then evaporated to dryness with mannitol to remove most silicon. The residues are redissolved in acid and passed through a cation exchange column to remove most metal cations. Then the eluate is passed through an anion exchange column twice (Fig. 2). The detailed procedure is shown in Appendix 3.

This method is designed to avoid the problem of precipitation and takes place in acid solution. Although the procedure of Nakamura et al. (1992) was followed without any significant change, no measurable boron peaks were found in the mass spectrometry. I changed the concentration of HF for conditioning the anion exchange resin and in the first two sets of samples got some data on the TIMS (see appendix 5 for detail), but I could not repeat these results.

In order to find out the reason for this failure, I added some boric acid solution (up to 1.0 μg B) to the $K_2B_4O_7$

Fig. 2. Flow diagram of HF dissolution with cation exchange and anion exchange resins extraction.



solution just before the mass spectrometry, but I still could not get any results. This made me think that the reason for failure was not a loss of boron, but because the boron extract I got was not pure enough and some elements in the solution influenced the boron analysis. Therefore I took two rock samples through the whole chemical procedure; one went through the anion exchange resin only once, but the other went twice. The two final eluates were dried under the protection of mannitol and the dried materials were dissolved in HCl and analyzed using ICP-MS for several elements. The results are listed in Table 2 and show that much Ti still remains after anion exchange twice. Maybe Ti and/or some other elements in the sample solution hindered the boron analysis. Therefore further purification of the sample solution is necessary. For example, using boron-selective anion exchange resin as the last step may be helpful to remove the interference elements. I have tried to alkalize the sample solutions after anion exchange once or twice, there were still significant or visible precipitates respectively. Therefore my suggestion is to try to remove more Si before using the boron-selective resin to purify boron.

Table 2. ICP-MS test for element extraction by ion exchange

Element	Syenite 840714-3#		Grey wacke 830815-1##	
	Amount in sample* (µg)	Amount extracted** (µg)	Amount in sample* (µg)	Amount extracted** (µg)
Na	7520	0.64	10200	0.12
Mg	5500	0.26	8050	0.03
Al	26600	178	33500	0.54
Si	79000	160	132000	18
Ti	1130	972	1480	1060
Fe	13000	0.38	22900	0.3
Zr		29		29
W		372		60

* Element amount in the rock sample before HF dissolution.
** Element amount remaining in the eluate from the anion exchange column.
\# Anion exchange only once.
\#\# Anion exchange twice.

3.4. Mass spectrometry

A variety of techniques have been used to determine the isotopic composition of boron (Thode et al. 1948, McMullen et al. 1961, Braman 1963, Nomura et al. 1973, Oliver et al. 1976, Duchateau and DeBievre 1983, Cook et al. 1985, Ramakumar et al. 1985, Spivack and Edmond 1986, Duchateau et al. 1986, Gregoire 1987, Xiao et al. 1988, Nakamura et al. 1992). Most workers use the metaborate of either sodium ($Na_2B_4O_7$) or cesium ($Cs_2B_4O_7$), with or without graphite as an activator, with thermal ionization mass spectrometry (TIMS, Ishikawa and Nakamura 1989, Bassett 1990). The boron species analyzed in these two methods are the molecular ions $Na_2BO_2^+$ and $Cs_2BO_2^+$. Sodium and Cesium have only one isotope in nature, ^{23}Na and ^{133}Cs respectively (Hodgman et al. 1961); boron has two (^{10}B and ^{11}B) and oxygen is mainly ^{16}O. Thus the molecular weights for $Cs_2BO_2^+$ are 308 and 309, for $Na_2BO_2^+$ is 88 and 89. Because the Cs ions are much heavier than the Na ones, the Cs method has higher precision (Nomura et al. 1982, Spivack and Edmond 1986). Uncertainty (2σ) for the former is 0.012%, and for the latter is 0.2%. But the AW of Cs is close to Nd (143 and 144) and Sm (150 and 151), so the presence of Cs might raise the background and influence the Sm and Nd ion measurement. In our laboratory, because Rb, Sr, Sm, Nd and boron are analyzed on the same instrument, we must worry about these mass interferences. Rubidium is a possible substitute for cesium, but it would increase the blank for Rb and Sr. Potassium was chosen here: it has three stable isotopes: ^{39}K, ^{40}K and ^{41}K, their proportions are 93.08%, 0.012% and 6.91% respectively (Hodgman et al. 1961). The ion ratio analyzed here is molecular ion 121 (MI121) to molecular ion 120 (MI120). The ions at mass 121 are $^{39}K^{39}K^{11}B^{16}O^{16}O^+$, $^{40}K^{39}K^{10}B^{16}O^{16}O^+$ and $^{39}K^{39}K^{10}B^{16}O^{17}O^+$; the ions at mass 120 are $^{39}K^{39}K^{10}B^{16}O^{16}O^+$; the ions contain ^{41}K or ^{18}O must be heavier than 121. Thus only the corrections for ^{17}O and ^{40}K are necessary. Adopting Spivack and Edmond's (1986) method, the $^{11}B/^{10}B$ ratio can be calculated as follows:

$$(^{11}B/^{10}B)=(MI121/MI120)-(0.00079+0.00026)$$
$$=(MI121/MI120)-0.00105$$

where 0.00079 is for the oxygen isotope correction (Catanzaro et al. 1970), and 0.00026 is for potassium correction, calculated from the potassium isotope ratio:

$$(^{40}K/^{39}K)\times2=(0.012/93.08)\times2=0.00026$$

Boron isotopic compositions will be expressed as deviations in parts per thousand from a standard as follows (Nakamura et al. 1992):

$$\delta^{11}B\ (‰)=\{[(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{standard}]-1\}\times10^3$$

The isotope determinations were performed on a VG isomass 354 mass spectrometer, and the detailed procedure is given in appendix 4. The boron standard used for concentration and isotope determinations is National Bureau of Standards standard reference material (NBS SRM) 951, and the spike is NBS SRM 952. Both of them are boric acid, certified for total H_3BO_3, absolute abundance ratio $^{10}B/^{11}B$, ^{10}B and ^{11}B atom percent. NBS SRM 951 was repeatedly analyzed with varying sample sizes (0.1-1.0 μg) to determine the analytical precision. The measured $^{11}B/^{10}B$ ratios corrected for oxygen and potassium isotopes are given in Table 3 together with those of NBS SRM 952. Ten separate analyses of NBS SRM 951 gave a mean $^{11}B/^{10}B$ ratio of 4.050 ± 0.08% (2σ). It seems that the limit of analysis of boron could be as low as 0.1 μg of boron.

The average $^{11}B/^{10}B$ value obtained for NBS SRM 951 is slightly higher than the certified value of 4.04362 ± 0.00137 (Catanzaro et al. 1970) and those (4.045-4.046) obtained by using the $Cs_2BO_2^+$ method without graphite (Ramakumar et al. 1985, Spivack and Edmond 1986). But my $^{11}B/^{10}B$ ratio is quite similar to that obtained using $Cs_2BO_2^+$ with graphite, e.g. 4.0512 for Nakamura et al. (1992) and 4.05037 for Xiao et al. (1988). The higher ratios maybe due to adding graphite, thus in any case the measured ratio should be normalized by that of NBS SRM 951 ($^{11}B/^{10}B$ = 4.050), to remove this bias.

Table 3. Measured 11B/10B of NBS SRM 951 and 952*

No.	Sample size (B µg)	Mass 121/120	11B/10B	Standard deviation (2 sigma) (%)	S.D. for all measurement (2 sigma) (%)
NBS SRM 951 boric acid					
1	1	4.0501	4.0490	0.010	
2	2	4.0495	4.0484	0.036	
3	1	4.0517	4.0506	0.036	
4	1	4.0498	4.0488	0.022	
5	0.13	4.0533	4.0522	0.046	
6	0.26	4.0535	4.0525	0.012	
7	0.13	4.0499	4.0489	0.028	
8	0.1	4.0500	4.0489	0.020	
9	0.13	4.0533	4.0522	0.010	
10	0.5	4.0499	4.0489	0.036	
Average			4.0500		0.083
NBS SRM 952					
1	0.2	0.05430	0.05325	0.030	
2	0.2	0.05445	0.05340	0.026	
Average			0.05333		

* Using dipotassium metaborate method

The relative standard deviation of the potassium metaborate method for standard NBS SRM 951 measurement is 0.08%, which is lower than the sodium metaborate method (i.e. 0.2% for Agyei and McMullen 1978), but higher than the cesium metaborate method (i.e. 0.012% for Spivack and Edmond 1986). The potassium metaborate method is considered acceptable.

Boron isotope ratios obtained for silicate rock samples and meteorites in the only two sets of samples which were successfully analyzed, are listed in table 4. Generally speaking, the whole procedure for boron isotope analyses of meteorites is not successful, only five measurements in two sets of samples (three silicate samples in each set were analyzed) give reasonable results. In most case the boron peaks are too small to be analyzed or absent.

Table. 4 Boron isotope measurement

Sample Number	Sample	11B/10B	Boron content* (µg)	Measured boron** (µg)	Standard Deviation### (%)
6705#	Grey wacke***	0.83111	13.0	12.4	0.080
6707#	Grey wacke***	1.05699	8.3	8.0	0.076
6708#	Grey wacke***	0.88022	8.8	8.4	0.099
6903##	Grey wacke***	4.0043			0.014
6911##	Potter****	4.0442			0.015

* Known by PGNAA analysis.
** Measured using isotope dilution method.
*** Terrestrial rock sample.
**** Meteorite.
\# Measurement of B abundance using isotope dilution mass spectrometry.
\## Measurement of B isotope composition.
\### Two sigma.

CHAPTER 4. DETERMINATION OF BORON ABUNDANCE

4.1. Analytical method

Boron concentrations in our meteorite samples were analyzed in the McMaster Nuclear Reactor (MNR) of Canada and the National Institute of Standard and Technology (NIST) nuclear reactor of USA by PGNAA (Prompt Gamma-ray Neutron Activation Analyses) using the boron peak at 478 keV. PGNAA is a good method for trace boron analysis in rocks (Curtis et al., 1980) and the cold neutron beam of the nuclear reactor of NIST can provide a good test for the data analyzed in MNR. But for meteorite analysis, there is a special difficulty compared with the analysis of terrestrial rocks, which is the interference of nickel.

Fig. 3 shows typical PGNAA spectra of a standard terrestrial rock, a meteorite and a blank from MNR. Comparing the spectra of meteorites and terrestrial rocks, the nickel peak (465 keV) and the small peaks, 1, 2 and 3, made the measurement of background adjacent to the boron peak difficult in meteorite spectra. But the measurement of

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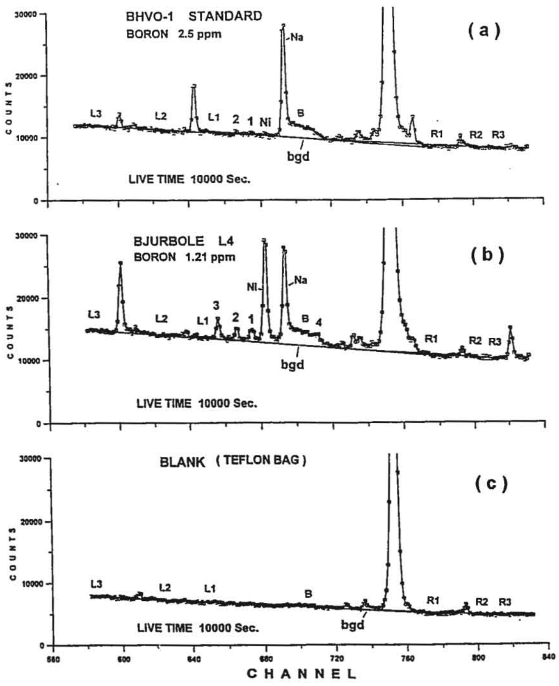


Fig. 3. PGNAA spectra of a standard (a), a meteorite (b) and a blank (c) from MNR. The solid squares represent the channels of backgrounds and the boron peak; 1, 2 and 3 are small peaks; peak 4 is cobalt. L1, L2 and L3 are three chosen left backgrounds of boron peak; R1, R2 and R3 are three chosen right backgrounds. The straight lines, L1-R1, L2-R2 and L3-R3, marked by bgd, were used to calculate the background underneath the boron peak. The vertical scale is total counts.

background seriously influences the precision and accuracy of the analysis of small amounts of boron, so requires careful correction. The method used to measure the background is a "three point method". We chose three left background points, L1, L2, and L3, (402, 426, and 443 keV respectively) and three right background points, R1, R2 and R3, (551, 541 and 525 keV), away from the boron peak (478 keV), which show almost no interferences. Each "point" is an average of 5 or 7 channels. We calculate straight lines between the three pairs of points, L1-R1, L2-R2 and L3-R3 respectively, and the background underneath the boron peak, taking the average of the three. All counting data were expressed as counts per second per channel (c.s^{-1}).

Two geological standards were used in this analysis: BHVO-1 and W-1. They were sealed in teflon bags occupying a volume similar to the meteorites. The standards were analyzed many times and the average of measured counts per second per microgram of boron (c.s^{-1}.μg^{-1}) for MNR is 0.1051, for NIST is 0.1159; these figures measure the analytical sensitivity of the two facilities.

The magnitude of the analytical blank is important for samples with less than 1 μg boron. The samples are packed in bags made of clean thin (0.001 inch thick) teflon sheet, which were suspended in the neutron beam. Teflon bags were analyzed as blanks and we also analyzed the empty neutron beam with nothing in it as the *system background*, which is mainly scattered γ-rays from the environment of the beam. The counts of blanks and system backgrounds were translated into boron by dividing by the sensitivity. The blanks and system backgrounds have been analyzed repeatedly and the results are listed in table 5.

Table 5 shows that the blank is mainly from the environment of the neutron beam. The boron in a teflon bag is about 0.03 - 0.04 μg and is less important. The system background in NIST is about 0.1 μg of boron lower than that in MNR.

For analyses of low boron content, correction for interfering elements must be considered. The boron peak (478 keV) occupies the range of 468 - 487 keV (Döppler broadening). In this range, there is a strong peak of sodium (472 keV), which is the strongest peak of that element, and a peak of cobalt (484keV, peak 4 in Fig. 3). In order to avoid these interferences, only 11 channels (475 - 482 keV), were measured for boron (Fig. 3). Within this field there are still four small peaks which should be treated as interference: Ca (476), Fe (479), Mg (480) and Ni (480) (Kitto 1987, Lone et al. 1981). Four strong peaks of these elements were chosen as reference peaks, and the intensity ratio of interference peak to reference peak was measured or adopted from Kitto (1987). For each standard or meteorite, the reference peaks were counted, the counts of interference peaks were calculated and subtracted from the total boron counts.

Table 5. The measurement of blank and instrument background

Reactor	MNR		NIST	
	C/S**	B*	C/S**	B*
System background	0.0149	0.14	0.0045	0.04
Teflon bag + system bg.	0.0174	0.17	0.0097	0.08
Boron in teflon bag		0.03		0.04

* Boron content in micro gram

** counts per second

For the evaluation of these interferences, we calculated the equivalent boron for each standard and meteorite by dividing the interference peak counts by the c.s^{-1}.μg^{-1} boron of each reactor. The results are summarized in table 6. The level of the interference mainly depends on the difference of the equivalent boron between the meteorites and the standards. In the analysis of 1 g samples, a boron concentration of 0.5 ppm represents 0.5 μg boron. Table 6 shows that this difference for Ca does not exceed 0.01 μg and is negligible. The differences for Mg and Fe may reach 0.08 μg, thus corrections for high Mg (>15%) and Fe (>20%) in meteorites are necessary. The difference for Ni may be as much as 0.18 μg of boron, therefore the correction of Ni for most meteorites is important. Both standards and meteorites were corrected for these four elements.

Table 6. Minor interference elements and equivalent boron for PGNAA in MNR and NIST

Element	Energy##	Concentration %		Maximum C/S		Maximum equivalent boron (ppm)		
		Stand.*	Meteor.**	Stand.	Meteor.	Stand.	Meteor.	M-S#
Ni	480	0.008, 0.012	0.0 to 2.1	0.0	0.018	0.0	0.18	0.18
Mg	480	4.0, 4.4	3.9 to 23.5	0.002	0.010	0.02	0.10	0.08
Fe	479	7.8, 8.5	0.5 to 35.0	0.002	0.010	0.02	0.10	0.08
Ca	476	7.9, 8.1	0.3 to 8.5	0.003	0.004	0.03	0.04	0.01

Stand. Standards BHVO-1, W-1.
Meteor. All meteorites analysed
* Concentration in standards (Govindaraju 1989).
** Concentration in meteorites (Mason 1971).
\# The difference of maximum equivalent boron in the meteorite and the standard.
\#\# Energy of interference peak.

4.2. Analytical quality

4.2.1. Precision:

All analytical results are listed in Table 7. Some samples (e.g. Ivuna, Orgueil, Murchison, Allende, Mokoia, Nulles, Farmington, Knyahinya, Holbrook, L'Aigle, Mocs, Suizhou, Parnallee, Bishopville, Norton County, Tatahouine, Juvinas and Stannern) were determined more than once. Samples were re-mounted for every irradiation, since the counting geometry effect can be an important source of error (the neutron beam is stronger in the center and the sensitivity of the detector is higher). The differences in multiple results of a sample in the same reactor are mostly less than 0.1 ppm, usually less than 0.05 ppm; one pair (Bishopville) differ by 0.2 ppm, and the B content is higher, close to 1.5 ppm (Table 7). The standand deviation (1σ) for one reactor is usually about 0.05 ppm, that is about 10% or smaller (Table 7, Fig. 4).

Most samples have been analyzed in both NIST and MNR. Generally speaking, agreement of the data is good (Table 7, Fig. 5). The relative standard deviations, calculated from all data, from both reactor systems, are usually close to 15% or smaller. But when the boron contents are close to or

Table 7. Boron abundances in meteorites

No.	Sample Name	Type		PGNAA Sample Weight [g]	Boron Conc. [NIST] [ppm]	Boron Conc. [MNR] [ppm]	Ave. Boron Conc. [ppm]	Relative S.D. [%]	No. of Analyses
1	IVUNA	CI1		0.7286		0.67	0.65	4.4	2
						0.63			
2	ORGUEIL	CI1		1.2106		0.78	0.78	0.9	2
						0.77			
3	COLD BOKKEVELD	CM2		1.0277	0.57	0.53	0.55		
4	MURCHISON*	CM2	(1)	0.9275	0.47	0.49	0.49	3.9	4
					0.51				
					0.47				
			(2)	1.0869	0.49	0.51			
5	ALLENDE	CV3		1.1488	0.40	0.35	0.35	15.2	5
					0.31	0.41			
					0.29				
6	MOKOIA***	CV3	(1)	1.0610	0.55	0.60	0.56	12.5	4
			(2)	0.1222		0.47			
						0.63			
7	WESTON	H4		1.2598	0.39	0.51	0.45		
8	PANTAR	H5		1.2946	0.40	0.40	0.40		
9	RICHARDTON	H5		1.3261	0.69	0.78	0.74		
10	DRESDEN	H6		1.2823	1.10	1.15	1.13		
11	NULLES	H6		1.3718	0.66	0.65	0.65	1.5	3
						0.64			
12	BJURBOLE	L4		1.2818	1.20	1.23	1.21		
13	SARATOV	L4		1.2936	0.43	0.49	0.46		
14	FARMINGTON	L5		1.3290	0.34	0.43	0.38	14.5	6
					0.35	0.47			
					0.36				
					0.34				
15	KNYAHINYA*	L5	(1)	1.5760	0.66	0.65	0.68	6.4	7
						0.67			
			(2)	1.3924	0.66	0.77			
					0.68				
					0.64				
16	BRUDERHEIM	L6		1.1612	0.87	0.87	0.87		
17	HOLBROOK	L6		1.5189	0.68	0.61	0.68	9.6	3
						0.74			
18	L'AIGLE	L6		1.4198	0.39	0.47	0.49	12.0	5
						0.53			
						0.53			
						0.51			
19	LEEDEY	L6		1.5409	0.38	0.43	0.40		
20	MOCS	L6		1.3372	0.41	0.48	0.46	10.3	3
						0.50			
21	MODOC	L6		1.2134	1.07	1.09	1.08		
22	PEACE RIVER	L6		1.3608	1.20	1.15	1.17		
23	SUIZHOU	L6		1.5182		0.58	0.56	5.1	2
						0.54			
24	PARNALLEE***	LL3	(1)	1.1944	2.41	2.18	2.34	5.9	3
			(2)	0.7914		2.43			
25	INNIS FREE	LL5		1.4497	0.51	0.62	0.56		
26	ST. SEVERIN	LL6		1.4192	0.37	0.51	0.44		
27	ABEE	E4		1.3959	1.22	1.17	1.19		
28	INDARCH	E4		1.3046	0.81	0.86	0.83		
29	HVITTIS	E6		1.5046	0.54	0.56	0.55		
30	BISHOPVILLE	AUB		0.7599	1.46	1.48	1.41	7.8	3
						1.28			
31	NORTON COUNTY	AUB		1.2430	0.28	0.37	0.33	14.3	3
						0.35			
32	TATAHOUINE	DIOG		1.0829	0.02	0.10	0.06	66.7	3
						0.06			
33	JUVINAS**	EUC	(1)	1.2250	0.72	0.61	0.63	11.2	4
			(2)	1.1459	0.62	0.55			
34	SERRA DE MAGE	EUC		0.9367	0.08	0.15	0.11		
35	SIOUX COUNTY	EUC		1.2100	0.66	0.66	0.66		
36	STANNERN**	EUC	(1)	1.0693	1.10	0.86	0.92	14.9	4
			(2)	1.0927	0.95	0.78			

* Two samples have been taken from one piece of meteorite.
** Two pieces of one meteorite from two sources.
*** The first sample is a mixture of fine powder and coarse grains, the second is the coarse grain only.

Fig. 4. Analysis precision, with error bars for ±1 s.d. Meteorite repeat analyses from Table 4. Point "a" is the standard BCSS-1.

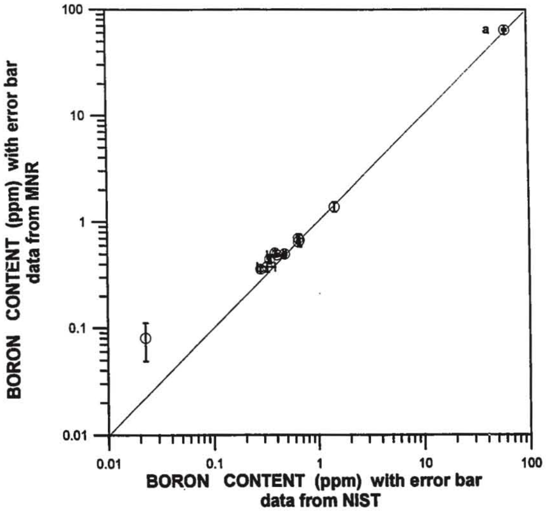
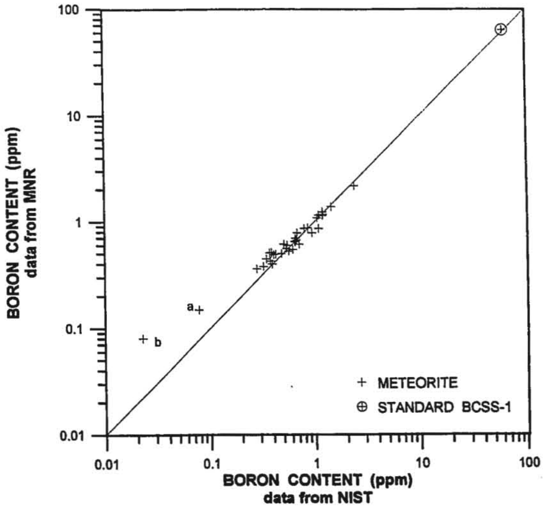


Fig. 5. Comparison of boron contents measured in MNR and in NIST. Point "a" is Serra de Magé (Euc.), "b" is Tatahouine (Diog.).



lower than 0.1 ppm, the relative errors become larger (about 50%) and demonstrate a small systematic error (Fig. 4 and 5). This may be due to over-correction for blank in NIST or under-correction in MNR. Table 5 shows that the teflon bags gave slightly higher boron in NIST (0.04) than in MNR (0.03), but such a small systematic error is negligible. A high boron sample, standard BCSS-1, was analyzed in NIST and in MNR, and the measured boron concentrations 62.3 ppm and 63.7 ppm are in very good agreement.

The average boron concentration, calculated from the data from both reactor systems, will be used as the boron content in that meteorite (Table 7).

4.2.2. Accuracy:

As mentioned above, separate analyses of BCSS-1 gave results which agreed well. Two meteorites (Murchison and Knyahinya) were analysed in two different parts of the same sample. Two others (Stannern and Juvinas) were analysed in samples from two different museums. The analytical results in Table 7 show similar mean values, except for one aberrant result for Knyahinya. This indicates that the distribution of boron in meteorites is relatively homogeneous and the accuracy of analyses is probably acceptable. Therefore the relatively small amount of sample (about 1 g) can be taken as representative of the whole meteorite. A better way to measure the accuracy would be to measure boron contents in the same meteorites using another method, such as isotope dilution. However this was not feasible because boron isotope measurements were not successful.

4.2.3. Boron contamination

All the meteorites analyzed have low boron abundance, close to or below 1 ppm (the only exception is Parnallee). Juvinas and Stannern, from two different collections and in different preservation states, give about the same boron content. This suggests that boron contamination is not a serious problem and that these samples, except Parnallee, are quite clean. Also, it seems that the sample appearance categories (Table 1) do not influence the analytical results. The linear relationship of boron and sulphur for carbonaceous chondrites and average ordinary chondrite (see following chapters) proved the cleanness of most of these meteorites too.

Parnallee and Mokoia have been analyzed as two samples respectively. First sample is the mixture of fine powder and coarse grains, and the second sample is coarse grains

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only whose diameter is larger than 0.3 mm. It is clear that the first sample is more strongly influenced by the sample preparation in this laboratory than the second one, but the two samples give similar results for these two meteorites (Table 7). Thus, the boron contamination from sample preparation is negligible.

CHAPTER 5. BORON IN METEORITES

5.1. Boron concentration in meteorites

The range and mean values of boron concentration in different groups of meteorites are listed in Table 8 and plotted in Fig. 6. The mean values are similar, from 0.5 to 0.9 ppm; and the ranges overlap, mostly from 0.3 to 1.4 ppm. There are three exceptions: two of these are the diogenite Tatahouine and the eucrite Serra de Magé, which have very low contents, only 0.06 and 0.11 ppm respectively; the third is the LL3 meteorite Parnallee, with 2.29 ppm. Curtis and Gladney (1985) analyzed Parnallee too and got only 0.48 ppm. The Parnallee sample analyzed here was the only meteorite which was too small to trim all its surfaces by chisel, although one surface was removed by fine sandpaper; the high boron content of this sample may thus be due to terrestrial contamination, and will not be used in the following discussion.

Table 8. Distribution of boron abundances (ppm) in different groups of meteorites

Group	No. of Analyses	Falls*		No. of Analyses	Antarctic meteorites**	
		Average	Range		Average	Range
CI	2	0.72	0.65 - 0.78			
CM	2	0.52	0.49 - 0.55	1	1.30	
CO				1	0.63	
CV	2	0.46	0.35 - 0.56	1	0.79	
H	5	0.68	0.40 - 1.13	16	0.73	0.19 - 1.95
L	12	0.70	0.38 - 1.21	14	0.86	0.37 - 1.97
LL***	2	0.50	0.44 - 0.56	6	0.64	0.34 - 1.19
E	3	0.86	0.55 - 1.19	2	1.45	0.20 - 2.69
Aub.	2	0.88	0.34 - 1.41	2	0.79	0.79 - 0.79
Diog.	1	0.06		2	0.60	0.35 - 1.03
Euc.	4	0.58	0.11 - 0.92	4	3.34	0.95 - 6.29
How.				3	3.63	1.00 - 6.98
Ure.				2	0.81	0.76 - 0.86

* present work
** unpublished data
*** Pamallee is excluded

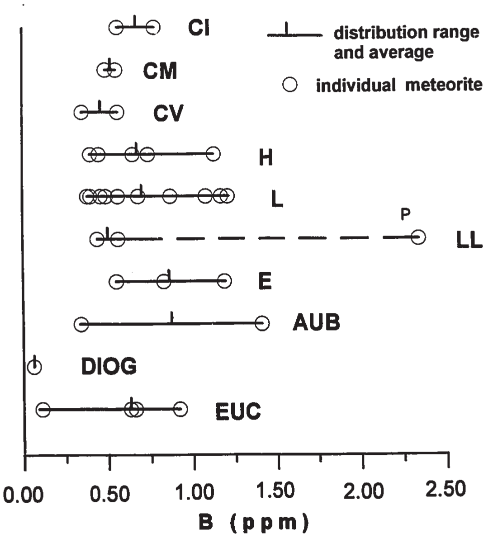


Fig. 6. Boron in meteorite falls. The variations of boron contents in different types of meteorites are small. "P" is Parnallee whose boron content is suspicious.

5.2. Comparison with previous data

Curtis et al. (1980) and Curtis and Gladney (1985) analysed some interior pieces of meteorite falls by PGNAA. For comparison, their results and the present results are summarised in Table 9. Generally speaking, the agreement of the present analytical results with their data is good. For seven specimens the differences are smaller than 0.15 ppm. In this work, three meteorites (Richardton, Knyahinya and Parnallee) give significantly higher boron than previous data; one (Weston) has a much lower content. All except Parnallee fall within the ranges shown on Fig. 6.

5.3. Comparison with boron data of Antarctic meteorites

Some Antarctic meteorites have also been analyzed for boron: detailed results are unpublished, but were summarized in an abstract (Shaw et al. 1992) and are listed in Table 8. The similarity to the present work for the H, L, and LL groups, indicates that most of these have not undergone any alteration which remobilised boron. Individual values of two carbonaceous chondrites, one enstatite chondrite and several achondrites are higher than for falls and require explanations. Although some may indicate analytical error

Table 9. Comparison of previous data and present results

Meteorite	Type	Boron (ppm) Curtis et al. 1980	Boron (ppm) Curtis and Gladney 1985	Boron (ppm) Present work
Orgueil	CI1		0.87	0.78
Cold Bokkeveld	CM2		0.40	0.55
Murchison	CM2	0.56	*0.42 (0.27 - 0.56)	0.49
Allende	CV3	0.27	0.33	0.35
Weston	H4	1.29		0.45
Richardton	H5	0.24	0.23	0.74
Nulles	H6	0.69	0.76	0.65
Saratov	L4	0.39	0.42	0.46
Knyahinya	L5		*0.24 (0.20 - 0.27)	0.68
Bruderheim	L6	0.69	0.73	0.87
Leedey	L6	0.12	0.39	0.40
Parnallee	LL3		0.48	2.34

* Average and range.

or contamination effects, these results nevertheless may be real; this is most likely for the eucrites and howardites.

CHAPTER 6. BORON SOLAR SYSTEM ABUNDANCE

The solar system abundance (SSA) of boron is of considerable interest and several estimates have been published (Table 10), using three kinds of data:

1. Average in some types of chondrites (Cameron et al. 1973, Curtis et al. 1980).
2. Average in CI meteorites (Curtis and Gladney 1985).
3. Average in CI meteorites, using the boron abundances in other meteorites adjusted by the ratio of the contents of similar elements, (Cu, Ag, Sb, Ge, Ga, S, Se and Sn for ordinary chondrites; Se, Te, Zn, Sn, In, Bi, Tl, Cd and Cs for carbonaceous chondrites, Anders and Ebihara 1982).

Using the composition of CI meteorites as a solar system abundance has been widely accepted (Woolum 1988, Anders and Grevesse 1989). However there was only one reliable boron value for CI meteorites (Curtis and Gladney 1985), this is the 0.87 ppm found in Orgueil (Table 9). Since boron concentrations vary in each group (Fig. 6), using one sample to represent a group is unrepresentative, and an average of multiple analyses is preferable. Matrix material is chemically similar in all four major groups: CI, CM, CO and CV (McSween and Richardson 1977, Scott et al. 1988). Anders (1964) noted and others (e.g. Krähenbühl et al., 1973) have confirmed that this consistency of matrix composition extends to a wide variety of minor and trace elements whose only common property is volatility. Although the correspondence is inexact for CO and CV chondrites (McSween,1977, Takahashi et al., 1978 a, b), volatile and moderately volatile elements have abundances in the carbonaceous chondrites that are directly proportional to matrix content. This observation led Wood (1963), Anders (1964) and Larimer and Anders (1967) to propose that the carbonaceous chondrites are mixtures of two components, high temperature and low temperature. Variations in the abundance and composition of the high-temperature component (chondrules, isolated grains and aggregates) of carbonaceous chondrites are largely responsible for their chemical variations (Dodd 1981, p. 54). The low temperature component (matrix, including sulfides) appears to be chemically unfractionated (Dodd 1981, p. 55) and pristine (MacPherson et al. 1985). On this basis we can use the boron content in the matrix of carbonaceous chondrites to represent the solar system abundance.

Table 10. Boron solar system abundance

Author	Method	Boron abundance*
A.G.W. Cameron et al., 1973	Reappraisal of fluorimetric analysis of 1 C2 and 3 C3 & C4 meteorites (Quijano-Rico and Wänke 1969)	350
D. Curtis et al., 1980	Logarithmic average of PGNAA analyses of 2 carbonaceous and 8 ordinary chondrites	6.6 (+6.5, -3.3)
E. Anders and M. Ebihara, 1982	Reappraisal of 34 PGNAA analyses (Curtis, 1980)	24 (±7)
D. Curtis and E. Gladney, 1985	PGNAA of Orgueil	21 (±2)
E. Anders and N. Grevesse, 1989	Reappraisal of Curtis and Gladney (1985).	21.2
This work	See text.	16.9 (±2.2)

* Solar system abundances in atoms/1.0E+6 Si

Alpha-track images revealed that in carbonaceous chondrites, boron and lithium are mainly concentrated in the matrix (Shaw et al. 1988 a; Shaw et al. 1988 b). In order to estimate the relationship between the boron contents and matrix contents, seven carbonaceous chondrites are available (Table 11). Six of them (Ivuna, Orgueil, Cold Bokkeveld, Murchison, Allende and Mokoia) are from the present work, one (Mighei) is from Curtis and Gladney (1985), in which the interior fragments of the meteorites were analyzed by PGNAA too. Matrix contents are from McSween (1979, for CM) and McSween (1977, for CV). Boron contents vs. matrix are plotted in Fig.7 and show a linear relationship. The least squares regression line is

$$Y_B=0.004547X+0.2332 \qquad (1)$$

where X is the matrix content (%), Y_B is the boron concentration (ppm). The correlation coefficient r=0.80, and the s.d. of Y_B is S=0.0938.

From the r value we can conclude that the boron content and matrix content in carbonaceous chondrites have good positive correlation. From equation (1), the calculated boron content in matrix ($Y_{B,H}$, when X=100) is 0.69±0.09 ppm (±1 S), and in the average chondrule ($Y_{B,CH}$, when X=0) is 0.23±0.09 ppm; the boron ratio of chondrule/matrix is 0.33. In order to get the boron solar system abundance, the $Y_{B,H}$ is

Table 11. Boron content and matrix proportion in carbonaceous chondrites

Meteorite	Type of Meteorite	Matrix Content Vol.%	Boron Content ppm
Ivuna	CI1	100 (1)	0.65 (4)
Orgueil	CI1	100 (1)	0.78 (4)
Cold Bokkeveld	CM2	74.2 (2)	0.55 (4)
Murchison	CM2	63.6 (2)	0.49 (4)
Mighei	CM2	60.7 (2)	0.42 (5)
Mokoia	CV3	39.8 (3)	0.56 (4)
Allende	CV3	38.4 (3)	0.35 (4)

(1). Assume the matrix content of CI meteorite is 100%.
(2). McSween and Richardson 1977.
(3). McSween 1977.
(4) Present work.
(5) Curtis and Gladney 1985.

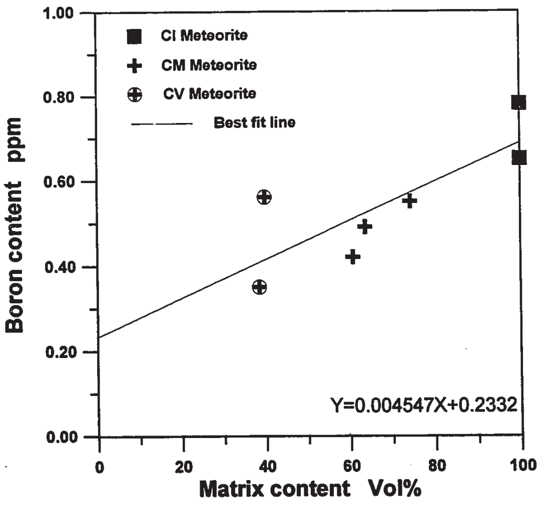


Fig. 7. Correlation of matrix and boron contents in carbonaceous chondrites.

then normalized to units of atoms per 10^6Si, giving

$$B_{SSA}=\frac{Y_{B,M}\times10^{-6}}{Y_{Si,CI}\times10^{-2}}\times\frac{W_{Si}}{W_B}\times10^6 \qquad (2)$$

where B_{SSA} is the boron solar system abundance, $Y_{Si,CI}$ is the Si content in CI meteorite (%), W_{Si} and W_B are the atomic weights of silicon and boron respectively. Substitute W_{Si}=28.09, W_B=10.81, $Y_{B,CI}$=0.69±0.09 ppm, $Y_{Si,CI}$=10.64 % (Anders and Grevesse 1989, mean CI chondrites), we get B_{SSA}=16.9±2.2 (atoms/10^6Si).

In order to test this solar system abundance we return to equation (1), and compare the calculated boron contents in matrix and chondrules with other data.

The only direct measurement of the boron content in chondrules and matrix of carbonaceous chondrite was the analysis of a polished thin section of Allende (CV3) by the ion-microprobe (Shaw et al. 1988 a). Here $Y_{B,CH}$ (including chondrules, clasts and inclusions) was 0.57 ppm, and $Y_{B,M}$ was 3.4 ppm. Inclusions make up about 70% of the meteorite, thus the boron content of this thin section must be about 1.4 ppm. This result is 4 times higher than that determined by bulk analysis in present work (0.35 ppm) and from Curtis and Gladney's (1985) analyses (0.33 ppm). Therefore the ion-probe data are unreliable.

Olsen et al. (1994) analyzed the boron concentration in some minerals of a H-chondrite inclusion in a IIE iron meteortie, Watson, using an ion microprobe. The measured boron contents in ol, opx, cpx and fp are 0.13, 0.38, 0.21 and 1.3 respectively. These measured boron contents in olivine, orthopyroxene and clinopyroxen are similar to the calculated boron content in chondrules from equation (1), 0.23±0.09 ppm.

If boron is mainly concentrated in the matrix then it should have positive correlation with other elements which mainly exist in the matrix (including sulfides) too, such as sulphur. In addition to the data in Table 11, we took two carbonaceous chondrites from Shaw et al. (1988 a), fifteen ordinary chondrites from Table 7. All data were normalized to the Si content of each meteorite and to the SSA of Anders and Grevesse (1989) for sulphur (5.15×10^5) and to the present work for boron (16.9). The data for chondrites were processed as follows. Let

$Y_{B,i}$ = boron concentration in each meteorite (ppm)
$Y_{S,i}$ = sulphur concentration in each meteorite (wt%)
$Y_{Si*,i}$ = silica concentration in each meteorite (wt%)
S_{SSA} is the solar system abundance of sulphur
B_{SSA} is the solar system abundance of boron

and let W_B, W_S, W_{Si*} be the atomic or molecular weight of

boron, sulphur and silica, 10.81, 32.06, 60.09 respectively. If $A_{B,i}$ and $A_{S,i}$ are the abundances of boron and sulphur normalized to 10^6Si atoms and the SSA for chondrule or each meteorite, then

$$A_{B,i}=\frac{Y_{B,i}\times10^{-6}}{Y_{Si*,i}\times10^{-2}}\times\frac{W_{Si*}}{W_B}\times10^6\times\frac{1}{B_{SSA}}=32.89\times\frac{Y_{B,i}}{Y_{Si*,i}} \qquad (3)$$

$$A_{S,i}=\frac{Y_{S,i}\times10^{-2}}{Y_{Si*,i}\times10^{-2}}\times\frac{W_{Si*}}{W_S}\times10^6\times\frac{1}{S_{SSA}}=3.639\times\frac{Y_{S,i}}{Y_{Si*,i}} \qquad (4)$$

The normalized abundances in all chondrites are listed in Table 12, and plotted in Fig. 8. The normalized abundances of boron and sulphur in chondrules of carbonaceous chondrites can also be calculated by equation (3) and (4), using their silica content 44.3%, sulphur content 0.48 (McSween et al. 1983), and boron concentration 0.23 ppm (calculated from equation 1). The calculated results are 0.04 and 0.17 for S and B respectively. The average chondrule content is plotted in Fig.8(a) too.

Fig. 8(a) shows that normalized boron and sulphur abundances are well correlated in carbonaceous chondrites, and the regression line passes close to the calculated chondrule composition. Thus, the boron and sulphur abundances in carbonaceous chondrites can be considered as a mixture of matrix and chondrule. For ordinary chondrites,

Table 12. Contents and silicon-SSA normalized abundances of boron and sulphur in chondrites

Chondrite		Silica Content* %	Boron Content* ppm	 Normalized abundance**	Sulphur Content* %	 Normalized abundance**
Ivuna	CI1	22.71 (7)	0.65 (1)	0.941	6.70 (7)	1.074
Orgueil	CI1	22.69 (4)	0.78 (1)	1.131	5.40 (4)	0.866
ALHA 83100	CM2	27.81 (2)	0.60 (2)	0.710	3.19 (2)	0.417
Cold Bokkeveld	CM2	27.33 (7)	0.55 (1)	0.662	2.98 (7)	0.397
Mighei	CM2	30.80 (6)	0.42 (3)	0.449	3.60 (6)	0.425
Murchison	CM2	29.07 (4)	0.49 (1)	0.554	2.64 (4)	0.330
ALHA 77003	CO3	34.02 (2)	0.50 (2)	0.483	1.79 (2)	0.191
Allende	CV3	34.23 (4)	0.35 (1)	0.336	1.47 (4)	0.156
Mokoia	CV3	33.40 (7)	0.56 (1)	0.551	2.46 (7)	0.268
Weston	H4	36.59 (8)	0.45 (1)	0.404	1.94 (8)	0.193
Pantar	H5	36.30 (9)	0.40 (1)	0.362	2.16 (9)	0.217
Richardton	H5	39.00 (10)	0.74 (1)	0.624	1.05 (10)	0.098
Bjurbole	L4	42.00 (10)	1.21 (1)	0.948	1.48 (10)	0.128
Saratov	L4	40.48 (4)	0.46 (1)	0.374	2.10 (4)	0.189
Farmington	L5	40.79 (11)	0.38 (1)	0.306	1.75 (11)	0.156
Knyahinya	L5	41.01 (4)	0.68 (1)	0.545	2.19 (4)	0.194
Bruderheim	L6	39.26 (4)	0.87 (1)	0.729	2.26 (4)	0.209
Holbrook	L6	38.84 (4)	0.68 (1)	0.576	1.98 (4)	0.186
L'Aigle	L6	39.20 (4)	0.49 (1)	0.411	2.40 (4)	0.223
Leedey	L6	40.32 (4)	0.40 (1)	0.326	2.34 (4)	0.211
Mocs	L6	39.66 (12)	0.46 (1)	0.381	2.34 (12)	0.215
Modoc	L6	39.84 (4)	1.08 (1)	0.892	2.09 (4)	0.191
Suizhou	L6	39.77 (5)	0.56 (1)	0.463	2.41 (5)	0.221
St. Severin	LL6	40.62 (4)	0.44 (1)	0.356	2.12 (4)	0.190

* The number in brackets is the reference. (1) present work; (2) Shaw et al. 1988b; (3) Curtis et al. 1980; (4) Jarosewich 1990; (5) Huang and Xiao 1989; (6)Curtis and Gladney 1985; (7) Wiik 1356; (8) Mason and Wiik 1965; (9) Konig 1964; (10) Easton and Elliott 1977; (11) Buseck et al. 1966; (12) Wiik 1969.

** SSA and Si normalized abundances

Fig. 8 (a). Boron vs. Sulphur in carbonaceous chondrites. All data are normalized to Solar System abundance of S (Anders and Grevesse, 1989) and B (present work). "s" is from Shaw et al. (1988 b), "c" is from Curtis and Gladney (1985). Unlabeled are from present work.

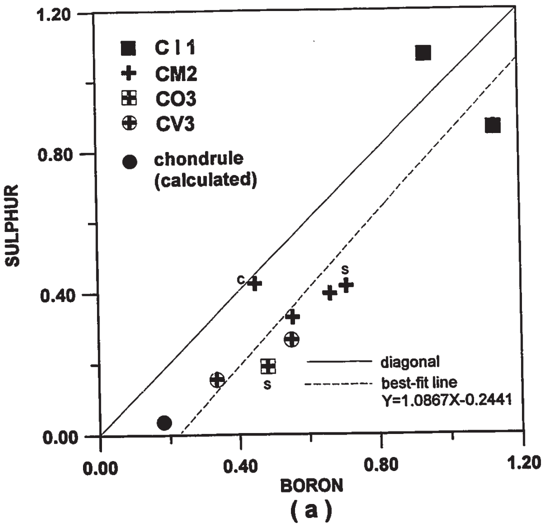
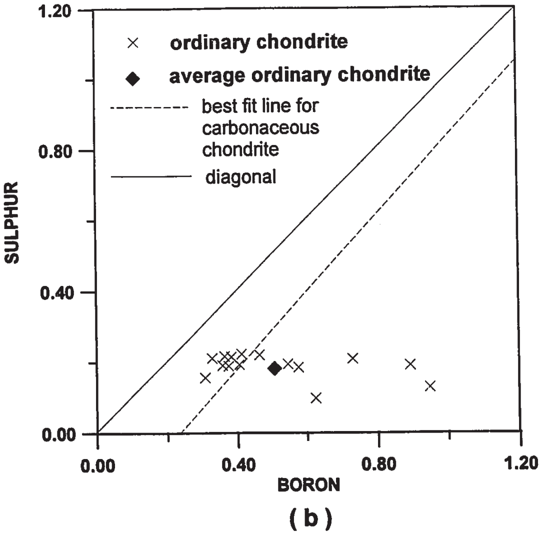


Fig. 8 (b). Boron vs. Sulphur in ordinary chondrites. All data are normalized to Solar System abundance of S (Anders and Grevesse, 1989) and B (present work).



normalized boron and sulphur abundances show no linear correlation at all in Fig. 8(b), but the average ordinary chondrite lies beside the best fit line calculated from carbonaceous chondrites. It seems that the original boron content in ordinary chondrites was controled by the ratio of matrix/chondrule too, but after that boron was redistributed.

Curtis and Gladney (1985) calculated the Si and CI normalized B and S abundances in some chondrites, and plotted the mass weighted averages of normalized B and S abundances in different chondrite types. They found that these abundances are similar in all types of chondrites, and concluded that boron is similar with sulphur, has condensation temperature in the range between 400 and 900 °K. The present work indicates that although the linear relationship between boron and sulphur exists for carbonaceous chondrites and the average ordinary chondrites, the normalized abundances of boron in chondrites are usually higher than sulphur, so most meteorites in Fig. 8 lie below the diagonal. That is because the ratio of concentrations chondrule/matrix is larger for boron than that for sulphur. In another word, boron is less depleted in chondrules than sulphur and may have a higher condensation temperature.

CHAPTER 7. NUCLEOSYNTHESIS OF BORON

Now it has been widely accepted that our cosmos was formed by the Big Bang 10 to 20 billion years ago and after that most elements were synthesised 5 to 8 billion years ago (Tu 1984). The elements then condensed and solidified from the solar nebula and formed our solar system. The age of condensation and solidification are 4.6-4.7 and 4.5-4.6 Gyr respectively (Tu 1984, Tilton 1988). In the following two chapters the formation and condensation of boron will be discussed.

7.1. Solar Photospheric abundance of boron

Solar system abundances can be estimated from the solar photosphere for most elements. But the strongest lines of atomic boron fall in the far ultraviolet and infrared solar spectrum, thus its abundance is poorly determined. A few tentative identifications of boron lines in stellar spectra have been made (Table 13). The only positive evidence for the presence of boron in the Sun is provided by Kohl et al. (1977) using photoelectric measurements near 2500Å which were made with a rocket-borne high-resolution spectrometer, and the measured boron abundance is 400 (+390, -200) atoms/10^{12}H.

Table 13. Boron abundance of the solar photosphere

Author	Method	B Abundance (Atoms/10^{12} H)
Engvold (1970)	Absence of the (0,0) band of BH at 4332Å in the spectra of sunspots	<320*
Hall and Engvöld (1975)	Absence of lines at 16240 and 16245Å of photospheric spectrum	<=120 (±60)
Kohl et al. (1977)	Photoelectric measurements of the solar spectrum near 2500Å	400* (+390, -200)
Anders and Grevesse (1989)	Reappraisal of Kohl et al. (1977)	400* (+390, -200)

* Converted from the original logarithmic form.

The solar system abundance of H is $2.79\times10^{10}/10^6$Si (Anders and Grevesse 1989). Therefore the boron solar system abundance calculated from meteorites in chapter 7, $B_{SSA}=16.9\pm2.2$ atom/10^6Si, can be converted to $B_{SSA} = 606\pm79$ atoms/10^{12}H. This is 1.5 times Anders and Grevesse's (1989) boron content of the solar photosphere (Table 14). In the 1970's and before, the calculated boron solar system abundance from meteorites (e.g., 350 atoms/10^6Si = 12500 atoms/10^{12}H, Cameron 1973) was much higher. Therefore, some tried to explain this difference as depletion of boron in the solar photosphere (Weller, 1977), or enrichment of boron in meteorites (Mills 1968, Cameron 1973). In 1980, Curtis et al. got a lower boron solar system abundance from the average of some chondrites, 6.6 atoms/10^6Si (= 240 atoms/10^{12}H) which is similar to the photosphere abundance (Table 13), and concluded that it is no longer necessary to consider processes to account for any difference. The present work based on the boron content in CI meteorites and the matrix of carbonaceous chondrites suggests a real difference of abundance between meteorites and solar photosphere.

Table 14. Solar system abundances of light elements from meteorites and solar photosphere.

Element	Li	Be	B
Abundance from meteorites (Atoms/10^{12} H)	2050	26.2	606*
Abundance from solar photosphere (Atoms/10^{12} H)	14.5	14.1	400
Ratio of meteorite to solar photosphere	141	1.9	1.5
Critical temperature (10^{6} °K)**	2	3.5	5

* From Chapter 6, Table 7. Other data from Anders and Grevesse (1989); calculated from Si-normalized data (meteorites) and logarithmic H-normalized data (photosphere).

** Arnould and Forestini (1989).

Besides boron, there are twelve elements whose contents in meteorites are significantly higher than in the photosphere, i.e. the ratio of former to latter is larger than 1.25. They are Li, Be, P, Mn, Ga, Ge, Ag, Sn, Tb, Ho, Tm and Pb (Anders and Grevesse 1989). Of these elements, Li and Be are depleted by nuclear reactions at the bottom of the convection zone of the Sun (Reeves 1971); P, Ga, Ag, Sn, Tb, Ho and Tm are poorly determined in the photosphere, due to severe blending of their few available spectral lines, lack of accurate transition probabilities or both. The remaining three elements are Mn, Ge and Pb. It is difficult to imagine an enrichment process which is specific for Mn, Ge, Pb and B. Therefore the difference of the abundances of boron in CI meteorites and in the solar photosphere can be better explained only by other methods include a depletion in the Sun by nuclear reactions.

Because of the similar depletion behavior, we will compare boron with lithium and beryllium (Table 14). The critical temperatures, at which the light elements begin to be destroyed, are listed in Table 14 too. This table shows that Li is strongly depleted in the solar photosphere, Be and B are moderately depleted, and the lower the critical temperature is, the stronger the depletion. Thus the abundances of light elements in meteorites are original

abundances, which are related only to the nucleosynthesis. Their abundances in the solar photosphere results from both nucleosynthesis and destruction in the Sun.

7.2. Boron nucleosynthesis

The abundance data of the elements are the basis of the theory of nucleosynthesis. Now, the relatively reliable abundance enable us to discuss boron formation. Since the mid-1950's, various models of the production of light elements by spallation reactions have been proposed, and two types are widely discussed: 1. bombardment of the interstellar medium (ISM) by galactic cosmic rays (GCRs); 2. spallative reaction in the surfaces of flaring stars .

A good model should predict the element and nuclide ratio produced from that mechanism correctly. In order to evaluate those models, Table 15 lists recent calculations of nuclide ratios by the two kinds of spallative nucleosynthesis models (Walker et al. 1985). Column 1 of Table 15 lists the element and nuclide ratio based on meteorites. The ratio $^{11}B/^{10}B$ in meteorites is poorly known (see chapter 3), and the only measurements of $\delta^{11}B$ (Shima 1962, Shima 1963, Agyei and McMullen 1978) show a wide

Table 15. Calculated nuclide ratios based on various spallative models and observed ratio

Column number	1	2	3	4	5	6	7	8
Author	Observed ratio** based on meteorites	Walker et al. (1985)						
Type		Bombardment of the ISM by GCRs				On flaring stars		
Model		GCRs	GCRs+ E^{-3} (f=1.05)	GCRs+ E^{-5} (f=0.131)	GCRs+ E^{-7} (f=0.028)	gamma =3	gamma =5	gamma =7
Element*								
Li	2046	168	1400	470	260			
Be	26	15	31	17	15			
B	606	251	850	460	410			
Nuclide*								
6Li	153	69	380	120	83			
7Li	1893	99	1000	350	180			
9Be	26	15	31	17	15			
10B	121	71	170	91	82			
11B	485	180	680	370	330			
Ratio								
7Li/6Li	12.3	1.4	2.63	2.92	2.17	2.9	4.8	5.2
11B/10B	4.0***	2.5	4.05	4.05	4.05	5.2	9.9	14
10B/6Li	0.791	1	0.45	0.76	0.99	0.31	0.38	0.76
10B/9Be	4.65	4.7	5.5	5.4	5.5	6.1	10	26
11B/6Li	3.17	2.6	1.8	3.1	4	1.6	3.8	10.6
11B/9Be	18.7	12	22	22	22	32	99	360

* Atoms/10^{12} H.

** Anders and Grevesse 1989, except B (this work).

*** see text

range, from -58 to +2.2; thus for this discussion, we adopt the terrestrial atom ratio of NBS SRM 951, $^{11}B/^{10}B=4.0$, as the boron isotopic ratio in meteorites, and this was used to calculate ^{11}B and ^{10}B from B_{SSA}.

The important role played by GCRs in the formation of the light elements was first discussed by Reeves et al. (1970) and subsequently confirmed by more detailed calculations (e.g. Meneguzzi et al. 1971, Mitler 1972, Weller et al. 1977 and Walker et al. 1985). GCRs are high-energy charged particle fluxes, and their major components are protons (85%) and α particles (14%), leaving 1% as the nuclei of Li, Be, B and some heaver elements. The dominating targets in ISM are CNO (^{12}C, ^{14}N, and ^{16}O) and ^{4}He (Arnould 1986). Walker et al. (1985) calculated the ratio of nuclides produced by the reaction of GCRs and ISM. The energy spectrum they used has the form

$$\Phi_i(E) = \alpha_i(E + E_0)^{-2.6} \qquad (1)$$

where Φ_i is the intensity of the particle "i", and is a function of its energy E per nucleon; E_0 is a constant; α_i is a coefficient for particle "i". The calculated results are listed in column 2 of Table 15. This model can not explain the nuclide ratios in meteorites; it is obvious that the calculated ^{7}Li and ^{11}B are too small relative to other nuclides, therefore the calculated ratios of $^{7}Li/^{6}Li$, $^{11}B/^{10}B$,

$^{11}B/^{6}Li$ and $^{11}B/^{9}Be$ are smaller than the observed values in column 1.

In order to solve this problem, Walker et al. next considered adding a low energy component of the cosmic ray flux which generates the needed ^{11}B, via the $^{14}N(p,\alpha)^{11}C(\beta^{+})^{11}B$ reaction and some ^{7}Li via $^{4}He(\alpha,p)^{7}Li$, while leaving the ^{6}Li, ^{9}Be and ^{10}B abundances relatively undisturbed. Thus the GCR flux function becomes:

$$\Phi_i(E) = \alpha_i(E + E_0)^{-2.6} + f_i E^{-\gamma} \qquad (2)$$

here f_i is a constant (normalization factor); γ is chosen from 3 to 7; other symbols are the same as in equation (1). Their calculated results are listed in columns 3, 4 and 5 of Table 15. The nuclide abundances and ratios agree with the observed data except for ^{7}Li which is still too small. They conclude that most ^{7}Li was formed in the Big Bang (Truran 1984, Boesgaard 1985, Arnould 1986).

The theory that spallative reactions in the surfaces of flare stars might form the light elements was first given by Fowler et al. (1955), and later discussed by Fowler et al. (1962), Reeves (1971) and Canal et al. (1975). Walker et al. (1985) also calculated the nuclide ratios based on the production in a transported flare spectrum of the form

$$\Phi_i(E)=\alpha_i E^{-\gamma} \qquad (3)$$

where γ is a constant and experimentally ranges from 3 to 7; other symbols are the same as in equations (1) and (2). The calculated ratios are listed in column 6, 7 and 8 of Table 15. Compared with column 1, they indicate that both the values involving B, Be are high when γ=5 or 7, i.e. ^{11}B is overproduced compared to Be. Although they look good for γ=3, all values involving ^{6}Li look bad. Also, the $^{7}Li/^{6}Li$ ratios are too small and unsatisfactory at all values of γ. This theory has also been criticized on very general grounds, on the basis of the fact that the enormous energy requirements are inconsistent with a stellar origin (Ryter et al. 1970). Therefore the nucleosynthesis solely in a flare mechanism cannot give good explanation for the light element formation. The boron solar system abundance and the light element ratio can be better explained only by the bonbardment of ISM by GCRs in which a very intense low energy in the form of E^{-5} is added.

CHAPTER 8. ELEMENT FRACTIONATION AND BORON CONDENSATION TEMPERATURE

Although Curtis and Gladney (1985) concluded that boron and sulphur have same normaized abundances in meteorites and thus have similar condensation temperatures at the low end of the range of moderately volatile elements, present work shows that boron has a higher normalized abundance than sulphur and may have higher condensation temperature (Fig. 8). It is desirable therefore to reappraise the relationship of the abundances of the elements and their condensation temperature. First it is noted that Higgins and Shaw (1984) analyzed boron in fertile unaltered mantle xenoliths, compared the depletion factors of boron and some other moderately volatile elements and estimated the temperature of condensation of boron as approximately 1,200°K. Next will be considered 33 moderately volatile elements (condensed between FeS and Mg-silicate) and refractory elements (condensed at a higher temperature, Larimer 1988, Palme et al. 1988). Their abundances in different types of chondrites are listed in Table 16. Lanthanum was chosen to represent rare earth elements which have similar condensation temperatures and normalized

Table 16. Element abundances and condensation temperatures in chondrites

Elem.	Cond. Temp. (°K)	Abun. Unit	Element abundance CI	CM	CO	CV	H	L	LL	EH	EL	CI and Si normalized abundance CM	CO	CV	CH*	E**
S	648	%	6.25	3.11	2.42	2.12	1.98	2.1	2.11	4.92	2.96	0.391	0.264	0.227	0.194	0.385
Zn	660	ppm	312	180	120	120	51	58	58	295	295	0.453	0.262	0.258	0.104	0.555
Sn	720	ppm	1.72	0.85	0.88	0.88	0.6	0.7	0.33	1.4	1.4	0.388	0.349	0.343	0.214	0.477
Ge	825	ppm	32.7	24	18	18	11	10	9	44	31	0.577	0.376	0.369	0.187	0.692
Ga	918	ppm	10	8.8	7.8	7.8	5.2	5.2	5.2	20	14	0.692	0.532	0.522	0.308	1.027
Na	970	ppm	5000	3190	3561	3635	6602	7048	7048	5786	6157	0.501	0.486	0.487	0.812	0.697
K	1000	ppm	558	498	415	415	747	913	830	581	747	0.701	0.508	0.498	0.883	0.683
Cu	1037	ppm	126	116	108	108	91	93	81	193	110	0.723	0.585	0.574	0.428	0.738
Rb	1080	ppm	2.3	1.7	1.45	1.25	2.9	3.1	3.1	2.6	2.5	0.581	0.430	0.364	0.776	0.652
P	1151	ppm	1220	1047	960	1091	1178	960	960	1920	1004	0.674	0.537	0.599	0.512	0.740
As	1157	ppm	1.86	1.9	2	2	2.1	1.5	1.3	3.7	2.7	0.803	0.734	0.720	0.555	1.036
Mn	1190	ppm	1990	1936	1859	1471	2401	2633	2711	2091	2168	0.764	0.638	0.495	0.755	0.626
Au	1225	ppm	0.14	0.18	0.18	0.18	0.23	0.16	0.17	0.4	0.31	1.010	0.877	0.861	0.811	1.519
Li	1225	ppm	1.5	1.5	1.8	1.8	1.7	1.8	1.8	2.1	0.58	0.786	0.819	0.804	0.693	0.575
Cr	1277	ppm	2660	2942	3284	3421	3558	3626	3695	2737	2189	0.869	0.843	0.861	0.802	0.553
Si	1311	%	10.64	13.54	15.59	15.89	17.11	18.57	18.98	16.69	20.19	1.000	1.000	1.000	1.000	1.000
Fe	1336	%	19.04	21.64	24.18	23.6	27.45	21.93	19.63	30.6	23.19	0.893	0.867	0.830	0.751	0.848
Mg	1340	%	9.89	11.99	13.85	14.62	14.03	14.91	15.21	11.06	14.43	0.953	0.956	1.003	0.871	0.739
Co	1351	ppm	502	560	700	618	834	551	481	900	700	0.877	0.952	0.824	0.789	0.955
Ni	1354	%	1.1	1.34	1.52	1.64	1.74	1.24	1.07	1.83	1.38	0.957	0.943	0.998	0.777	0.876
Pt	1411	ppm	0.99	1.3	1.7	1.7	1.3	0.78	0.8	1.1	2.2	1.032	1.172	1.150	0.604	0.922
U	1420	ppb	8.1	13	15	17	13	14	14	9	8	1.202	1.204	1.339	0.945	0.592
V	1450	ppm	56.5	75	92	96	74	77	75	54	60	1.043	1.111	1.138	0.791	0.586
Ca	1518	ppm	9280	13508	14723	18725	12436	13222	13722	9005	5360	1.144	1.083	1.351	0.825	0.474
La	1520	ppm	0.2347	0.317	0.387	0.486	0.295	0.31	0.315	0.235	0.19	1.061	1.125	1.387	0.767	0.541
Ti	1549	ppm	436	540	779	959	719	719	779	570	599	0.973	1.219	1.473	0.984	0.783
Ru	1573	ppm	0.712	0.83	1	1	1.1	0.75	0.5	1	1	0.916	0.959	0.940	0.732	0.824
Y	1592	ppm	1.56	2	2.4	2.4	2.2	2.1	2	1.3	1.3	1.007	1.050	1.030	0.810	0.489
Ir	1610	ppm	0.481	0.56	0.74	0.77	0.77	0.49	0.36	0.57	0.53	0.915	1.050	1.072	0.739	0.675
Sc	1644	ppm	5.82	8.15	9.6	11.3	7.95	8.6	8.35	5.7	7.4	1.100	1.126	1.300	0.844	0.645
Al	1650	ppm	8680	11484	15189	17041	11325	11908	11855	9473	11167	1.040	1.194	1.315	0.795	0.688
Os	1814	ppm	0.486	0.67	0.78	0.78	0.82	0.51	0.38	0.64	0.76	1.083	1.095	1.075	0.772	0.832
Re	1819	ppm	0.0365	0.051	0.058	0.058	0.079	0.046	0.035	0.053	0.061	1.098	1.085	1.064	0.964	0.905

* Ordinary chondrite, calculated from H, L and LL chondrites weighted by their fall frequency.

** Enstatite chondrite, calculated from EH and EL chondrites weighted by their fall freqwency.

abundances. The condensation temperatures of elements in Table 16 were taken from Wasson (1985, appendix G), who listed the fifty per cent condensation temperatures at a pressure of 10^{-4}atm for sixty four elements. Eighteen of these were not chosen because of the incompleteness or the inaccuracy of their abundances. Here refractory elements are divided into two subgroups: low refractory ($T_c \leq 1400$°K), and high refractory ($T_c > 1400$°K).

The abundances of all these elements (Table 16) were taken as follows. CI meteorites are taken from Anders and Grevesse (1989). Abundances of the fourteen elements Si, Ti, Al, Cr, Mg, Ca, Fe, Mn, Co, Ni, K, Na, P, and S of all othe types of meteorites are adopted from Jarosewich (1990): for CM, CV, H, L and LL chondrites, the data are his mean of meteorite falls; for CO, EH and EL, the data are his mean of found meteorites. The six elements Sc, V, Rb, La, Ir and U are from Kerridge and Matthews (1988, appendix 3). The remaining thirteen trace elements (Li, Cu, Zn, Ga, Ge, As, Y, Ru, Sn, Re, Os, Pt and Au) are from Mason (1971); since CO and CV are not separated, the abundances of C3 are used for both CO and CV subgroups.

The elemental data have been normalized to the mean Si in the same type and to the CI abundance. The normalized

element abundances for total ordinary chondrites (CH in Table 16) are calculated from H, L and LL chondrites weighted by their fall frequency, 33.2%, 38.3% and 7.9% respectively (Sears and Dodd 1988). The abundances for total enstatite chondrites are calculated fron EH ad EL weighted by their fall frequence, 0.84% ad 0.72% respectively (Sears and Dodd 1988).

The normalized element abundances of CM, CO and CV meteorites have been plotted against the condensation temperatures in Fig. 9 which shows that for the moderately volatile and low refractory elements, the normalized abundances have strong positive correlation with condensation temperature. For the highly refractory elements, the normalized abundances are constant, about 1.05±0.15. U, Ca, La, Ti, Sc and Al, have much higher abundances in CV meteorites (Fig. 9 c).

In Fig. 10 are shown the abundances for the mean ordinary chondrite (CH) and the mean enstatite chondrites (E). The linear relationship of moderately volatile and low refractory elements in ordinary chondrites (Fig. 10 a) is not as clear as it is in CM, CO and CV carbonaceous chondrites, and totally disappears in enstatite chondrites (Fig. 10 b).

Fig. 9 (a). CI-Si normalized element abundances and condensation temperatures in CM meteorites.

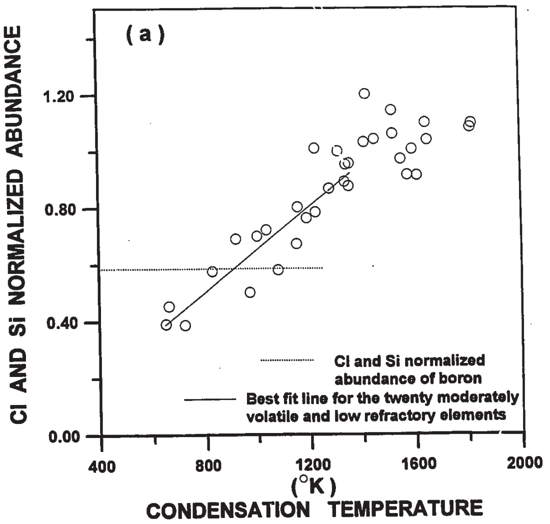


Fig. 9 (b). CI-Si normalized element abundances and condensation temperatures in CO meteorites.

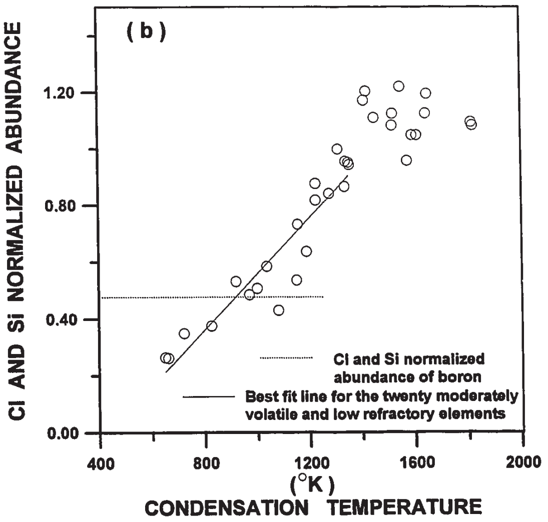


Fig. 9 (c). CI-Si normalized element abundances and condensation temperatures in CV meteorites.

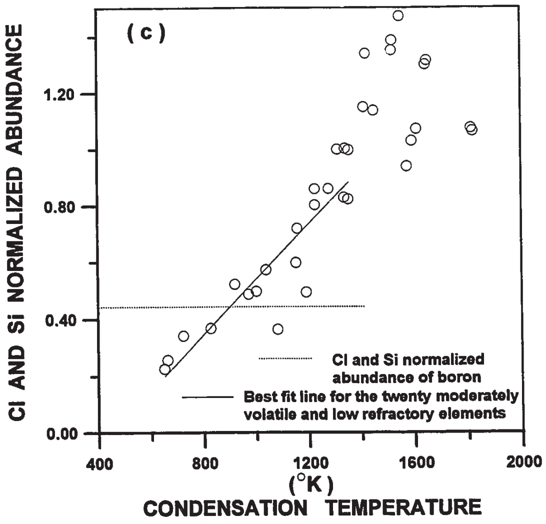


Fig. 10 (a). CI-Si normalized element abundances and condensation temperatures in ordinary chondrites.

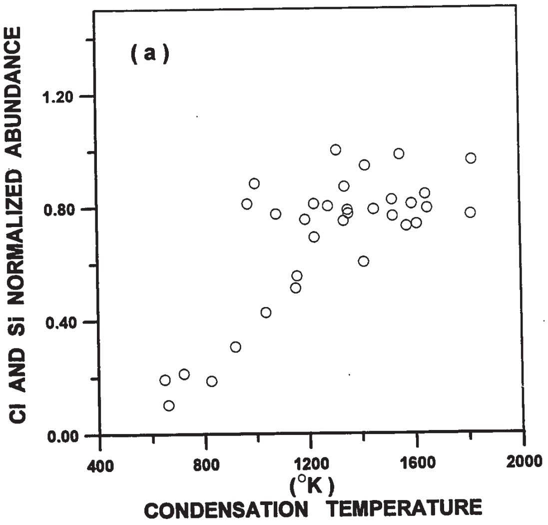
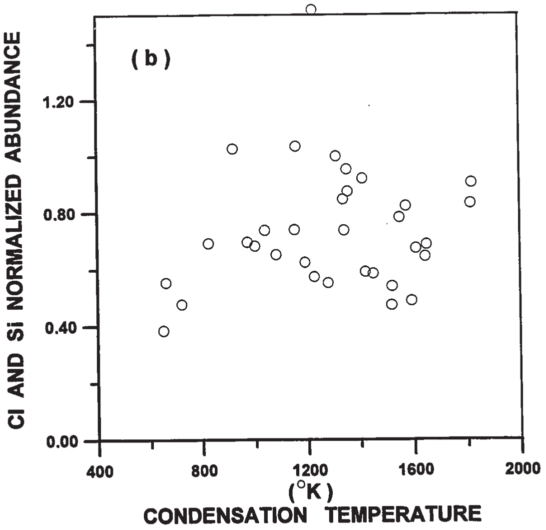


Fig. 10 (b). CI-Si normalized element abundances and condensation temperatures in enstatite chondrites.



There was a long-standing contention between two major theories which were used to explain the chemical compositions and the formation of chondrites: the two component theory and the volatile loss theory. Wood (1963), Anders (1964), Larimer and Anders (1967) and Anders (1968, 1975) described the two component theory: chondrites are composed of two components, one component has been heated to high temperatures losing moderately volatile elements more or less completely (high-temperature fraction = chondrules, metal grains); the other component is a low-temperature fraction (= matrix) contains moderately volatile elements.

Wasson and Chou (1974), Wai and Wasson (1977) and Wasson (1985) presented and explained the volatile loss theory. They studied the direct relationship of condensation temperatures and the moderately volatile element abundances, and found a strong correlation between CI and Si normalized abundances and their condensation temperatures for CM meteorites and ordinary chondrites. They concluded that these results can be understood in terms of a model in which volatiles are lost as gases prior to condensation or as finely divided solids that are incompletely agglomerated, and the condensation/agglomeration efficiency gradually decreases as a function of time (Wai and Wasson 1977).

Fig. 7 showed that the boron content in the matrix of CM, CO and CV meteorites is similar, and approximately equal to that in CI meteorites. This is true for other elements (McSween and Richardson 1977), and supports the two component theory. On the other hand, the linear relationship of CI and Si normalized abundances and the condensation temperatures for the moderately volatile elements and low refractory elements in carbonaceous chondrites is clear, and so the volatile loss theory is supported by present work too. Thus there is support for both these two theories.

No matter what is the detailed process of the formation of chondrites, the linear correlation of normalized abundances and condensation temperatures can be used to estimate the condensation temperature of boron. The average CI and Si normalized boron abundances for CM, CO and CV chondrites are 0.59, 0.48 and 0.44 (adopted or calculated from Table 12) and have been marked in Fig. 9 (a), (b) and (c), respectively. According to the best fit lines in Fig. 9 (a), (b) and (c), the related 50% condensation temperature at a pressure of 10^{-4} atm for boron should be about 910°K (900 - 920°K), between that of Ge (825 °K) and Na (970 °K), similar to that of Ga. In the light of the mineral phase stability of equilibrium nebular condensates (Dodd 1981, p. 57), the boron might condense in the end of the condensation of alkali feldspars, before the condensation of troilite. The analysis of Olsen et al. (1994) for a silicate inclusion which has a composition of H-chondrites, in the IIE iron meteorite, Watson, shows that 1.3 ppm boron occurs in alkali feldspar (which condenses at about 1000 °K), which is 6 to 10 times higher than the 0.13 ppm in olivine (which condenses at 1444 °K) and the 0.21 ppm in clinopyroxene (which condenses at 1450 °K) and 3.4 times higher than the 0.38 ppm in orthopyroxene (condenses at 1349 °K, Dodd 1981, p. 57). It seems that when the temperature decreases from 1450 to about 1000 °K, the proportion of boron condensed increases. Although the per centages of minerals and the boron concentration in the whole meteorite are unknown, the average boron content of these four minerals (0.5 ppm), is close to the average boron content in H chondrites (0.68 ppm, Table 8). Thus maybe boron is mainly exists in the silicates in meteorites.

CHAPTER 9. CONCLUSIONS

The present study of boron has shown that:

1. Alkali fusion followed by boron selective anion exchange resin purification method is unsuitable for silicates because of the precipitation in the chemical procedure and the consequent loss of boron. But the ion exchange procedure described here can be used to extract boron from water sample and calcite rocks, if they can be dissolved in HCl and have no precipitation when the solution is alkalized by NH_4OH, for their boron isotope analysis.

2. The boron obtained from the HF dissolution with cation exchange and anion exchange resins purification is not completely separated from other elements, and should be further purified for isotope analyses.

3. Although the standard deviation of the potassium borate mass spectrometry is larger than the cesium method, it is less than the sodium method, and is acceptable for boron isotope analyses.

4. The analyses of boron in meteorites by PGNAA can give reliable data, when the boron content is higher than 0.3 ppm, the 1σ relative standard deviations are equal to, or smaller than 15%.

5. Most meteorites have boron contents of 0.3 to 1.4 ppm. The average boron concentrations in different groups of meteorites are quite similar, from 0.5 to 0.9 ppm.

6. Normalized boron and sulphur abundances of carbonaceous chondrites and average ordinary chondrite show a linear relationship, and the boron contents in carbonaceous chondrites are the results of a mixture of matrix and chondrules. In carbonaceous chondrites, boron is mainly concentrated in the matrix (0.69 ppm), which is diluted by chondrules (0.23 ppm).

7. The boron solar-system abundance is 16.9±2.2 (atoms/10^6Si).

8. Boron solar system abundance support the nucleosynthesis model, in which the boron was formed by the continually bombardment of ISM by the GCRs, in which a very intense low energy is added.

9. Boron condensation temperature is about 910°K, between Ge (825 °K) and Na (970 °K), similar to Ga (918 °K).

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APPENDIX 1. REAGENT PREPARATION FOR ANALYSIS OF BORON ISOTOPE IN METEORITES

In order to decrease the analytical blank of boron, some reagents have been purified.

Water and hydrochloric acid. Because mannitol can suppress the evaporation of boron in water and hydrochloric acid (Feldman 1961, Ishikawa and Nakamura 1990), it can be used for their purification. The mannitol (Aldrich Chemical Company) was dissolved into the laboratory Milli-Q and analytical grade 37% HCl (CALEDON Laboratories Ltd) at a ratio of 2 g l^{-1}. These solutions then were put into a quartz still, and sub-boiling distilled. The same amount of mannitol is added into the distilled water and hydrochloric acid and distilled again. The double distilled water and hydrochloric acid were analyzed by isotope dilution, and their boron contents are about 4 ng/g and 5 ng/g respectively.

Ammonia hydroxide. In alkali solutions, boron is in the tetrahedral form, and is not volatile, therefore it is easier to purify ammonia hydroxide than water and acids.

The analytical grade ammonia hydroxide (Fisher Scientific Limited, NH_3 29%) was put into the quartz still, and sub-boiling distilled. The cooling water was cooled by ice in order to increase the velocity of distillation. The boron content in distilled ammonia hydroxide was determined by isotope dilution, and is about 0.7 ng/g.

Hydrofluoric acid. Mannitol (Aldrich Chemical Company) was added to the analytical grade 49% HF (Fisher Scientific Limited) at the ratio of 2 g l^{-1}. This solution was sub-boiling distilled in a two-bottle still made of teflon. The mixture of hydrofluoric acid and Mannitol was heated under the boiling temperature of HF, and the condensation bottle was cooled in water. The same amount of mammitol was added into the distilled HF and the solution was again distilled in a two-bottle still made of teflon. The double-distilled HF was analysed and its boron content is about 5 ng/g.

All solutions, include standards, acids, spike, potassium hydroxide etc., were made by dissolution of reagents in the mannitol distilled water, and were stored in FEP teflon bottles.

Potassium solution. Analytical grade potassium carbonate (BDH Chemicals) was dissolved in 0.1 N HF to give about 0.01 M K solution.

Mannitol solution. Analytical grade mannitol powder (Aldrich Chemical Company) was dissolved in mannitol distilled water to obtain a 1% (about 0.055 M) solution.

Graphite. Super pure (99.999%) graphite (Metron Incorporated) was suspended in 50% ethanol-50% water solution (v/v) to give 40 mg graphite/ml.

Boric acid. U.S. National Bureau of Standards Standard Referece Material (NBS SRM) 951 boric acid was used as a standard for the boron isotope measurements. The boric acid was dissolved in double-distilled pure water to obtain a 1000 μg/g B solution as the stock solution, and then diluted with double-distilled pure water to obtain a 100 μg/g B solution for the ordinary boron standard measurements. NBS SRM 952, boric acid enriched in ^{10}B, was used as a spike for isotope dilution mass spectrometry (IDMS). The spike was made by dissolving weighed NBS SRM 952 into weighed double distilled water to give 41.996 μg/g B.

Boron selective resin. Amberlite IRA 743 boron-selective resin was ground and wet screened to 55-100 mesh BSS. 2.0 ml of boron-selective resin was transferred to a polypropylene column whose internal diameter is 0.6 cm, rinsed with 10 ml of water, 5 ml of 3 M ammonia solution, 10 ml of water, 10 ml of 2 M HCl and 2×10 ml of water. Store the column in this situation.

Cation- and anion- exchange resins. Bio-Red AG 50WX12 and AG 1-X4 cation and anion exchange resins (200 - 400 mesh) were cleaned alternately with double distilled 6 N HCl and water several times, and stored in double distilled pure water.

Potassium carbonate. Analytical grade of potassium carbonate (BDH Chemicals) was used to fuse rock samples. No boron was found in this potasium carbonate when I analyzed using isotope dilution.

APPENDIX 2. PROCEDURE OF ALKALI FUSION WITH BORON-SELECTIVE ANION EXCHANGE RESIN PURIFICATION

The basic procedure of alkali fusion with boron-specific anion exchange resin purification is as follows:

Step 1. Weigh about 0.5 g rock powder into a 20-ml platinum crudible and mix it thoroughly with 2.5 g of potassium carbonate. Dry the crucible charge in an oven at 110°C for at least 1 hour. Fuse the mixture on a small flame at first by heating the tilted crucible tangentially and increase heating to full blast for 30 minutes when the vigor of the fluxing and effervescence subside.

Step 2. Cool the crucible to room temperature, put 10 ml water into the crucible and warm it on a small flame to about 90°C to transfer most parts of the fusion cake to a 50-ml polypropylene centrifuge tube. Very carefully drip 2M HCl into the centrifuge tube until the solution is acid and the fusion cake is dissolved thoroughly. Put drops of water and then HCl into the crucible to dissolve the rest of the fusion cake remaining in the crucible, and put all the solution in the centrifuge tube.

Step 3. Drip 3M NH$_4$OH to the test tube very cautiously to alkalize the solution to pH larger than 10. Separate the precipitate by centrifuging for 10 min.

Step 4. Transfer 2.0 ml of Amberlite IRA-743 resin (55-100 mesh) to a column which has internal diameter 0.6 cm. Rinse with 10 ml of water, 5 ml of 3M ammonia solution, 10 ml of water, 10 ml of 2M hydrochloric acid and 2×10 ml of water; this is also the procedure for regeneration between samples.

Step 5. Transfer the clear supernatant centrifugate to the resin column at a flow rate of 2 ml min^{-1}. Remove most of the potassium and other ions by rinsing the column with 10 ml of water, 5 ml of ammonia solution and 10 ml of water in that order. Elute the boric acid from the column with 2×5 ml of 2M HCl and collect the eluate in a polypropylene centrifuge tube. Repeat step 4 and 5 to purify boron sample again and collect the eluate in a teflon beaker.

Step 6. Put mannitol solution to protect boron at a ratio of 10 µg of mannitol per µg of boron. Heat the beaker to about 70 °C under an infrared light to dry the solution. Stop heating just before the solution is absolutely dried. Put KOH solution at a ratio of 2 µg potassium to 1 µg of

boron to dissolve the dried sample. Heat the solution just to dryness under an infrared light. This is the sample for the analysis by mass spectrometer.

Because no boron peaks were found when these samples were analyzed on the mass spectrometer, I have also tried some variations of chemical procedure and the results are listed in Table 17. It seems that all of these procedures can not avoid the precipitation and the following loss of boron when the solution was alkalized.

Table 17. The variations of the chemical procedure of alkali fusion with boron-selective anion exchange resin purification

No.	Variations of chemical procedure	Purpose	Result
1	Different size of resin grain	To improve ion exchange	No significant difference larger size of grain of resin need large volume
2	Different size of resin volume	To improve ion exchange	1.5-2.0 ml of IRA-743 resin (50-100 mesh) is enough to purify boron
3	Wash the precipitate by water or 3M NH4OH at the end of step 3	To wash back the boron if it is abstracted by the surfaces of precipitate	No boron was washed back, maybe the boron is in the structure of precipitate
4	Use only water to extract boron from the fusion cake and put this solution directly to the ion exchange column as in step 5	To avoid alkalization which cause the precipitation and the following boron loss	More than half boron still remained in the residue of the fusion cake
5	Methyl borate distillation after step 2	To purify boron without alkalization	Usually the yeild is smaller than 75% and need too much reagents (HCl etc.)
6	In the first step, use HF dissolution (silicon to be retained in solution) and followed by step 3	To try different way to dissolve rock smple	The precipitate still removed most boron when the sample solution was alkalized
7	In the first step, use HF dissolution (silicon to be lost by volatilization) and followed by step 3	To avoid precipitation by removing Si	Some Si still remains in the sample, thus there was precipitate when the solution was alkalized, and boron was lost
8	Different sample weight, from 0.3 to 0.8 g	To control the total amount of anion to avoid the saturation of resin	0.5 g of rock sample do not let the resin to be saturated
9	Different ratio of sample to potassium carbonate in variation 4	To try to get all boron when the fusion cake was dissolved into hot water	Some boron still remained in the residue of fusion cake

APPENDIX 3. PROCEDURE OF HF DISSOLUTION WITH CATION EXCHANGE AND ANION EXCHANGE RESINS PURIFICATION

The basic procedure of this method is as follows:

Step 1. Grind rock chips to minus 200 mesh by using an agate mortar and pestle. Weigh 0.3 g of rock powder to a teflon bomb. The sample was soaked with 0.3 ml 1% mannitol solution. Put spike for the IDMS (isotope dilution mass spectrometry). Add 2 ml of concentrated (about 30N) HF and tighten the cap using a wrench. Heat the sample-containing bomb in an oven at 75°C for 3 days.

Step 2. Cool the bomb to room temperature, open the cap, transfer the mixture of solution and solid into a 15 ml centrifuge tube. Rinse the bomb by 0.5 ml concentrated HF twice, and add that HF to the centrifuge tube. Centrifuge the solution for 10 min. Transfer the supernatant to a teflon beaker. Rinse the residual fluoride with 1 ml of 30N HF twice, after centrifuge, these supernatants were added to the teflon beaker too.

Step 3. Evaporate this solution very carefully to dryness on a hot plate at about 70 °C, stop heating when the solution was just dried. Add 0.5 ml of 6N HCl to the beaker to dissolve the dried sample and subsequently evaporate the solution to dryness at 70 °C to convert the sample to chloride.

Step 4. Transfer 3 ml of cation exchange resin AG 50WX12 into a polypropylene column. The resin bed was cleaned twice by 5 ml of 6 N HCl and then conditioned using 3 ml of 0.02 N HF. The chloride-form sample was then loaded onto the column, the solution flowing from the column was collected. The beaker was then rinsed with 0.5 ml of 0.02 N HF and this solution was loaded onto the same column. Rinse the column using 5 ml of 0.02 N HF as an eluent and collect all the eluate in a Teflon beaker. This solution was evaporated on a hot plate to nearly dryness.

Step 5. 0.3 ml of anion-exchange resin AG 1-X4 (200-400 mesh) was loaded onto a polyethelene column and cleaned with 2 ml of 6 N HCl twice and conditioned with 3 ml of 3 N HF. 0.6 ml of 3 N HF was added to the dried sample and warmed to 80 °C for 15 min. in a tightly sealed Teflon beaker. After cooling, the sample was loaded onto the anion-exchange column. 0.25 ml of mixed acid, composed of 2 N HCl and 0.5 N HF, was added to dissolve any sample

remaining in the beaker and this solution was also loaded onto the column. Wash the column using 1.2 ml of mixed acid. The boron fraction was then collected in a Teflon beaker using 2 ml 6 N HCl as an eluent. Add 0.02 ml of mannitol solution to protect the boron and evaporate it to nearly dryness.

Step 6. The sample was dissolved in 0.6 ml of 3N HF and goes through the anion exchange resin again following the procedure discribed in step 5 using the same column. The final boron fraction collected in a Teflon beaker containing potassium solution and mannitol to give B/K mole ratio of 2 and 50 µg of mannitol to 1 µg B, respectively. Evaporate this solution to dryness and the dried sample is stored for analysis by mass spectrometry.

Because no detectable boron peaks were found, some variations of chemical procedure have also been tried and the results are listed in Table 18.

Table 18. The variations of the chemical procedure of HF dissolution with cation exchange and anion exchange resins purification

No.	Variations of chemical procedure	Purpose	Result
1	Condition the anion exchange resin using 0.3 ml of 0.02 N HF at step 5	This is the original procedure of Nakamura et al. (1992)	No boron peaks were found when the sample was analyzed on the mass spectrometer
2	Add 3 drops of 3% phosphoric acid when evaporating the sample solution at steps 3, 4 and 5	To avoid complete dryness and the following loss of boron	The sample still did not run on mass spectrometer
3	Use different volume of cation and anion resin at steps 4 and 5	To avoid of saturation of cation and anion resin	The sample still did not run on mass spectrometer
4	At step 3, after evaporation of sample solution in HF (before add HCl) add some HF to redissolve the dried material and redry it again	To remove more silicon	No boron peaks were found when the sample was analyzed on the mass spectrometer
5	Use different weight of rock powder at step 1, from 0.1 to 0.8 g	To avoid saturation of cation and anion resin	The sample still did not run on mass spectrometer

APPENDIX 4. MASS SPECTROMETRY

The mass spectrometry procedure was mainly adopted from Nakamura et al. (1992) and Xiao et al. (1988).

Prior to sample loading, the Ta filaments used were outgassed for 15 min. at 10^{-6} Torr when heated to brightness. The filaments were then allowed to oxidize by the ambient atmosphere for at least one day.

These filaments were first treated with 1 µl of the graphite-ethanol-water slurry containing about 40 µg of graphite to coat the filament. Just before complete dryness of the graphite, the boron sample dissolved in 1 µl of 0.02 N HF was loaded on the graphite layer. The filament was then dried slowly with a current of 2.0-2.5 A passing through the coated filament.

A set of samples and standards was loaded into the mass spectrometer and the evacuation was started. When the vacuum reached 3×10^{-7} Torr, the filament current was rapidly raised to 0.5 A and then increased a further to 0.8-0.9 A slowly. In this range, K^+ (m/e=39) appeared and was used to focus the ion beam. When the ion current of K^+ was 1×10^{-12} A, $K_2{}^{11}BO_2{}^+$ becomes detectable with the Faraday cup collector. The filament current was then slowly increased until the ion current of $K_2{}^{11}BO_2{}^+$ reached about 1×10^{-12} to 1×10^{-11} A. The ratio of $K_2{}^{11}BO_2{}^+$ to $K_2{}^{10}BO_2{}^+$ was then measured against a base line at *m/e*=118.5. 150 to 300 ratios were collected in 10 to 20 blocks.

Because no detectable boron peaks were found in samples extracted from rock powder, the following variations of methods of analysis have also been tried:

1. without coating of graphite; but there is no difference for samples extracted from rock powder.
2. using the Daly detector to analyse weak boron peaks; but the boron peaks were still too small to be analyzed.
3. starting the analysis when the vacuum reached 6×10^{-7} Torr; there is no improvement.

The mass spectrometry analyses for silicate rock sample were not successful. Dr. Nakamura suggested that the type of graphite is important for the mass spectrometry. He said:

> "We have tested several types of graphite and finally found that spectroscopic graphite is the most suitable to get stable and high itensity measurement of B. The grain size of graphite is also another factor." (Nakamura 1993, private letter).

Thus the author recommends for the further mass spectrometry work:

1). to try different types of graphite for coating the filament;
2). to try negative ion mass spectrometry.

APPENDIX 5. EFFECT OF CHANGING THE CONCENTRATION OF HF TO CONDITION AG1-X4 ANION EXCHANGE RESIN

After checking the whole procedure, I found one disagreement in the paper of Nakamura et al (1992). In the section 3.3, when discuss the anion exchange chromatography, they said:

> "In order to further purify the boron obtained by the above procedure, we subsequently adopted the ion-exchange chromatography in F^- form".

But in their analytical procedure (section 2.3.3.2), just before loading the sample to the anion exchange resin, they said:

> "0.3 ml of anion-exchange resin was loaded onto a polypropylene column and cleaned with 2 ml of 6N HCl at least twice and conditioned with 0.3 ml of 0.02 N HF. 0.6 ml of 3 N HF was added to the dried sample obtained after the major cation separation and warmed to a temperature of 80°C for 15 min. in a tightly sealed Teflon beaker. After cooling to room temperature, the sample solution was loaded onto the anion-exchange column."

The relative selectivity of F^- and Cl^- for AG 1-X8 are 1.6 and 22 respectively (Bio-Red 1993), the data for AG 1-X4 should be similar. Thus after cleaning using 2 ml of 6N HCl, the 0.3 ml resin must be in Cl^- form no matter its original form is F^- or OH^-, but 0.3 ml of 0.02 N HF can not change the resin from Cl^- to F^- form. In order to change 0.3 ml of AG 1-X4 resin from Cl^- to F^- form, we need at least 4 ml of 1 N HF or 1.4 ml of 3 N HF. In their procedure the anion resin before loading of sample was Cl^- form, but not F^- form. Therefore I tried to use 2-3 ml of 3N HF to condition the anion exchange resin, to convert the resin from Cl^- form to F^- form and then load sample solution onto the column.

The first two sets of samples, just after I changed the concentration of HF, gave some data (Table 4). The data of two isotope analyses and three boron concentration analyses are reasonable. But after that I have analyzed many sets using 3 N HF to condition the anion exchange resin or using 0.02 N HF, and have not get any results.