THE USE OF BORON CONCENTRATIONS IN FOSSIL MATERIALS AS A PALEOSALINITY INDICATOR

Thesis by

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ABSTRACT

The $^{10}B(n,\alpha)^{7}Li$ nuclear reaction has been used in conjunction with alpha-sensitive plastic track detectors to determine boron concentrations in various biologically precipitated minerals. A correlation between the boron concentration in the water in which the precipitating organisms grew and the boron concentration in the materials analyzed was found in specimens of *Mytilus edulis*, related bivalves, diatoms, and siliceous sponge spicules. *M. edulis* shell boron concentrations in aragonite ranged from about 5 ppm in specimens from 5 ^{o}/oo salinity water to about 15 ppm in specimens from 35 ^{o}/oo salinity water. Salinities can not be distinguished quantitatively using carbonate shells beyond the general distinction of marine, brackish, or nearly-fresh water. Fossil shells showed evidence for some loss of boron from aragonite. Freshwater diatomites contained less than 10 ppm B, while marine diatomites and unconsolidated marine core samples contained about 100 ppm. Detailed studies of live-collected sponge spicules established that individual spicules larger than 20-25 microns in diameter can be analyzed, and that there is a correlation with water salinity for sponges from regions of low water temperature and high productivity. Measured concentrations ranged between nearly 0 for fresh-water sponges to 600-700 for marine sponges. However, spicules from sponges from tropical, low-productivity marine locations contained markedly less boron. The exact relationships between B concentration in the spicules and concentration in the water, temperature, nutrient supply, and food sources for the sponges are not known. Pleistocene spicules from deep-sea cores tended to contain somewhat less boron than might be anticipated by comparison with live-collected spicules based on present water temperatures and nutrient supplies. It is uncertain whether the lower concentrations are the result of diagenetic processes or the unknown effects of differences in the food supply and/or environmental conditions. Until the significance of the boron concentration in spicules is understood more fully, paleosalinity determinations will not be possible. If a relationship between boron content and water temperature or nutrient supply can be defined, it may be possible to use boron concentrations in spicules to trace oceanic circulation patterns in the past.

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I. INTRODUCTION

One of the keys to the interpretation of marine paleoenvironments is a means of determining paleosalinities. In addition to understanding the geologic history of particular locations, it would also be desirable to understand the history of the oceans on a broad geographic scale. It is believed that the composition of the oceans has been fairly uniform (within a factor of two of present ionic composition) since the Middle or Late Precambrian (Rubey, 1951; Lowenstam, 1961; Moore, 1971; Holland, 1972). However, even a factor of two difference in either direction of the total ionic composition or in the contents of one or more of the major ionic species would have profound effects on marine life as we know it today, and also on sedimentary and diagenetic processes occurring on the ocean floor. If the proportions of the different ions were significantly altered, the pH of the sea would change, and the CO_2 equilibrium between the ocean and the atmosphere would be upset (Rubey, 1951; Sillén, 1961; Garrels and Perry, 1974). The ability of organisms to tolerate changes in salinity is closely tied to their needs for and abilities to regulate their internal ionic composition and osmotic pressure. Most marine invertebrates are <u>stenohaline</u> (able to survive only in water of normal salinity) and have fluids which are isotonic (of equal salt concentration) with sea water. When they are subjected to changes in salinity they are unable to maintain the internal fluid composition which they require for survival; when placed in water of reduced salinity they absorb water and increase their volume. Organisms which can tolerate salinity variations are euryhaline. They may either be able to tolerate wide variations in internal concentration and not be as seriously affected by the changes in internal fluid volume and composition, or they may have the capability of regulating their internal fluid composition independently of the external medium (Gunter, 1947; Pearse and Gunter, 1957). Few organisms are able to withstand variations in salinity greater than 25% from normal marine conditions.

At this point a definition of salinity is in order. It is "the total amount in grams of solid material dissolved in 1 kg of seawater when all the carbonate has been converted to oxide, all the iodine and bromine have been replaced by chlorine, and all the organic matter has been completely oxidized" (Duxbury, 1971). In practice, precipitation of silver halides is used to determine the water chlorinity (the sum of the masses of all the halides, chloride, bromide, and iodide contained in 1 kg of water), and is typically determined to a precision of ± 0.05 $^{o}/oo$. The salinity is calculated from the chlorinity by assuming a constant halide/total salt ratio, or determined from the water density (Mason, 1966). It has been found that, within the uncertainties of measurement, the following elements occur in constant ratio to the total salt content: sodium, potassium, rubidium, cesium, magnesium, strontium, boron, sulfur, fluorine, chlorine, and bromine. Variations of only 1 % are found in the ratio of calcium to total salt (Broecker, 1974). Together, these elements make up over 99 % of the dissolved solids in sea water (Mason, 1966). Both chlorinity and salinity are commonly expressed in units of g/kg of water or parts per thousand (^{o}/oo); sea water has a chlorinity of about 19 ^{o}/oo and a salinity of about 35 ^{o}/oo. Except for very localized situations such as industrial pollution or estuaries of rivers which drain very unusual types of rocks, variations in salinity are due to varying degrees of dilution by water or concentration by evaporation of water.

A survey of the literature of boron concentrations in sea water from a wide variety of locations indicates that the ratio of B/Cl is constant to within about 10 %, independent of the body of water, sample depth, and latitude. Data obtained as early as the 1930's agree well with data obtained since 1970. A summary of a large number of analyses is contained in Table I. It can be concluded that even for semi-isolated basins such as the Baltic and Mediterranean Seas, the proportionality of B to Cl is maintained.

It is believed that some changes in sea water composition have occurred, in particular changes in the Ca/Mg ratio, the SiO_2 content, and the saturation depth for calcite. These changes have been attributed to the rapid increase in abundance during the Cretaceous of a variety of planktonic organisms, including foraminifera, coccolithophoridae, diatoms, and radiolarians (Loeblich and Tappan, 1964; Garrison and Fischer, 1969; Berger and Winterer, 1974; Lowenstam, 1974; Bosellini and Winterer, 1975). These organisms precipitate opal or low-magnesium calcite. Before the Cretaceous, biogenic carbonates were composed mainly of high-magnesium calcite and aragonite. Each form has different solubility characteristics. The shift of the major biologic production of calcium carbonate from continental shelf areas to the open oceans, coupled with the different solubility of

TABLE I: Boron Concentrations in Sea Water

Body of Water	Maximum B/Cl[a] B(ppm)/ 0/00	Miminum B/Cl[a]	Mean B/Cl[a]	Method	Author
Pacific Ocean			.239	electrometric	Moberg & Harding 1933
	.227	.221	.224	mannitol	Igelsrud, et al. 1938
	.225	.219		mannitol	Gast & Thompson 1958
	.246	.211		1,1'-dianthrimide	Gassaway 1967
	.243	.224		curcumin	Uppstrom 1974
Atlantic Ocean	.264	.224		electrometric	Rakestraw & Mahncke 1935
	.226	.205		mannitol	Noakes & Hood 1961
	.251	.239		mannitol	Ryabinin 1972
	.244	.239		mannitol	Barannik 1972
	.256	.226	.241	mannitol	Barannik, et al. 1972
Mediterranean Sea	.250	.224	.232	mannitol	Fossato 1969
(hypersaline)	.244	.235		mannitol	Barannik 1972

cont.

TABLE I (page 2)

Body of Water	Maximum B/Cl[a] B(ppm)/ 0/00	Minimum B/Cl[a]	Mean B/Cl[a]	Method	Author
Thames Estuary (hyposaline)	.24	.23		ferroin borodisalicylate	Matthews 1974
Baltic Sea (hyposaline)	.245	.230		curcumin	Dyrssen & Uppstrom 1974[b]
	.334	.219	.252	mannitol	Kremling 1975[c]

[a] B/Cl expressed in units ppm/ 0/00

[b] B(mg/kg) = 0.227 x CL(0/00) + 0.050

[c] Only 12 of 112 determinations had B/Cl > .270; only 5 had B/Cl > .290

carbonate produced in the open ocean, probably has had long-term effects on the oceanic Ca and Mg budgets (Lowenstam, 1974). The sudden increase in biogenic opal production and a possible decrease in abundance of previous Si-precipitating organisms probably also had significant effects on the dissolved SiO_2 distribution in the oceans.

Means of Paleosalinity Determinations

A. Mineralogy

In some cases the sediment mineralogy is determined wholly or partially by the salinity of the environment. Evaporites indicate hypersaline conditions. Because the major ionic composition of sea water is uniform, there is a definite sequence of salts which precipitate upon continued evaporation, beginning with iron and calcium carbonates, then gypsum, halite, and magnesium sulfate and magnesium chloride. A layered sequence of these minerals is indicative of a marine evaporite deposit, while the occurrence of a variety of other evaporite minerals such as borates or nitrates is associated with non-marine deposition (Krauskopf, 1967). The lack of major deviations from the sequence of minerals in marine evaporite deposits has been used as evidence in support of constant ionic composition of the sea (Moore, 1971; Holland, 1972).

Clay mineralogy may also be used to infer the salinity of the depositional environment. (See, for example, Millot, 1952; Murray, 1954; Grim and Johns, 1954; Keller, 1956.) Marine clays often contain abundant illite $[K_{1.0-1.5}Al_4(Si_{7-6.5}Al_{1-1.5})O_{20}(OH)_4]$, while kaolinite $[Al_4Si_4O_{10}(OH)_8]$ is associated with low-pH fresh-water bodies in regions with high precipitation rates and montmorillonite

$[(\frac{1}{2}Ca, Na)_{0.7}(Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4 \cdot nH_2O]$ formation is associated with high-pH freshwater bodies in arid regions. However, clay minerals are easily transported and the sites of formation and eventual deposition can be widely separated, sometimes by thousands of kilometers. The composition of the clays is also dependent on the composition of the starting material and the extent of equilibration during the weathering process. Further, salinity determinations are not quantitative.

B. Faunal assemblages

Traditionally, paleontologists have relied on fossils to indicate salinity. By analogy with modern counterparts, the salinity tolerance of the fossil organisms is inferred. However, one has no way of knowing whether the tolerances were the same in the past, particularly when there are no closely related extant forms. Organisms which can tolerate brackish water generally also can tolerate hypersaline water. Further, brackish-water regions tend to be populated by euryhaline marine species rather than fresh-water species (Pearse and Gunter, 1957). The greater the deviation from normal marine salinity, the fewer species are generally found. Often a decrease in size accompanies salinity deviations. An increased abundance of a limited number of species may be indicative of either hyper- or hyposaline conditions; the two cases are often indistinguishable in the fossil record, unless primary evaporite minerals such as gypsum, halite, or epsomite are also found. At best, the faunal assemblage can give only a qualitative indication of the paleosalinity.

C. Shell morphology and mineralogy

A few modern species of molluscs exhibit shell morphologies which differ with salinity (Eisma, *et al.*, 1976). However, the salinity-controlled features are limited to isolated species or genera and can not be used for paleosalinity determinations except when the proper organisms are found. In a few types of carbonate shells which contain both calcite and aragonite, the ratio of aragonite to calcite has been found to increase with decreased salinity (Dodd, 1963, 1966; Lowenstam, 1974; Eisma, 1966). For the species which have been shown to exhibit this phenomenon, the calcite/aragonite ratio in fossil shells can be used to determine paleosalinities. Diagenetic alteration of aragonite to calcite and temperature-induced variations in the ratio must, however, be considered (Lowenstam, 1974). It is cumbersome to systematically study a large number of organisms to find the few which have shell morphologies and/or mineralogies which vary with salinity. The use of these shells is obviously limited by their earliest occurrence in the fossil record.

D. Carbon and oxygen isotopic compositions

Carbon and oxygen isotopic compositions in carbonate shell material can be measured by mass spectrometry and used to determine salinities (Epstein and Mayeda, 1953; Keith, *et al.*, 1964; Mook and Vogel, 1968; Fritz and Poplawski, 1974; Grazzini, 1975; Williams, *et al.*, 1978). $\delta^{13}C$ and $\delta^{18}O$ are defined:

$$\delta^{13}C = 1000\left(\frac{^{13}C/^{12}C\ (\text{sample})}{^{13}C/^{12}C\ (\text{standard})}\right) - 1$$

$$\delta^{18}O = 1000\left(\frac{^{18}O/^{16}O\ (\text{sample})}{^{18}O/^{16}O\ (\text{standard})}\right) - 1.$$

C analyses are reported relative to the Peedee Belemnite (PDB) standard and O analyses are reported relative to Standard Mean Ocean Water (SMOW). The carbon isotopic composition of shells depends on the source of the carbon ingested by the precipitating orgnnism. Freshwater shells have C isotopic compositions ranging from $\delta^{13}C = -15.2$ to -0.6 while marine carbonate shells have compositions ranging from $\delta^{13}C = -1.7$ to $+4.2$ (Keith, et al., 1964). Oxygen isotopic ratios in freshwater vary as a function of latitude and the amount of water tied up in polar ice caps. The composition of brackish water depends largely on the composition of the fresh water that is mixed with sea water (Epstein and Mayeda, 1953). Oxygen isotopic compositions for freshwater carbonates range from $\delta^{18}O = +16.8$ to $+ 22.8$ and values for marine carbonates range from $\delta^{18}O = +25.6$ to $+30.5$ (Keith, et al., 1964). Thus, freshwater shells have C and O isotopic compositions that are highly variable but readily distinguished from marine shells. The variations in both carbon and oxygen compositions of shells due to water salinity variations are about an order of magnitude larger than those due to temperature variations (Epstein and Mayeda, 1953; Epstein et al., 1953). Under ideal circumstances, marine and freshwater shells can be readily distinguished, but quantitative salinity determinations are prevented by the large variations in isotopic composition of the freshwater sources (Epstein and Mayeda, 1953; Fritz and Poplawski, 1974). For fossil samples, uncertainties in these freshwater compositions become increasingly important. In addition, diagenetic effects must be considered for fossil specimens; re-equilibration of C and O isotopic compositions may occur (Lowenstam, 1961). The nature of the isotopic changes is dependent on the temperature and the composition of the water involved in the reactions. If isotopic variations within a single shell can be shown to have a correlation with growth increments or other features related to shell formation, it can be assumed that diagenetic alteration is minimal. In other cases, it may be difficult to determine the extent of alteration. Recrystallization of the shell as evidenced by microscopic examination is a clear indication of alteration of the isotopic composition (Lowenstam and Epstein, 1954; Odum, 1957; Lowenstam, 1961).

E. Trace elements

Some types of carbonate shells show a correlation of Sr and/or Mg concentration with water salinity (Chave, 1954; Lowenstam, 1961; Dodd, 1965); depending on the species, the relationship may be quite sensitive. However, the temperature-related variations in Sr and Mg carbonates are of comparable magnitude to the salinity effects. When combined with oxygen isotopic data, it is possible to distinguish qualitatively the contributions of salinity, temperature, and diagenesis to the final composition (Lowenstam, 1961).

A variety of other trace elements present in sea water have been investigated for possible correlations between salinity and concentrations in shell material and sediments, including boron, lithium, chromium, vanadium, copper, manganese, barium, lead, magnesium, iron nickel, cobalt, silver, zinc, tin, gallium, rubidium, beryllium, molybdenum, and sodium. Only boron was found to exhibit such a relationship with its concentrations in both shell material and clay minerals directly correlated to water salinity (Degens, *et al.*, 1957, 1958; Leutwein and Waskowiak, 1962; Potter, *et al.*, 1963; Cody, 1971; Veizer, *et al.*, 1977; Furst, *et al.*, 1976).

F. Boron

A variety of workers have investigated the use of the boron content of sediments as a paleosalinity indicator. (See, for example, Landergren, 1945a,b,1948; Frederickson and Reynolds, 1960; Eagar, 1962; Curtis, 1964; Spears, 1965; Walker and Price, 1963; Walker, 1964,1968; Fleet, 1965; Eagar and Spears, 1966; Levinson and Ludwick, 1966; Lerman, 1966; Cody, 1968,1970; Sukhorukov and Yemel'yanov, 1969; Harder, 1970; Couch, 1971; Dewis, *et al.*, 1972; Perry, 1972; Liss and Pointon, 1973; Bohor and Gluskoter, 1973; Kazakov, *et al.*, 1975; Timofeyev, *et al.*, 1976). The boron in sediments has been found to be associated primarily with clay minerals, and particularly with illite $[K_{1.0-1.5}Al_4Si_{7-6.5}Al_{1-1.5}O_{20}(OH)_4]$. It is bound frrmly in the clay crystal lattice, probably substituting for tetrahedrally-coordinated aluminum (Eugster and Wright, 1960; Stubican and Roy, 1962) and remains even when the clays are treated with HCl (to remove adsorbed boron). A correlation of boron in illite with water salinity has been found in many cases, but it is not always a reliable indicator. Generally the clay fraction is estimated or isolated by treatment of the sediments with HCl and KOH or NaOH. X-ray diffraction is then used to determine the fractions of illite and other clay minerals present (Frederickson and Reynolds, 1960; Walker and Price, 1963; Walker, 1964, 1968; Spears, 1965; Reynolds, 1965; Bohor and Gluskoter, 1973). Both the boron and the potassium concentrations in the clay fraction are measured. Making an assumption of how boron is distributed among the clay minerals present and that the potassium is found only in illite, the boron concentration in illite can be calculated.

Several problems are inherent in the use of B in illite for paleosalinity determinations.

1. Detrital K-feldspar is not removed in the chemical treatment and may give an anomalously high K content.

2. The illite may not have an ideal composition; the alkali site may contain cations other than potassium.

3. Mixed-layered illite/montmorillonite and illite/kaolinite occur commonly and are not readily handled.

4. The boron content of the illite may not reflect the final depositional environment, e.g., marine sediments redeposited in a lake will have high B contents.

5. The mechanism of B fixation in the crystal lattice is unknown and may occur during diagenesis, when the clays are in contact with a fluid whose composition differs from sea water.

6. The technique is not quantitative, and appears to need a separate calibration for each sedimentary section. Remarkable

variations in boron concentrations are observed by the different workers, ranging from around 150 ppm to 500 ppm for marine illites (Frederickson and Reynolds, 1960; Eagar, 1962; Walker and Price, 1963; Walker, 1964, 1968; Curtis, 1964; Spears, 1965; Reynolds, 1965; Levinson and Ludwick, 1966; Shaw and Bugry, 1966; Cody, 1970; Bohor and Gluskoter, 1973).

Scope of this Research

This research was undertaken to develop a quantitative technique for paleosalinity determinations based on the B content of biogenic minerals. The first goal was to find one or more groups of organisms which incorporate B into their mineralized tissues in proportion to B in the water, hopefully concentrating it relative to the water. Both carbonate and opal skeletal materials were studied. Although most of this work has been on live-collected specimens, some fossil forms have also been studied to establish the usefulness of biologic materials for paleosalinity determinations. By using fossil material, one can obtain direct evidence of the extent of diagenesis for a particular sample by a variety of techniques. The O and C isotopic compositions can be measured and used as an indicator of possible exchange with ground water. Infrared spectroscopy can provide a rapid identification of the mineral(s) present in the sample, thereby demonstrating possible recrystallization and/or dehydration of the original materials. The relative amounts of calcite and aragonite or the degree of crystallinity of siliceous skeletal material can be determined with X-ray diffraction. Chemical tests can be used to verify the composition of samples, particularly the electron microprobe. Examination of samples with a scanning electron microscope can reveal a great deal of information about the sample surfaces and can be conducted simultaneously with elemental analyses. On the basis of sediment petrography one can often determine that shell formation and deposition in the sediments occurred in the same place, thus avoiding the problem of detrital versus authigenic origin of clay minerals. In addition, it was hoped that better precision would be possible for paleosalinity determinations based on B in fossil materials than is presently available by other techniques. A B-salinity relationship which is valid at a high taxonomic level would ensure a good chance of finding appropriate organisms in the fossil record.

The radiographic method of boron determination is well-suited for this type of study. Analyses of very small amounts of material, such as individual sponge spicules (20 x 100 microns) are possible. It is nondestructive in the sense that the same samples can be re-analyzed many times, and are still available for additional experiments. One can readily obtain the spatial distribution of B and often determine when and why results are anomalous by microscopic examination of the actual sample analyzed. Chemical treatment of samples is minimal and chances of contamination or alteration are minimized. Because one can choose appropriate areas for B determination, a small amount of extraneous material does not interfere with analyses.

II. EXPERIMENTAL DESCRIPTION

The radiographic technique employed in this study is described in Furst, et al. (1976) (Appendix I). A more complete discussion of some general aspects of sample handling, data collection, and analysis is contained here. Boron determinations were made by placing a plastic detector which is sensitive to alpha particles over each sample. Neutron irradiation results in the emission of alpha particles from the $^{10}B(n,\alpha)^{7}Li$ reaction. Those alpha particles which are produced in the surface layers of the sample can enter the plastic detector and cause radiation damage. After irradiation, the detector is chemically etched. The radiation-damaged areas etch faster than the bulk plastic and conical-shaped holes or "tracks" result. The tracks can be counted with a scanning electron or optical microscope, typically at 1000x or greater magnification.

Two types of plastic alpha track detectors were used. A specially prepared cellulose nitrate (USF4-b) was obtained from Dr. E. V. Benton of the University of San Francisco. After storage in our laboratory for over a year, this material began to show locally excessive surface pitting and proved somewhat unreliable for obtaining countable tracks. The plastic employed for most analyses was Kodak-Pathe cellulose nitrate CA80-15, which is commercially produced specifically for alpha radiography. It generally has very smooth surfaces, a relatively uniform etching rate, and nicely developed tracks. Detectors from some of the latest irradiations had numerous small pits; apparently the plastic deteriorates with time and an effort must be made to use fairly fresh material.

All plastics were stored in mylar or other air-tight plastic wrappers to minimize background alpha tracks from atmospheric radon decay. The plastics were also kept in a freezer in the laboratory with a filtered air supply to minimize oxidation and exposure to smog.

Detectors were not etched until at least twenty-four hours after irradiation because complete registration appears to require exposure to oxygen or air for a period of about 24 hours in some plastics. The detectors were usually etched within two weeks after irradiation, or kept in a freezer if storage times longer than one month were anticipated. These precautions were taken to avoid introducing errors into observed track densities due to deterioration of the plastic.

The etching solution was 6 N. NaOH. The temperature was maintained at about 30° C to allow etch times which were long enough that minor variations in time did not significantly affect track development and short enough to be practical; etching times ranged from 60-110 minutes, depending on the track density, the counting procedure used, and the appearance of the tracks. The appropriate etching times were selected after determining that the observed track density was independent of etch time between 60 and 110 minutes at 30° C. Samples and standards were etched together to minimize possible differences in the degree of etching. After etching, detectors were generally mounted permanently on microscope slides with double sticky tape. After counting, samples were stored in darkness in order to avoid deterioration of plastics due to light.

Irradiation Conditions

All irradiations were carried out at the UCLA Nuclear Energy Laboratory. The thermal column of the reactor provided a well-thermalized uniform flux over a volume which was about 10" x 2" x 1", verified by fission track analyses using uranium foil flux monitors with mica detectors. Total fluences were between 1×10^{11}-5×10^{12} neutrons/cm^2, with irradiation times of approximately 30 minutes.

Standards

The B standards used in this work were epoxy-mounted polished sections of National Bureau of Standards SRM 610 and 612. These materials are soda lime glasses with a number of elements added in nominal concentrations of 500 ppm and 50 ppm, respectively. SRM 610 contains 351 ppm B, determined by isotope dilution, while the NBS gives no official value for the B in SRM 612 (National Bureau of Standards Certificates of analysis, 1972). SRM 610 has a uniform B distribution, but there are inhomogeneities of 20% or more on a 2-mm scale in SRM 612, in agreement with findings by Carpenter (1972). Thus, a specific area was chosen on each piece of 612 glass and independently calibrated relative to SRM 610, yielding B concentrations between 35 and 40 ppm. This is slightly higher than the 32.4 ppm found by Carpenter (1972). Both glasses contain Li in amounts comparable to B, and corrections were made assuming 350 ppm Li in SRM 610 and 33 ± 3 ppm in SRM 612. Because the concentrations in the lower-B standards are only known to 5-6% standard deviations (due to counting statistics and uncertainties in B and Li contents of the two glasses), the accuracy of B determinations in actual samples is also limited to about 6%. However, it should be noted that the conclusions drawn from the data obtained in this work depend only on the ratios of track densities and boron concentrations, and not on the absolute concentrations.

Blanks

Several types of blanks and control samples were used in B determinations. Each irradiation included two pieces of cellulose nitrate plastic irradiated facing each other, as a check on the cleanliness and surface condition of the particular sheet of plastic used. Polished sections of SiO_2 glass tubing and/or cleavage slices of single crystals of calcite (Hilton Deposit, San Diego Co., California) were included as a check on the extent of contamination during polishing and other sample handling procedures. These two materials were chosen because of the chemical similarity to the actual samples analyzed and because of their low B contents (<0.3 ppm in the calcite and less than 1 ppm in the glass). Typically, the track density for the plastic-on-plastic blank was about a factor of two higher than the calcite blank; this was attributed to a 4π geometry for track production in the plastic and a 2π geometry for track production in the other materials.

Background Track Density

The background track density in all types of detectors used was equivalent to about 0.3 ppm B and provides a limit to the sensitivity of the technique. The sources of these tracks are the $^{17}O(n,\alpha)$ reaction, recoil tracks from fast neutron interactions with the plastic and possibly a small contribution of proton tracks from the $^{14}N(n,p)^{14}C$ reaction. Oxygen and nitrogen are major constituents of the plastic detectors and therefore can not be excluded from the experiment. Detectors which were immersed in distilled water during irradiation had track densities comparable to those found for blanks. Because of the high oxygen content of water, it is apparent that the $^{17}O(n,\alpha)$ reaction is not a major contributor to the background track density. The contribution from fast neutrons can be minimized by irradiating samples with a well-thermalized neutron flux; irradiations for this work were carried out in the thermal column of the UCLA reactor, with a thermal/epithermal ratio of 50 or more. Additional background "tracks" arise from imperfections in the surface of the plastic detectors. Considerable effort has been extended toward obtaining plastics with smooth surfaces and handling them in such a way as to minimize damage to the surfaces. Unirradiated plastic had negligible track densities.

Interference from Lithium

The technique used in this work exploits the comparatively unique nuclear property of ^{10}B, its large cross section for the (n,α) reaction. Lithium is the only element which provides significant interference in B determinations with this track technique. The $^{6}Li(n,\alpha)^{3}H$ reaction has a cross section of 950 barns, with an alpha energy of 2.05 MeV (Lederer, Hollander, and Perlman, 1967). By comparison, ^{10}B has a cross section of 3840 barns; 90% of the alpha particles will have an energy of 1.47 MeV and 10% will have 1.9 MeV. If the sample is "infinitely" thick, i.e., thicker than the range of the alpha particles, the result will be a continuous distribution of track lengths from 0 to a maximum value dependent on the alpha energy. The tracks arising from the two different nuclei (B and Li) are therefore indistinguishable on the basis of length or width. Assuming that alphas from the two reactions are recorded with equal probability, the efficiency for detecting Li relative to B can be calculated by comparing the abundances of the appropriate isotopes, the reaction cross sections, and the alpha ranges for the two elements, as shown in Equation 1:

$$\frac{\rho(\mathrm{Li})}{\rho(\mathrm{B})} = \frac{{}^{6}\mathrm{Li}}{{}^{10}\mathrm{B}} \cdot \frac{\sigma({}^{6}\mathrm{Li})}{\sigma({}^{10}\mathrm{B})} \cdot \frac{R(\mathrm{Li})}{R(\mathrm{B})} \qquad (1)$$

where $\frac{\rho(\mathrm{Li})}{\rho(\mathrm{B})}$ is the track density ratio for Li relative to B; $\frac{{}^{6}\mathrm{Li}}{{}^{10}\mathrm{B}}$ is the ratio of concentrations of the two nuclei; $\frac{\sigma({}^{6}\mathrm{Li})}{\sigma({}^{10}\mathrm{B})}$ is the ratio of the cross sections for (n,α) reactions of the nuclei in parentheses; and $\frac{R(\mathrm{Li})}{R(\mathrm{B})}$ is the ratio of the ranges of alphas originating from ^{10}B and ^{6}Li. For a glass of the composition of NBS SRM 612 (used as a standard in this work), the ranges for Li and B alphas are 1.67 and 1.28 mg cm^{-2}, respectively (Northcliffe and Schilling, 1970), and the ratio of the two ranges is essentially independent of the material. For equal concentrations of B and Li in the material, a theoretical relative Li/B efficiency of 0.12 results.

The relative efficiency of detection of Li and B has also been determined experimentally. Materials containing either Li or B in known amounts were irradiated and tracks were counted in the detectors. A summary of the results is presented in Table II. The spodumene, petalite, and two of three LiF samples were powders which had been pressed into pellets; all of the other specimens were epoxy-mounted polished sections. Excellent agreement of detection efficiencies was obtained for the three B-containing materials, while the data for Li minerals show considerably more scatter. However, LiF has an order of magnitude more Li than the other materials, and some reduction in track density may have occurred due to self-absorption of neutrons in the thick solid LiF sample. $LiNbO_3$ has a very different alpha range because of the high atomic weight of Nb, and the calculated ratio of its range to that in the other materials may not be correct. Because the $LiNbO_3$ was a high purity synthetic preparation and was known to be stoichiometric in Li, its detection efficiency was included in the average. It is also conceivable that either the LiF or the $LiNbO_3$ were synthesized using Li with an unnatural isotopic composition. Efforts to determine the sources of Li used in manufacturing these particular materials were unsuccessful. In conclusion, the experimentally determined efficiency of detection of Li relative to B is 0.16. The discrepancy between the experimental value and the theoretical value of 0.12 is reasonable because the theoretical calculation assumed equal fractions of alphas would register for B and Li. In fact, only those above a certain energy will register, and therefore the Li efficiency is underestimated relative to B due to the greater alpha energy from the ^{6}Li reaction. The experimental value has been

TABLE II: Experimental Detection Efficiencies for B and Li

Mineral	No Samples Analyzed	wt% B	wt % Li	Range$^+$ (mg cm^{-2})	Track Density (Blank-corrected) 10^4 cm^{-2}	Detection Efficiency-B* 10^4 cm^{-2}/wt% B	Detection Efficiency-Li* 10^4 cm^{-2}/wt% Li	Average Efficiency
Colemanite	2	15.7	-----	1.12	538 7	37.3	---	
Hi B glass NBS SRM 93a	2	3.88	-----	1.22(B) 1.60(Li)	141 4	36.3	---	36.3 1.0
Lo B glass NBS SRM 92	2	0.22	-----	1.24	7.9 .5	35.3	---	
$LiNbO_3$	1	-----	4.7	2.34	47 2	----	6.8	
Spodumene NBS SRM 181,300	2	-----	2.96	1.62	3.7 .7	----	4.6	
Petalite NBS SRM 182	2	-----	2.01	1.63	12.1 .7	----	5.9	5.7 0.5
LiF(pellet)	2	-----	26.9	1.43	143 14	----	5.9	
LiF(solid)	1	-----	26.9	1.43	119 4	----	4.9	

Experimental relative efficiency $\frac{Li}{B}$ = 0.16 0.01

TABLE II (page 2)

+ Northcliffe and Schilling, 1970

* Corrected to one standard material, NBS SRM 93a, Hi B glass, 3.9% B, in order to eliminate effects of different alpha ranges due to different mineral compositions. The B efficiencies were calculated according to the equation

$$\text{Detection efficiency B} = \frac{\rho_{Bx}}{\%Bx} = \frac{\rho_{Bx(obs)}}{\%Bx} \cdot \frac{R_{B(\text{Hi B glass})}}{R_{Bx}}$$

where $\rho_{Bx(obs)}$ = observed track density due to B in material x

$\%Bx$ = weight % B in x

R_B = Range of alpha particle originating from B in designated material.

An analogous equation was used to calculate Li efficiencies. Units of efficiencies are tracks/cm^{-2} per % of element.

used in all subsequent corrections for ^{6}Li contributions to observed track densities. The uncertainty associated with the experimental efficiency is insignificant compared to other uncertainties used in calculating B concentrations. Appendix V contains results of flame emission lithium analyses of representative samples.

Contamination

During the course of the investigation of the boron concentration in carbonaceous chondrites (Appendices III, IV) it became apparent that airborne contamination posed a serious threat to B determinations in specimens with less than about 10 ppm and became a crucial problem in determinations at the 1 ppm level. As discussed in detail in the appendices, it was observed that second irradiations of crushed meteorite samples which were pressed into pellets never gave B concentrations which were lower than the first analyses, and frequently gave higher results; typically, the increases were about 1-3 ppm, but in the worst cases boron contents were ten times higher. The pellets were pressed as shortly as possible before the samples were assembled with plastic detectors and packed for irradiation, and stored between irradiations in plastic boxes inside larger plastic boxes in drawers or in a glove box in a laboratory with a filtered air supply. Since the contamination seemed to be correlated somewhat with the exposure time of the samples to air in the laboratory and no "stars" or clusters of tracks were observed, it was concluded that the contamination must be in sub-micron-size particles which preferentially adhere to radiation-damaged surfaces. Some samples of Murchison, which became contaminated the most easily, seemed to have a shiny coating after irradiation which was not readily removed with acetone or alcohol.

A variety of laboratory materials were analyzed for boron to determine which materials could be used to construct necessary tools for handling samples. A summary of these results is given in Table I of Appendix IV. Appendix IV also contains a detailed discussion of a series of experiments which were conducted to establish that B concentrations obtained for first irradiations of samples were indeed real and not wholly due to contamination.

In the work with shell material, the above contamination problems were less important. Almost all of the skeletal material had large enough B concentrations that the introduction of 1-2 ppm contamination was not a major contribution to the total measured concentration. In addition, the surfaces were always cleaned before packaging for irradiation by 30-60 seconds of polishing with fine aluminum oxide powder, so a fresh surface was always exposed, even when samples were irradiated a second time. The SiO_2 glass and calcite control samples, which were handled similarly, consistently showed low B contents (0.5 ppm or less).

Track-counting Procedures

Three methods were employed for counting tracks on irradiated, etched detectors. The data from fields of view corresponding to damaged areas on either the plastic or the epoxy mount were not included in the average for the sample; i.e., only "good" fields of view were used to obtain boron concentrations.

1. Tracks were etched as described above and counted with

transmitted light at about 1000x magnification, either directly with the microscope or by using a vidicon camera and a TV screen. The field of view (and hence the sample area) counted at one time is about 100 x 100 microns, although areas 5-10 microns in diameter can be used. Track densities less than about 10^7 cm^{-2} can be readily handled in this manner.

2. Tracks were etched for a shorter time to keep the track size smaller, gold-coated, and counted with an ISI Super-II scanning electron microscope at about 3500x magnification. This system had the advantage that much smaller objects could be analyzed because the field of view is about 10 x 10 microns. Greater magnifications could not be used since the electron beam caused decomposition of the plastic detectors. Thus, tracks from individual sponge spicules and diatoms with diameters as small as 15-20 microns could be counted. CRT images were photographed and tracks counted from the photographs. SEM track densities were systematically higher than optical track densities because a larger proportion of short tracks was counted.

3. Detectors were etched and gold-coated as in (2) and counted optically in reflected light at about 1000x magnification. This system is considerably faster than the SEM but can not be used when track densities are greater than about 5 x 10^7 cm^{-2}. Areas about 6 x 6 microns can be counted. However, small pits in the detector surfaces were readily visible and contributed to a very high background track density. Reflected light was used to count samples from only one irradiation.

For each method of track counting, criteria were developed which distinguished objects which should be counted as tracks from objects which should not be counted, such as dirt and small surface pitting of the detectors. Optical criteria were that the object must have a reasonable diameter in comparison to other tracks in the detector and a finite length which did not exceed the maximum alpha length of about 6 microns. SEM data were collected with the criteria of a reasonable track diameter and a clearly visible ring of light with a dark center. Samples and standards from each irradiation were counted in the same way. Consistent boron concentrations were obtained with each method.

Data Analysis

Groups of samples were counted and average track densities and boron concentrations were calculated for the group at a later time in order to prevent bias in track counting by adjusting the criteria for track identification so as to obtain track densities which agreed with expected values. All counting was done by one person to promote uniform application of the criteria. Measured track densities were corrected for background by subtracting the average of the blank track densities. Generally the calcite or silica glass blanks were used. The blank corrections were generally equivalent to less than 0.3 ppm for calcite and less than 0.7 ppm for SiO_2. The SiO_2 blanks apparently contain about 0.5 ppm B but were used primarily with siliceous materials which contained several hundred ppm B. The error in the blank correction is negligible. The final boron concentrations also are not significantly influenced if the plastic-against-plastic values are used.

The standard track densities were then corrected for the contribution from Li using the experimentally determined relative detection efficiency and the known Li concentration of the standards according to the equation

$$\rho_B^{standard} = \frac{\rho_{measured}^{standard} - \rho^{background}}{E\ (1 + \frac{Li}{B}_{standard})} \qquad (2)$$

where ρ is the track density, E is the experimentally determined relative detection efficeincy for Li relative to B (0.16, Table II), and B and Li are the concentrations of the two elements, respectively. The quantity $\rho_B^{standard}$ is the track density due to B in the standard. This was calculated individually for each standard. The values obtained were then averaged to yield a single number of tracks per unit area per ppm B. (For the samples analyzed in this work, contributions from Li to the track densities were negligible. If the ratio $\frac{Li}{B}$ is greater than 0.5, observed track densities must be corrected for Li contributions. Independent Li analyses are required.) When appropriate, corrections were also made for the differences in alpha ranges in the samples and the standards (Northcliffe and Schilling, 1970). These calculations had to be repeated for each irradiation. It was found that there was no detectable gradient in the neutron flux during irradiation, and no corrections were made for relative sample locations during an irradiation.

III. BORON IN SILICEOUS MATERIALS

In 1932 Goldschmidt and Peters published the results of spectroscopic analyses of a variety of biogenic carbonates and opals (amorphous hydrous SiO_2), indicating that radiolarian oozes and marine sponges tended to have significantly more boron than marine carbonate shells. They also reported low boron concentrations in freshwater diatomites (Goldschmidt, 1954). More recent work has confirmed the high boron contents of marine biogenic opal (Gross, 1967; Kolodny, _et al._, 1979). The relationship between boron concentrations in opal skeletal materials and water salinity was investigated with the goal of finding a suitable type of organism for use in paleosalinity determinations.

Several extant groups of opal-precipitating organisms are abundant in the fossil record, including silicoflagellates, diatoms, radiolarians, and sponges. The skeletons of the first three of these tend to be very delicate, porous, and small, presenting difficulties for analysis, particularly for analysis of individual specimens. Both diatoms and siliceous sponges occur in freshwater and marine environments. Because some representatives of each of these two groups can tolerate salinities other than normal marine, because they occur abundantly in the fossil record, and because material was readily available for study, these two groups were chosen for investigation.

Description of Diatoms

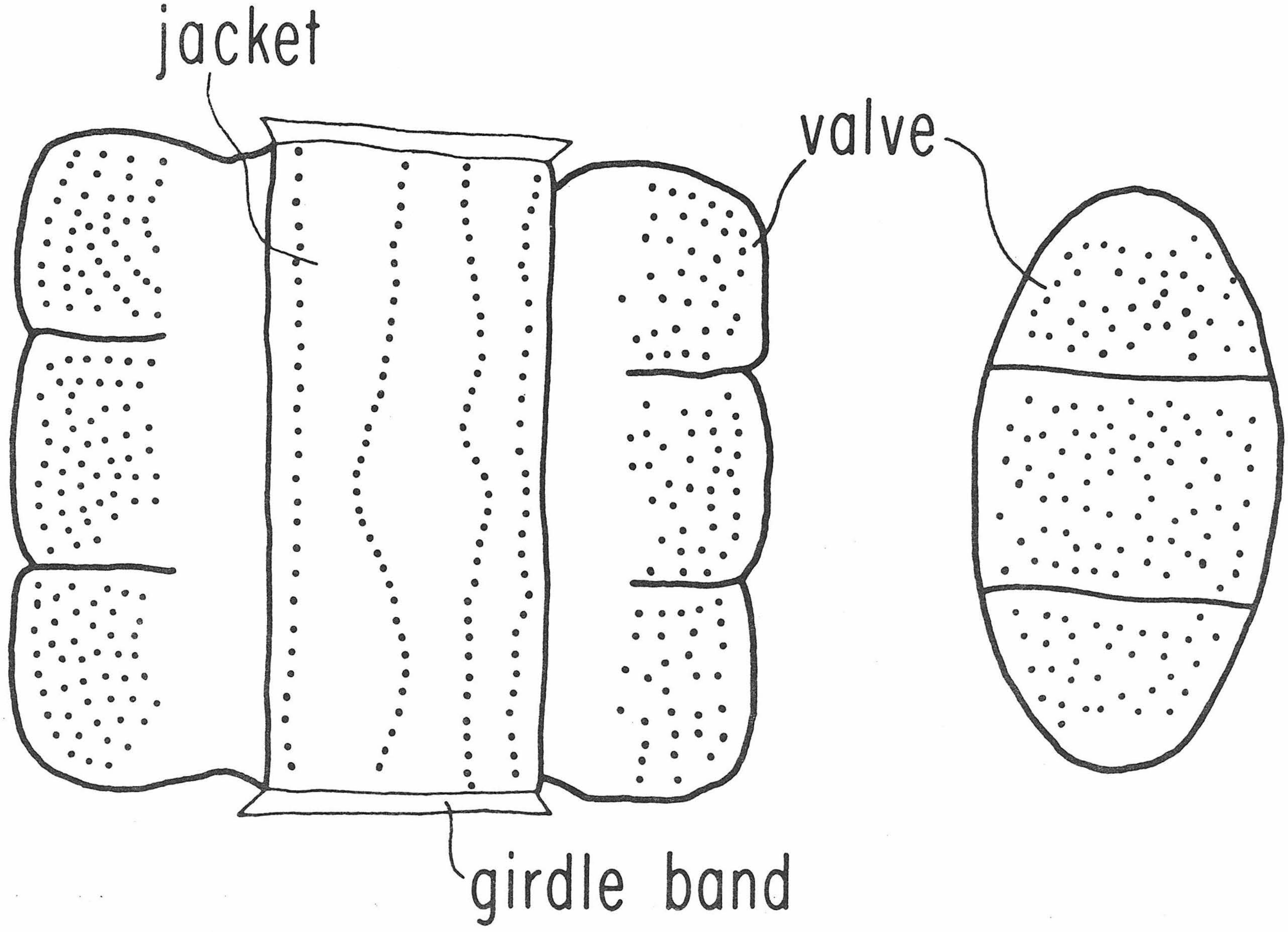
Diatoms belong to the group of Chrysophyta, or yellow-green algae. As photosynthesizers, they are primary producers in food chains. They are abundant in plankton, comprising about 70% of the mass and accounting for most of the organic carbon production in the open ocean (Lisitzin, 1977). Also occurring as shallow benthic and freshwater dwellers, diatoms may be unicellular, filamentous, or multicellular aggregates. The diatom cell wall is mineralized to a varying extent with opal (see, for example, Riemann, et al., 1965, 1966; Lewin and Riemann, 1969; Roth and de Francisco, 1977). The mineralized wall, or frustrule, has a box-like structure, with two flat valves of radial or bilateral symmetry. Each perforated valve is attached to a marginal valve jacket, and the two valve-plus-jacket assemblies are held together by an organic girdle band. (See Figure 1.)

Diatom cell walls have several layers; a single layer of opal is completely enclosed by an organic mambrane. Opal deposition occurs in vesicles inside the cell, with the newly precipitated material always in contact with the organic vesicle membrane. The membrane probably acts as a template or mold for SiO_2 deposition. (see, for example, Riemann, et al., 1966; Darley, 1974; Roth and de Francisco, 1977). In addition to the membrane, a layer of cations may be adsorbed on the surface of the frustrule, which seems to decrease the rate of dissolution of frustrules in contact with sea water after death, despite the undersaturation of sea water with respect to Si (Lewin, 1961).

Both boron and silicon have been established as essential

FIGURE 1

Diagram of the diatom Anaulus mediterraneus Grun. The siliceous valve and jacket and the organic girdle band are labelled. The long dimension of the valve is approximately 10 microns. From Coupin, year unknown.


jacket
valve
girdle band

nutrients for diatoms. Silicon uptake is aerobic and inhibited by the respiratory inhibitors KCN, NaF, iodoacetate, $NaAsO_2$, NaN_3, and fluoroacetate (Lewin, 1955). In its absence, new cell walls can not be constructed (Busby and Lewin, 1967). Silicon is apparently involved in amino acid or protein metabolism and in the synthesis of new proteins, particularly for the cell wall (Lewin and Chen, 1968; Coombs and Volcani, 1968). Cells deficient in boron are viable but can not reproduce (Lewin, 1965) or grow (Lewin, 1966a). The boron requirement of *Navicula pelliculosa* (Bréb.) Hilse was observed to increase with increased silicon content of the culture medium (Lewin, 1966b). B-deficient *Cylindrotheca fusiformis* Riemann and Lewin (1964) contained lower protein and RNA and higher lipid contents than cells cultured in the same medium with added boron. It was concluded that B may be needed for pyrimidine synthesis and that it may serve to detoxify phenolic compounds by forming complexes with them. Apparently boron is involved in enzymatic reactions since it is not used up after continued cell growth and divisions (Lewin and Chen, 1976). It is known that different species of diatoms concentrate boron relative to sea water to varying extents (Lewin, 1977).

Description of Sponges

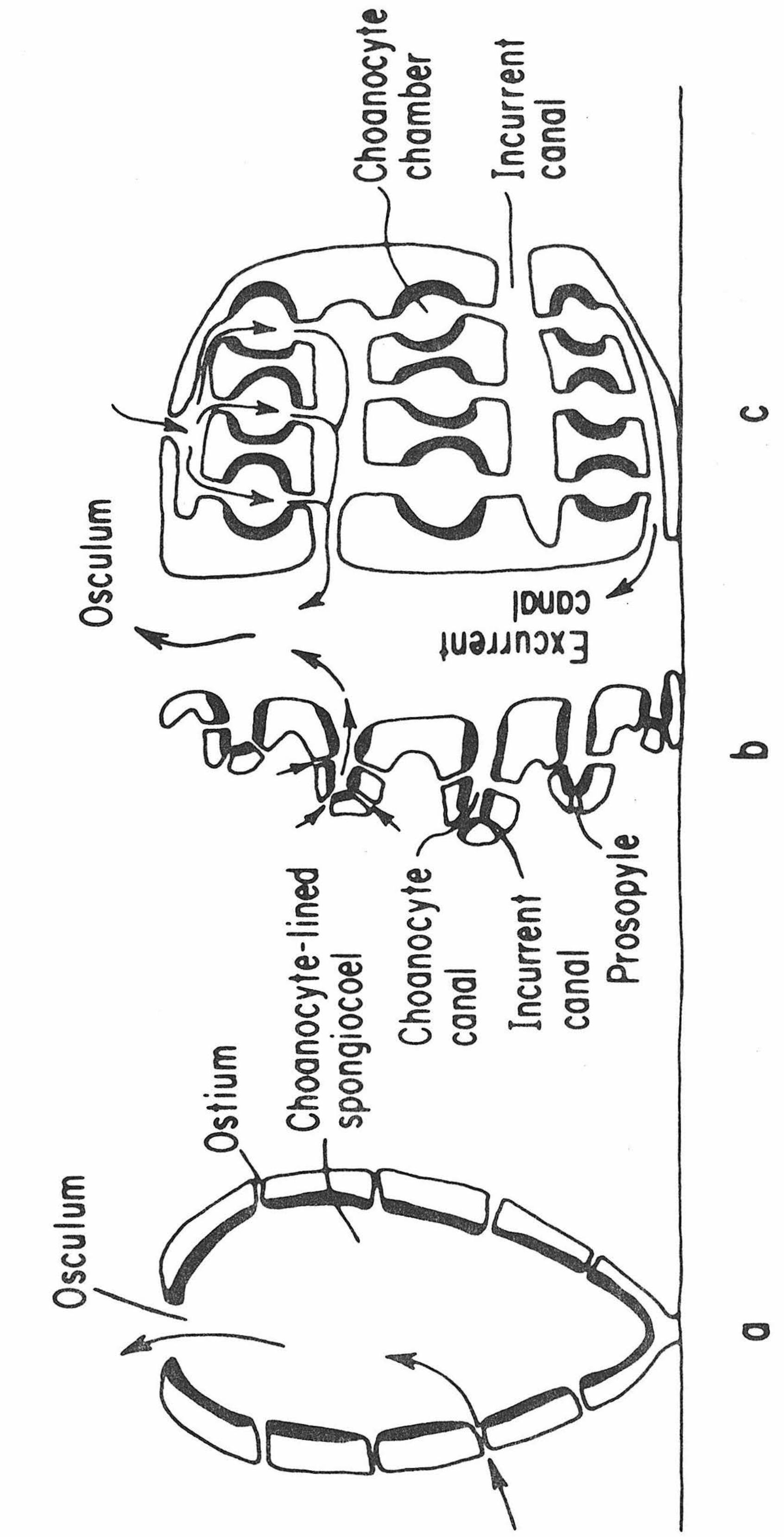
The phylum *Porifera*, or the sponges, represents the lowest form of multicellular animals. They possess no true tissues. There is no nervous system and each cell responds to environmental stimuli individually; however, isolated cells can not survive permanently. Digestion of food is intracellular, as in protozoans (Meglitsch, 1972;

Bergquist, 1978). Figure 2 is a diagram of a sponge. Water flows through numerous small pores or ostia, enters one or more passages lined with flagellated cells (choanocytes), and exits via one or more large openings, or oscula. The choanocytes create currents flowing through the sponge and gather small particles which are of the appropriate size (0.2-50 microns) almost indiscriminately and with high efficiency (de Laubenfels, 1955; Reiswig, 1971a; Bergquist, 1978). Reiswig (1971a) studied three species of sponges in Jamaica and found that two separate systems operate in trapping particles; objects 5-50 microns in diameter are captured by the cells lining the incurrent canals and particles in the bacterial size range (0.3-1 micron) are captured by the choanocytes. About 20% of the food is composed of microscopically resolvable particulate material and the remainder is microscopically unresolvable particulate matter. Dissolved organic compounds can presumably also be absorbed by sponges. Morphology is often environmentally determined, ranging from encrustations less than one millimeter thick to globular forms a meter in diameter. Sponges are bottom-dwellers, attached to either hard or soft substrates, and occur at all water depths (Meglitsch, 1972).

Sponges contain spicules or fibrous skeletal elements. In the class _Calcarea_, spicules are composed of calcite. In _Sclerospongia_, high-magnesium calcite, aragonite, and opal structures are found. Both _Demospongia_ and _Hexactinellida_ contain opal spicules, and _Demospongia_ may have proteinaceous fibers of spongin with or without siliceous spicules. (The common bath sponge contains only spongin fibers.) Spicules come in a wide variety of shapes even within one

FIGURE 2

Cross-sectional sketch of sponge body plans. (a) is an asconoid sponge. Two halves of a syconoid and a leuconoid sponge are depicted in (b) and (c), respectively. Appropriate parts are labelled and the arrows indicate the direction of water flow. All siliceous sponges have the complex body form (c). Calcispongia may have any of the three plans.


Osculum
Ostium
Choanocyte-lined spongiocoel
a
Choanocyte canal
Incurrent canal
Prosopyle
b
Osculum
Choanocyte chamber
Incurrent canal
Excurrent canal
c

sponge, often with several rays extending outward from a central point. Megascleres make up the framework of the organism and microscleres occur loose in the flesh. Taxonomy is based principally on spicule morphology.

Siliceous spicules are formed within a single cell. A central organic filament, composed of protein and probably also carbohydrate (Drum, 1968; Schwab and Shore, 1971; Shore, 1972), has a triangular cross section in *Demospongia* and a square cross section in *Hexactinellida* (Reiswig, 1971b). The filament diameter is about 0.5 microns (Reiswig, 1971b; Schwab and Shore, 1971). Opal is deposited in concentric tubular layers around the central filament; electron microscopy of etched spicules indicates that the layers are 0.2 to 0.3 microns thick in *Acarnus erithacus* (Schwab and Shore, 1971), and that the central filament occupies a canal or tube in the opal. The central filament may serve as a template for SiO_2 deposition (Reiswig, 1971b). Elvin (1971) measured growth rates of spicules in *Ephydatia muelleri* (Lieberkuhn), a freshwater sponge, and found that lengths increased at about 5 microns/hour and $5\text{-}30 \times 10^{-18}$ moles of silica were deposited per square micron of spicule area per minute, depending on the silica concentration in solution and the temperature.

Calcitic spicules are also intracellular precipitates. They contain no axial filament, but may have some impure calcite along the centers of the rays. Each spicule is a single crystal which is oriented in the sponge tissue. Initial crystallization occurs at the center of a group of cells which form the spicule; the cells are probably not completely separate from each other (syncytial) during the first stages of spicule formation (Jones, 1967).

Silicon and boron metabolism in sponges are not well understood. It is not known what functions they have other than their occurrence in spicules.

Experimental

General aspects of the analytical technique have been explained in Appendix I and in Chapter II. Details of sample preparation and analysis are described here.

A. Diatoms--sediment samples

Three core samples were obtained from the Scripps Institute of Oceanography collection. The diatom-rich fractions were collected by their settling rate in distilled water. Large diatoms were handpicked and mounted individually for irradiation by pressing them onto a piece of cellulose nitrate plastic which had been partially dissolved with a small amount of acetone on the surface. Smaller diatoms were collected on filter paper and irradiated as a layer on the filter paper.

B. Diatomaceous earth samples

Chips were broken off and ground with 600 grit SiC paper (Buehler) to form two plane parallel surfaces. Each chip was sandwiched between two plastic detectors for irradiation, with no further preparation.

C. Sponges--live-collected

Live-collected sponges were preserved in 70-75% ethanol or dried. Small pieces were cut off with a clean scalpel and soaked in 6% NaClO solution (commercial Chlorox) in plastic beakers until the soft parts were completely oxidized and bubbling had ceased (2-4 days). The spicules were collected in a fine sieve (20 or 37 micron mesh) and washed repeatedly with distilled water and then finally with spectroscopic quality methanol. They were then potted in E-7 epoxy and polished with aluminum oxide powder. Irradiation and track counting were carried out as described in Chapter II.

D. Sponges--sediment samples

Several deep-sea core samples were obtained which contained abundant fossil sponge spicules. A small portion of material from each core position was suspended in distilled water and sieved. The portion which did not pass through a 70 micron mesh was examined and large spicules were hand picked and potted in epoxy, as were the live-collected spicules. One core, V19-29, was thoroughly cemented with carbonate and required solution in dilute HCl before sieving.

Results

The results of all boron analyses of siliceous materials are listed in Table III. Documentation of all sample locations, sources, and water salinities is provided in Appendix II. Flame emission Li analyses of 10-100 mg aliquots of spicules from each of several sponges were obtained. In all cases, the Li concentrations were less than 10 ppm and no corrections for Li in spicules were necessary.

A. Reproducibility

The reproducibility of track analyses determined from SEM photographs at nominal magnifications of 5000 and 7000 times was established in two ways.

TABLE III: Boron Concentrations in Sponge Spicules

Sample and Location		Salinity ‰	[B] ppm	Classification
LIVE-COLLECTED SPONGES				
San Juan Islands, Washington		28-32		
	FP1		587	*Syringella* sp.
	FP2		506	*Myxilla* sp.
	PV2		521	
	PV3		430	*Iophon pattersoni*
	PV4		334	*Lyssodendoryx firma*
	WS1		499	*Syringella* sp.
	MV1		574	
	Egg1	0	< 7.5	*Spongilla*
San Nicholas Island, California		33.5		
	25765-1		596	*Staurocalyptus* sp.
	25765-2		690	*Aphrocallistes vastus*
	25765-2		699	
	25765-3		599	
	25765-4		574	Fam. *Craniellidae*
	25765-5		143	*Lissodendoryx* sp.
	25766-1		293	*Axinella* sp.
	25766-1		540	*Axinella* sp.
	25766-1		429	*Axinella* sp.
	25766-2		569	
	25767-2		693	
	25767-3		572	
	25767-3		177	
Catalina Island, California		33.5		
	26601		267	
	26601		523	
Magdalena Bay, Mexico		~36		
	4545-1		399	single spicules
	4545-2		367	single spicules
	4081-1		621	single spicules
	4081-2		648	single spicules
	4544-1a		398	single spicules
	4544-2		332	single spicules
Cedros Island, Mexico		~35	406	single spicules
Northumberland Str., Nova Scotia	YH4	32±1	670	*Haliclona oculata*
Eastport, Maine	YH12	32±1	505	*Isodictya palmata*
Massachusetts Bay, Massachusetts	YH7	31.6±.2	660	*Haliclona oculata*
	YH10		604	*Polymastia robusta*
	YH10a		698	*Polymastia robusta*
Woods Hole, Massachusetts†		20-30		
WH1 (H_2O_2)			550	*Microciona* sp.
WH2 (H_2O_2)			573	*Microciona* sp.
WH3 (H_2O_2)			550	*Microciona* sp.
WH13 (H_2O_2)			236	*Halichondria* sp.
WH14 (H_2O_2)			273	*Halichondria* sp.
WH15 (H_2O_2)			253	*Halichondria* sp.
WH13c (chlorox)			277	*Halichondria* sp.
Block Island, Rhode Island	YH8		841	*Suberites ficus*

Table III (cont.)

Sample and Location		Salinity ‰	[B]* ppm	Classification
New Haven, Connecticut	YH2	15-32	402	*Cliona celata*
	YH6		258	*Microciona prolifera*
Gloucester Point, Virginia	GP1	10-25	287	*Halichondria bowerbanki*
	GP2		428	*Lissodendoryx carolinensis*
North Carolina	CBS5	0	3.8	*Spongilla* sp.
Nassau, Bahamas	YH9	37±1	345	*Iotrochata birotulata*
Honduras	C1	36±1	100	*Thalysias juniperina*
	C2		353	*Iotrochata birotulata*
	C3		125	*Agelas clathrodes*
	C4		282	*Neotibularia nolitangere*
Jamaica	YH1	36±1	236	*Xestospongia muta*
	YH3		402	*Tethya crypta*
Puerto Rico	YH11	34±1	334	*Haliclona rubens*
Barbados	BB-1-1	36.0-36.75	315	
	BB-1-2		277	
	BB-1-4		331	
	BB-2-2		288	
	BB-2		505	
	BB-3-4 needles		288	*Geodia* sp.
	BB-3-4 round		96	*Geodia* sp.
	BB3		147	*Geodia* sp.
	BB4		78	*Geodia* sp.
	BB8		103	
Bermuda	Ber-1	37±1	61	*Calliospongia vaginalis*
Askö Island, Sweden	AI1	5.6-7.1	29.1	*Ephydatia fluviatilis*
	AI2		32.3	
	AI3		30.0	
Cataluna, Spain	YH5	?(>35)	484	*Axinella polypoides*
Arthur Harbor, Antarctica	AA1	32.5±.5	487	
	AA2		476	
	AA3		435	
	AA4		468	
	AA5		538	
	AA6		590	
CORE SAMPLES				
RC13-263 South Atlantic	450 cm	marine	361	
V19-20 E. Equatorial Pacific	0 cm-3		117	
	-4		241	
	120 cm-3		172	
	-4		252	
	850 cm-3		217	
	-4		243	
V23-42 North Atlantic	0 cm	marine	340	
	10		344	
	20		273	
	30		262	

Table III (cont.)

	30		546
	40		434
	50		608
	50		524
	60		470
	70		559
	90		437
	430		477
	450		408
	470		425
RC12-249 North Central Atlantic	160 cm	marine	649
SOCAL (Gulf of California)		marine	342
MSN Antarctic		marine	384

[*] Standard deviations of boron concentrations are usually 6% or less.

[†] The Woods Hole, Massachusetts samples were treated with hydrogen peroxide or Chlorox as indicated. All other sponges were treated with Chlorox.

1. Several SRM 610 (351 ppm) standards were included in each irradiation, and at least three were counted each time. Track densities for the standards from two irradiations which were counted using the SEM are shown in Figure 3. All of the standards from the 3/77 irradiation have track densities within one standard deviation (based on counting statistics) of the mean of the values of all standards counted at the same magnification, and all of the standards from the 4/77 irradiation have track densities within a two sigma standard deviation from the mean. Further, when the average track densities for each group of the 3/77 standards are normalized for the different areas counted, they agree to within 1 track per photo.

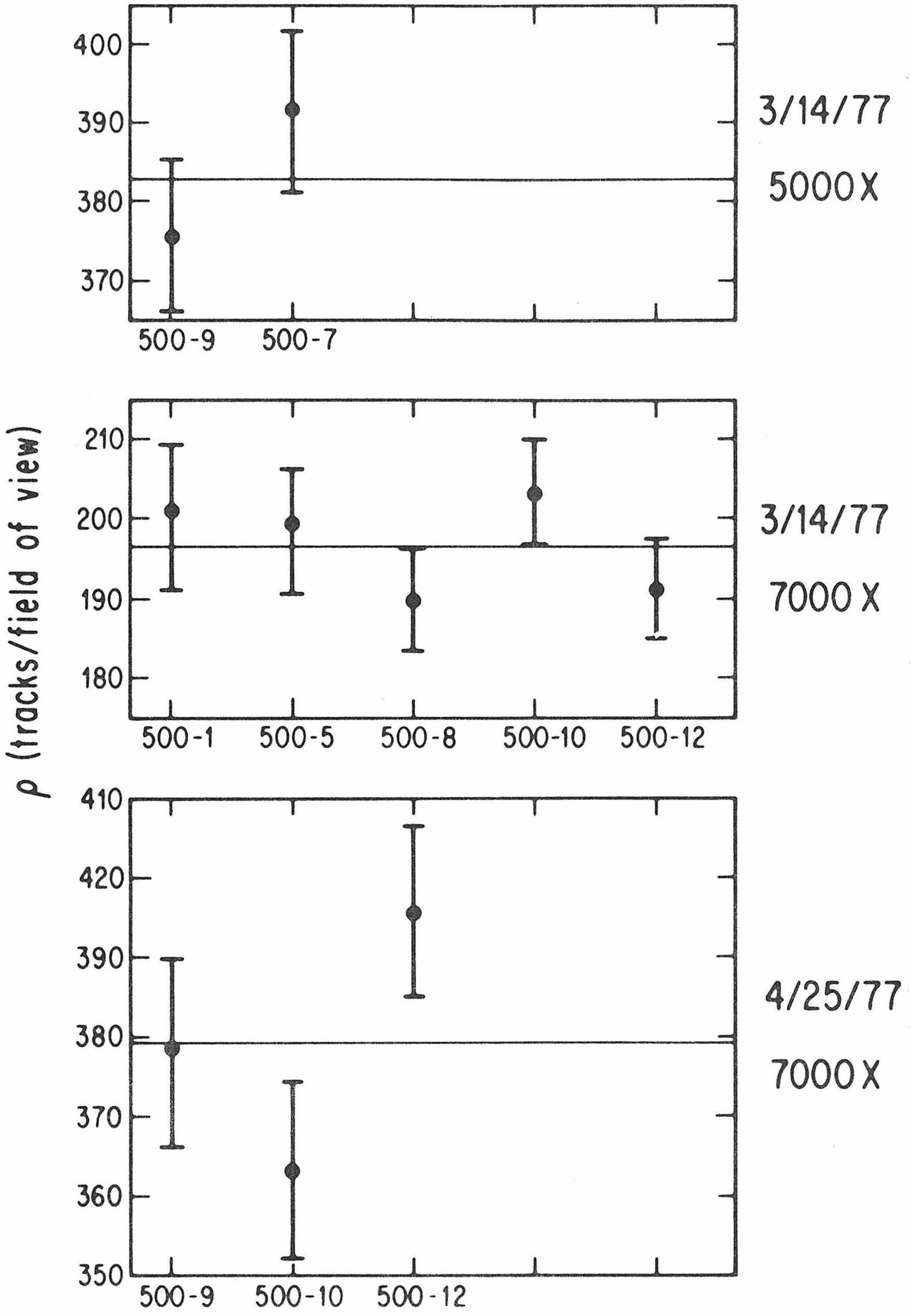
2. Two mounts of sponge spicules were reanalyzed; the second analyses of both samples agreed with the first in both cases to well within the 6% error of the determinations.

The reproducibility of the optically counted track data was established by repolishing and re-irradiating a number of samples on different occasions. Results showed consistency comparable to the SEM data, generally agreeing to better than the 6% standard deviation of each analysis. When there was a larger discrepancy, it could be attributed to contamination or other effects using independent evidence. Duplicate analyses of the same detector also agreed well in most cases. Even when they did not agree to within counting statistics, all analyses were averaged. Such discrepancies may have been due to sample inhomogeneities, but could also have represented track counting errors.

In general, samples and standards had B concentrations within a

FIGURE 3

Reproducibility of SEM track data. Track densities are plotted for three groups of standards from two irradiations. Error bars represent one sigma standard deviations based on counting statistics. The average track density for each group is indicated by a horizontal line. When corrected for the different areas of the fields of view, the average track densities for the 3/14/77 data at 5000x and at 7000x agree to within 1 track per field of view.


400
390
380
370
500-9
500-7
3/14/77
5000X
ρ (tracks/field of view)
210
200
190
180
500-1
500-5
500-8
500-10
500-12
3/14/77
7000 X
410
420
390
380
370
360
350
500-9
500-10
500-12
4/25/77
7000X

factor of 2-3 of each other and should have similar reproducibilities. Occasionally the data for a sample did not agree with results for similar samples from the same location. In such cases, the samples were rejected only if it could be demonstrated that there was good cause due to a reexamination of the sample. Several samples were reirradiated and gave results in agreement with the values obtained the first time; these B concentrations were considered valid and not rejected. The two values were averaged and included in any tabulations, figures, and other discussion of the results.

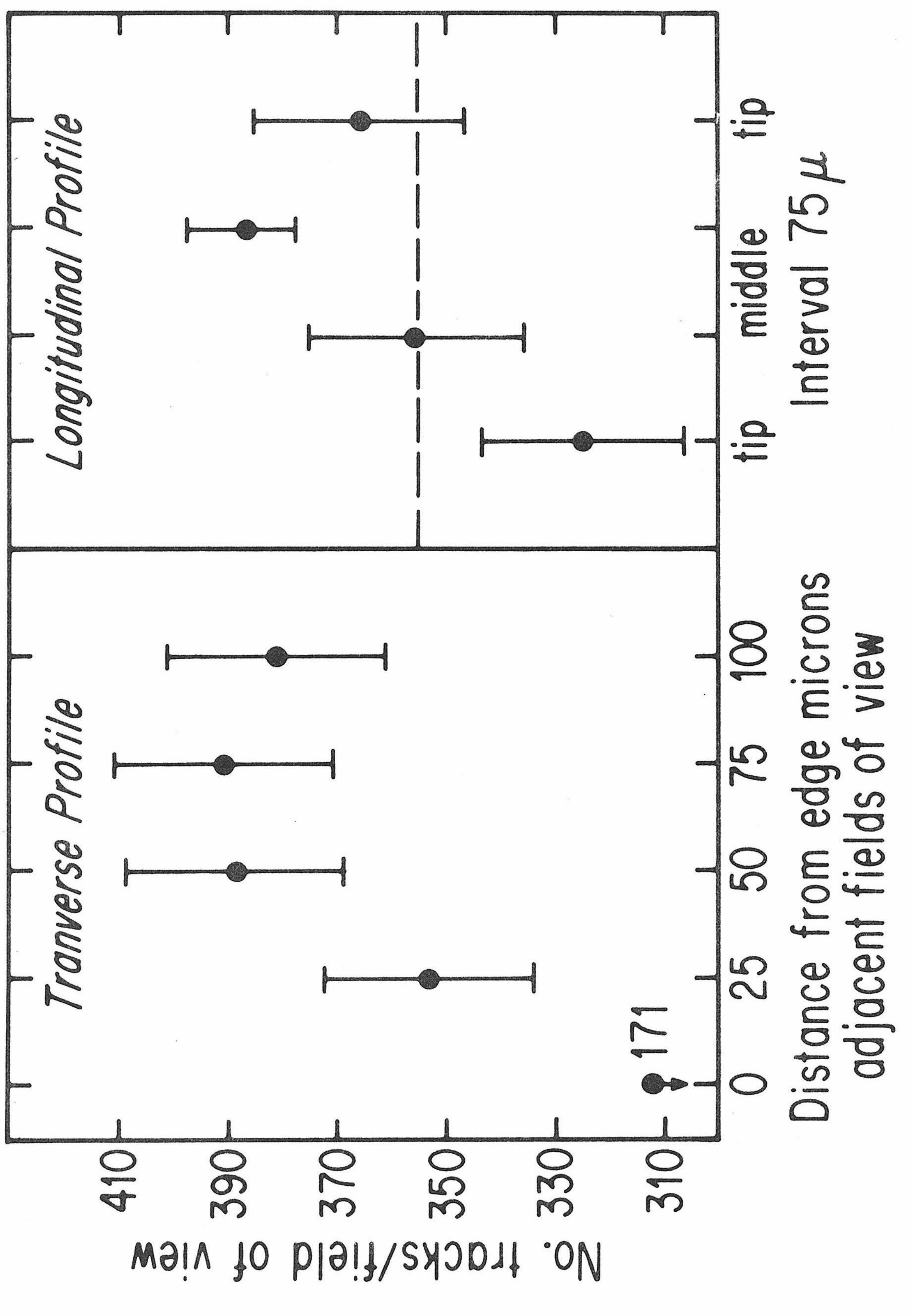
B. Uniformity of boron in spicules

Initial detailed studies of the boron distribution in individual sponge spicules were carried out using the scanning electron microscope for track counting. A typical traverse across a single large spicule is shown in Figure 4. The spicule edge is very clearly defined in the transverse profile and the boron concentration is uniform within counting statistics across the diameter of the spicule. The longitudinal profile is representative and does not indicate the most uniform case observed. There may be a slight decrease in boron concentration near one end of the spicule, but the low track density may also be due to inadequate opal thickness at the spicule tip. The boron concentration seems to be quite uniform (certainly better than 10%) within individual spicules on a scale of 5-10 microns. Because the spicules are composed of many layers of opal and organic material, it is likely that the boron is inhomogeneously distributed in these layers on a finer scale than can be resolved using tracks.

The uniformity of boron concentrations in different spicules from

FIGURE 4

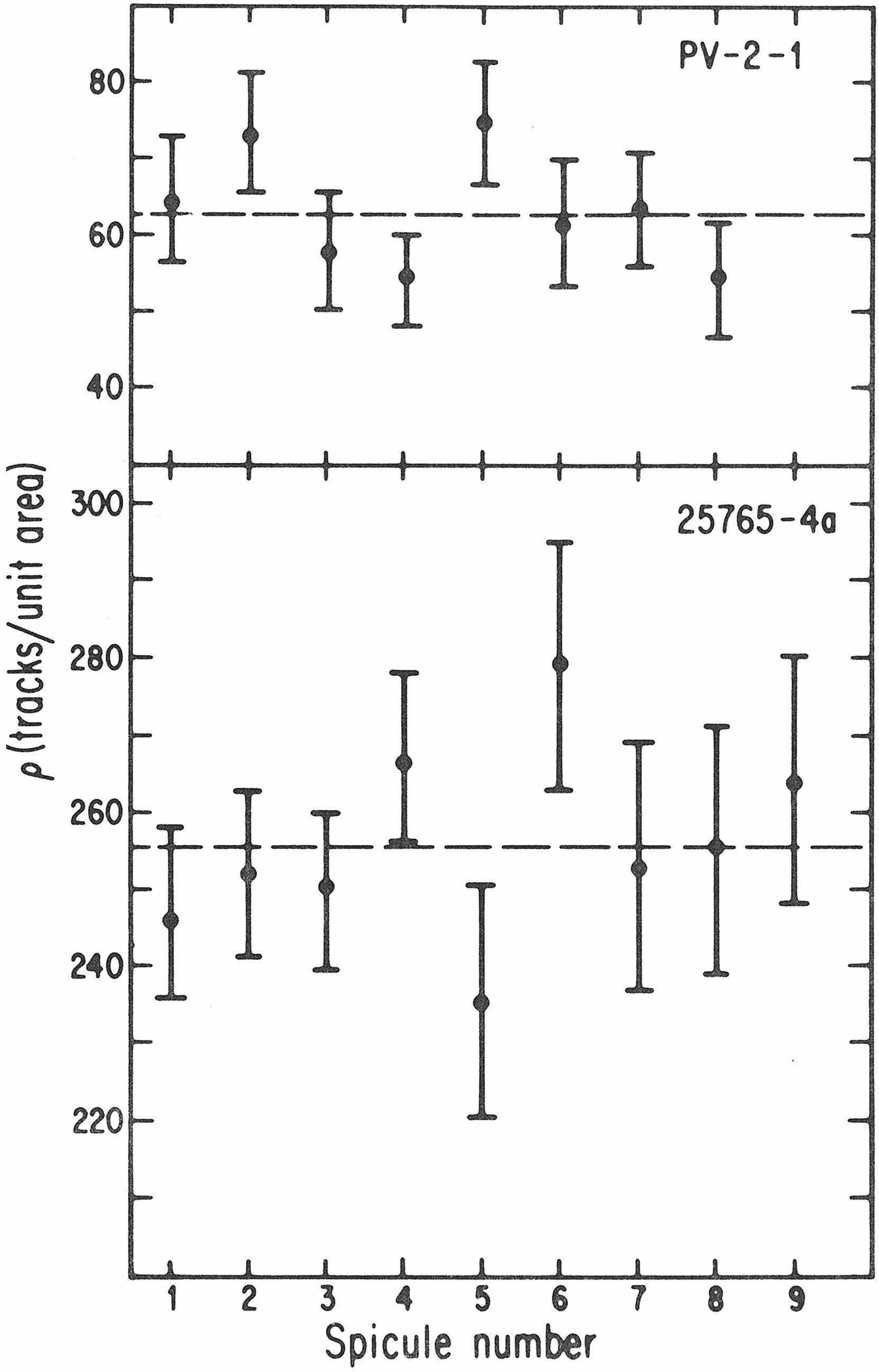
A typical traverse across a single large spicule. The transverse profile begins near the boundary of the spicule and goes more than half-way across the spicule. The error bars represent one standard deviation based on counting statistics. In the longitudinal profile, the dashed line indicates the average of the four points plotted, and the four high-density points from the transverse profile have been averaged and plotted as the third point on the longitudinal profile.


Tranverse Profile
Longitudinal Profile
No. tracks/field of view
410
390
370
350
330
310
171
0
25
50
75
100
Distance from edge microns
adjacent fields of view
tip
middle
tip
Interval 75 μ

the same sponge was also investigated. The observed track densities for nine spicules from one sponge and eight from another are plotted in Figure 4. The error bars indicate one standard deviation based on counting statistics, and the dashed line represents the average of all spicules. The boron contents of the different spicules are uniform within counting statistics, as observed in most live-collected specimens. However, several sponges were found which had different boron concentrations in spicules originating in different parts of the sponge or in spicules of different morphologies. Spicules from the fingerlike projections which supported a specimen of Polymastia robusta (Bowerbank) (YH 10) above a soft substrate had 15% more boron than spicules from the main mass of the sponge, with 5% counting statistics. Two specimens of Geodia from Barbados (BB3 and BB 4) each had concentrations which differed by a factor of three in different types of spicules. In both specimens, the spicules which had lower B contents were spherical or ellipsoidal in shape and had distinctive surface patterns (sterrasters); these spicules also were the only microscleres encountered which were large enough to analyze. It may be that there is a fundamental difference between boron concentrations in megascleres and microscleres. Because of their distinctive morphologies, many microscleres are easily recognized and can be excluded from analyses of individual spicules; usually they are sufficiently small that they are not retained by the sieves used in sample preparation. In general, it can be concluded that there is a uniform boron concentration in spicules from a single sponge, and that analysis of only one or a few spicules will result in a boron concentration representative of the whole sponge.

FIGURE 5

Plot of track densities for several spicules from each of two different sponges. Each point represents one spicule, and error bars represent standard deviations based on counting statistics. The differences in track densities for the two sponges are due to different irradiation conditions and different unit areas; PV-2-1 was counted optically and 25765-4a was counted using the SEM. Average track densities for each group of spicules are indicated with dashed lines.


PV-2-1
80
60
40
25765-4a
300
280
260
240
220
ρ (tracks/unit area)
1
2
3
4
5
6
7
8
9
Spicule number

C. Chemical form of boron in spicules

In order to verify that the Chlorox treatment did not change the boron content of the spicules due to contamination or possible leaching from opal in the basic solution, two experiments were conducted. First, a sponge was divided into two parts and one part was treated with Chlorox. Spicules from the treated and the untreated parts were mounted and analyzed separately, yielding B contents which agreed within counting statistics. Second, several samples were treated with hydrogen peroxide instead of Chlorox, which is an acidic solution. The boron concentrations also agreed well with those found in sponges of the same species from the same location. Subsequent analyses were carried out on Chlorox-treated spicules because of the shorter time required to oxidize the soft parts of the sponges (peroxide digestion required one week or more).

The portions of the spicules analyzed were interior surfaces. There is probably some organic material inside the spicules which is not oxidized by Chlorox, and the possibility that this organic material is rich in boron can not at present be ruled out; the layers of opal and protein/carbohydrate within the spicules are far too narrow for different concentrations to be resolvable using tracks. It is hoped that a definitive indication of the chemical form of the boron in the spicules can be obtained using nuclear magnetic resonance spectroscopy.

D. Selection criteria for boron data from sponge spicules

After polishing, the epoxy spicule mounts were carefully examined with a microscope in reflected light and the spicules appropriate for analysis were selected. It was found that the following criteria for spicule selection were necessary to obtain reproducible boron concentrations which agreed with other spicules from the same sponge and/or other sponges from the same location.

1. Spicules had to have diameters greater than 20 microns. It was found that narrower spicules gave low track densities, presumably because the portions remaining after polishing were thinner than the range of the alpha particles (6-7 microns), and epoxy as well as spicules was being analyzed.

2. The spicules couldn't be part of a dictyonine skeleton. One specimen of *Aphrocallistes vastus* had very large variations in the boron content of its spicules, even in a single section perpendicular to the long direction of the spicule. However, the specimen was not alive at the time of collection, and SEM study of a fragment revealed significant enlargement of the central canal, reflecting partial solution of the interior of the spicule. It is possible that other specimens would have more uniform boron concentrations.

3. Root-like spicules which anchor and support some soft-substrate sponges were also excluded because early analyses of several of these spicules yielded low B concentrations relative to spicules from the main portions of sponges. However, the low B contents may actually have been related to other factors (see discussion below) and it is possible that this criterion is not really needed. Also, these very large (around 1 mm in diameter) spicules did not polish well and the analyses would have been excluded on that basis.

4. The spicule surface must be well-polished and free of pits

and cracks because extraneous material collects readily in holes and extensive pitting is evidence for dissolution of the spicule by water. The surface analyzed must be from the interior of the spicule; material adsorbed or cemented on the exteriors of spicules should be excluded from good boron determinations.

5. The central canal of the spicule must be present but not significantly enlarged. The absence of a central canal is an indication that the spicule is calcareous rather than siliceous. If the canal is greatly enlarged due to solution of opal after the sponge died, the walls of the spicule may be too thin and the same problem with low B analyses occurs as in criterion (1).

All of these criteria can readily be applied to fossil spicules. The first four have also been applied to live-collected specimens, but not necessarily to all of the spicules actually analyzed. Mounts of live-collected specimens generally contained so many spicules that it was difficult to keep track of exactly which ones were analyzed, and there was generally very little variation in polish, size, and diameter of the central canal in each type of spicule from a single sponge. Several specimens from key locations had only very small spicules and individual spicules could not be analyzed. Suspensions of these spicules were collected on filter paper and analyzed as bulk samples. Of course, this technique can not be used for sediment samples because of the large amount of non-spicule material present. It should be emphasized that the first three criteria deal with readily observable morphological features of spicules and present no problem for selection of spicules from sediment samples. Indeed, objects smaller than 20 microns in diameter are difficult to handle individually.

E. Intersponge variations in boron concentration

Different sponges from the same marine location tend to have boron concentrations which agree with each other, independent of species, but there are some notable exceptions. Brackish-water sponges and sponges from tropical locations have variable boron contents. Marine sponges from more northerly areas have boron concentrations ranging about 10 per cent from the mean for each location, with 6% standard deviations for each determination. Table IV compares boron concentrations from sponges from each of several locations from which two or more species met the selection criteria. It is apparent that representatives from temperate locations show good agreement and those from tropical locations show poor agreement. Thus, it can be concluded that the observed boron concentrations are independent of species, but appear to be a function of some environmental factor. The groups of sponges from Barbados and from Southern California included both *Demospongia* and *Hexactinellida*, so it can be concluded that the boron concentration is independent of taxonomic group at the class level. (No spicules from *Sclerospongia* were analyzed.)

A comparison of boron concentrations found in spicules from representatives of the same genera from different locations is found in Table V. When the comparison is between locations which are both tropical or both temperate, the concentrations are in good agreement; when tropical and temperate specimens are compared, as in the case of *Haliclona*, the agreement is poor. The *Axinella* specimen from

TABLE IV: Comparison of Boron Concentrations in Different Sponges from the same Marine Locations

Genus and Species	Sample	[B], ppm	Location
Haliclona oculata	YH 7	660 ± 32	Massachusetts
Polymastia robusta	YH 10	604 ± 30	
Xestospongia muta	YH 1	236 ± 13	Jamaica
Tethya crypta	YH 3	402 ± 22	
	BB 1	308 ± 30	Barbados
	BB 2	505 ± 19	
Geodia, sp.	BB 3	147 ± 7	
Geodia, sp.	BB 4	78 ± 11	
	BB 8	103 ± 25	
Syringella, sp.	FP 1	587 ± 35	Washington
Myxilla, sp.	FP 2	506 ± 30	
	PV 2	521 ± 31	
Iophon pattersoni	PV 3	430 ± 26	
Syringella, sp.	WS 1	499 ± 30	
	MV 1	574 ± 34	
Thalysias juniperina	C 1	100 ± 8	Honduras
Iotrochata birotulata	C 2	353 ± 19	
Agelas clathrodes	C 3	125 ± 9	
Neotibularia nolitangere	C 4	282 ± 17	
Staurocalyptus, sp.	25765-1	596 ± 34	California
(Hexactinellida)	25765-3	599 ± 14	
Lissodendoryx, sp.	25765-4	574 ± 25	
(Hexactinellida)	25766-2	569 ± 30	
(Hexactinellida)	25767-2	693 ± 53	
(Demospongia)	26601	523 ± 19	
	AA 1	487 ± 31	Antarctica
	AA 2	476 ± 30	
at least 4 genera,	AA 3	435 ± 28	
not identified	AA 4	468 ± 30	
	AA 5	538 ± 36	
	AA 6	590 ± 36	

TABLE V: Comparison of Boron Concentrations in Sponges from the same Genera but Different Locations

Sample	Location	[B], ppm	Genus & Species
FP 1	San Juan Islands, Washington*	587 ± 35	Syringella
WS 1	San Juan Islands, Washington*	506 ± 30	
C 2	Gulf of Mexico—Honduras	353 ± 19	Iotrochata birotulata
YH 9	Bahamas	345 ± 20	
YH 4	Nova Scotia	670 ± 33	Haliclona
YH 7	Massachusetts Bay	660 ± 32	
YH 11	Puerto Rico	334 ± 19	
25766-1	California (small spicules)	485 ± 55	Axinella
YH 5	Spain—Mediterranean (hypersaline)	484 ± 25	

* The two sites in the San Juan Islands are separated by about 10 km.

California had very small spicules which were analyzed as a bulk sample. The Mediterranean location is slightly hypersaline and intermediate between "temperate" and "tropical" in climate.

F. Correlation of the boron content of live-collected spicules with salinity and other environmental factors

Live-collected sponges were obtained from the locations shown in Figure 6. Table III gives the results of boron analyses of these specimens, and Appendix II provides documentation of the sample sources and water salinities.

The observed boron concentrations are plotted against salinity in Figure 7. It is apparent that samples of the same species from the same location (the three sponges at 6 ^{o}/oo, each group of samples at about 25 ^{o}/oo, and two of the sponges from 28-32 ^{o}/oo) have boron concentrations which agree within counting statistics. Fresh-water spicules contain 5 ppm B or less, and brackish-water spicules have boron contents between the fresh-water and the high group of marine values. The average boron concentrations for each location are plotted in Figure 8; a clear trend of the data is shown with the dashed lines.

The obvious environmental difference between tropical and temperate locations is water temperature. Most of the sponges were collected in shallow water (less than 100 feet), and the water temperature was measured at the collecting site for the Southern California sponges. Boron concentrations have been plotted relative to published surface water temperatures for the marine specimens in Figure 9. The grouping of the warm- and cold-water points is striking.

FIGURE 6

Map showing sample locations. The small dots indicate live-collected sponges and the large dots indicate cores.

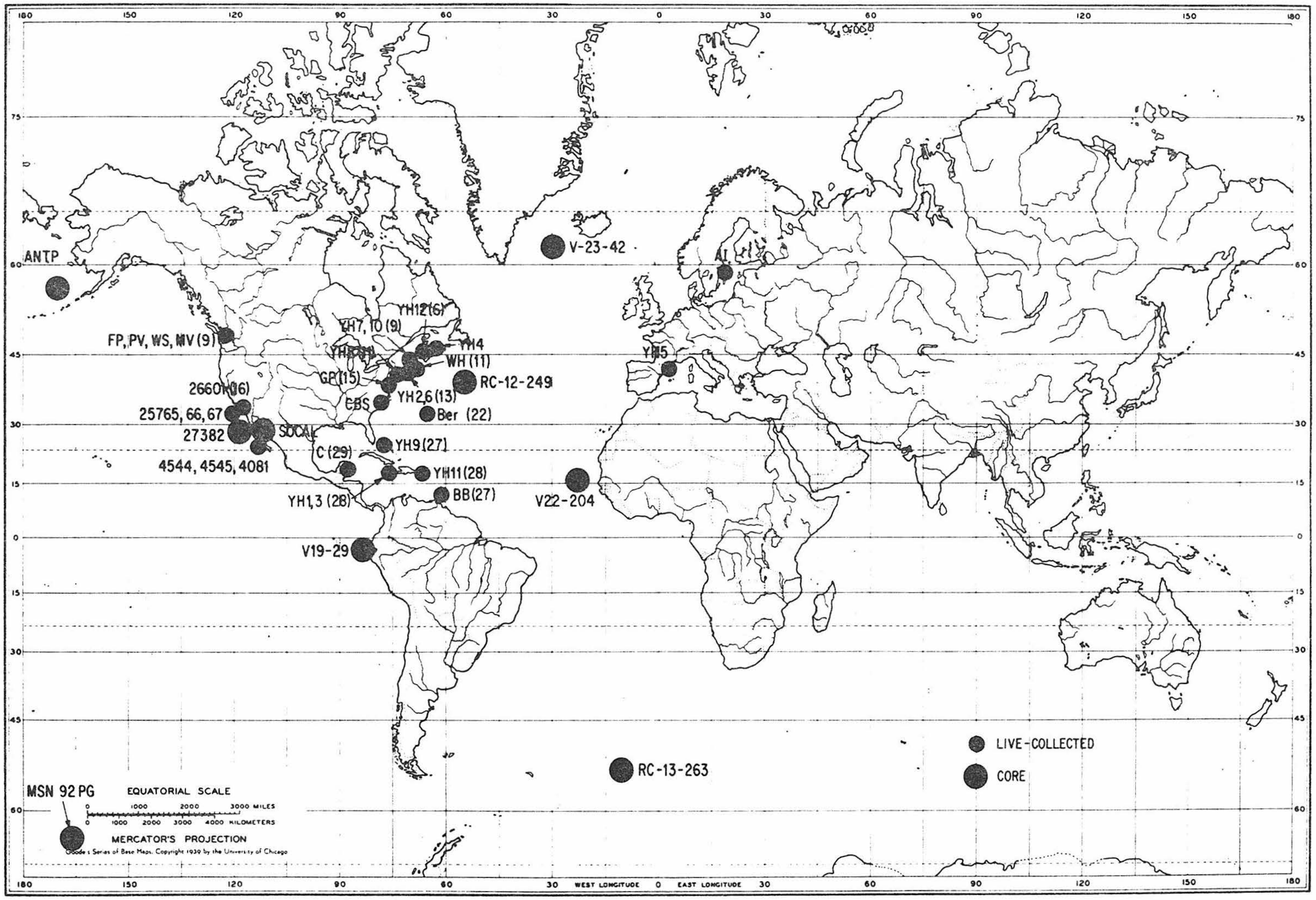

ANTP
V-23-42
AI
FP, PV, WS, MV (9)
YH12(6)
YH7, 10 (9)
YH8
YH4
WH (11)
GP(15)
RC-12-249
YH5
2660K(16)
25765, 66, 67
27382
SOCAL
CBS
YH2,6 (13)
Ber (22)
YH9 (27)
C (29)
4544, 4545, 4081
YH11 (28)
YH1,3 (28)
BB (27)
V22-204
V19-29
RC-13-263
LIVE-COLLECTED
CORE
MSN 92 PG
EQUATORIAL SCALE
0 1000 2000 3000 MILES
0 1000 2000 3000 4000 KILOMETERS
MERCATOR'S PROJECTION
Goode's Series of Base Maps. Copyright 1930 by the University of Chicago
180
150
120
90
60
30
0
75
45
15
WEST LONGITUDE
EAST LONGITUDE

FIGURE 7

Plot of boron concentration versus salinity for spicules from live-collected sponges. Each point represents the average of spicule analyses (generally 5 or more) for a single sponge. Representative error bars indicating standard deviations based on counting statistics are shown. Interspicule variations are comparable to these standard deviations. The large uncertainties in salinity for the brackish-water samples are due to large seasonal and annual fluctuations at the sample locations; each of these sponges may have been exposed to the entire range of variation. The closed circles represent sponges from cold (less than 15° C) nutrient-rich water and the open circles represent sponges from warm (greater than 15° C) nutrient-poor water.

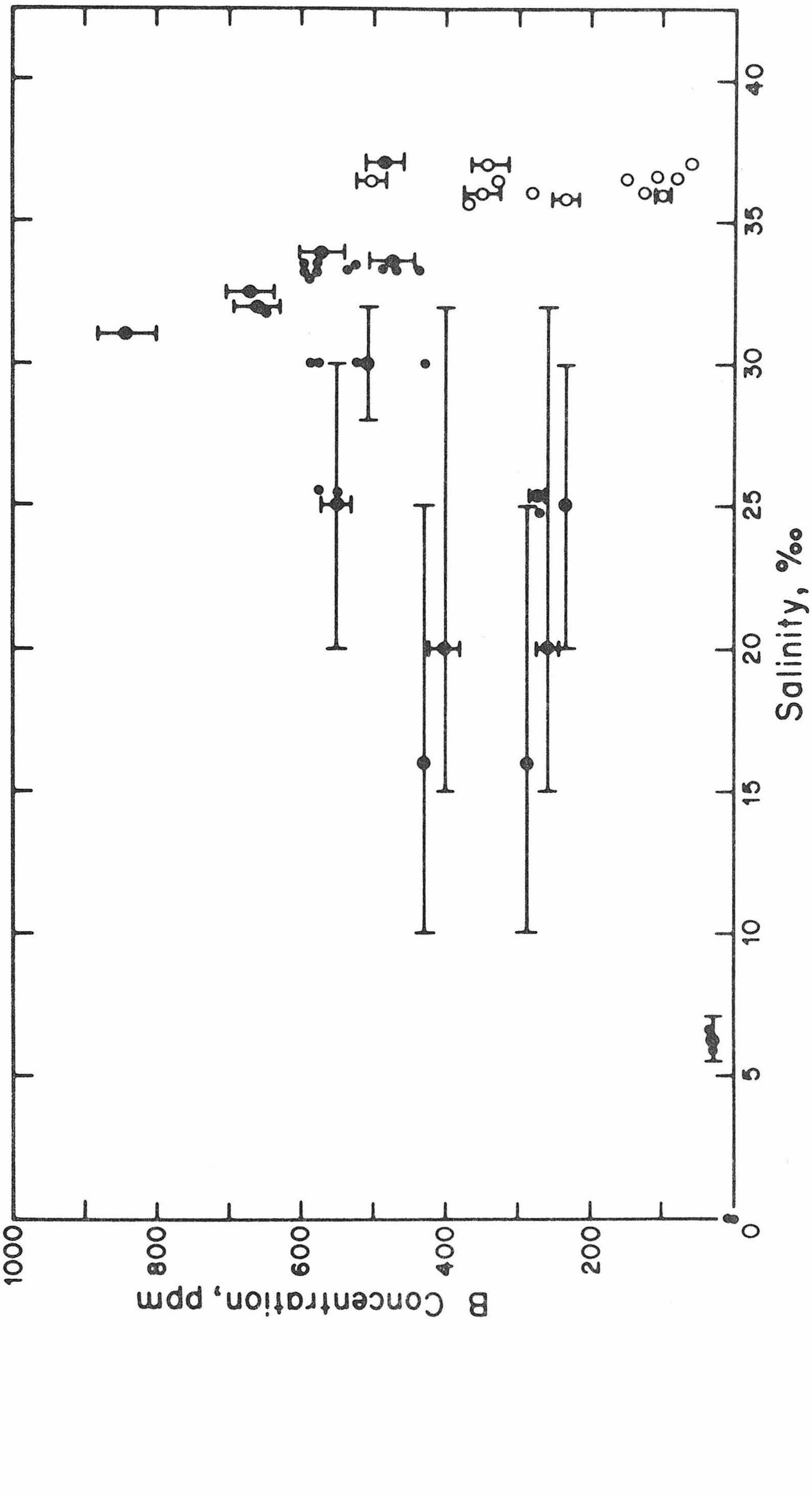

B Concentration, ppm
1000
800
600
400
200
0
Salinity, ‰
0
5
10
15
20
25
30
35
40

FIGURE 8

Plot of B concentration versus salinity for sponge sample locations. Each point represents the average of the boron concentrations of all samples analyzed from each location. The error bars represent the range in boron concentrations for all samples analyzed and the ranges in water salinity. When error bars for salinities are absent, the variations are small (± 1 ^{o}/oo or less). The closed circles represent areas of low water temperature (less than 15° C) and high nutrient supply; open circles represent tropical regions (greater than 15° C) with low nutrient supply. The dashed lines indicate a range for the trend of boron concentrations with salinity for cold-water sponges.

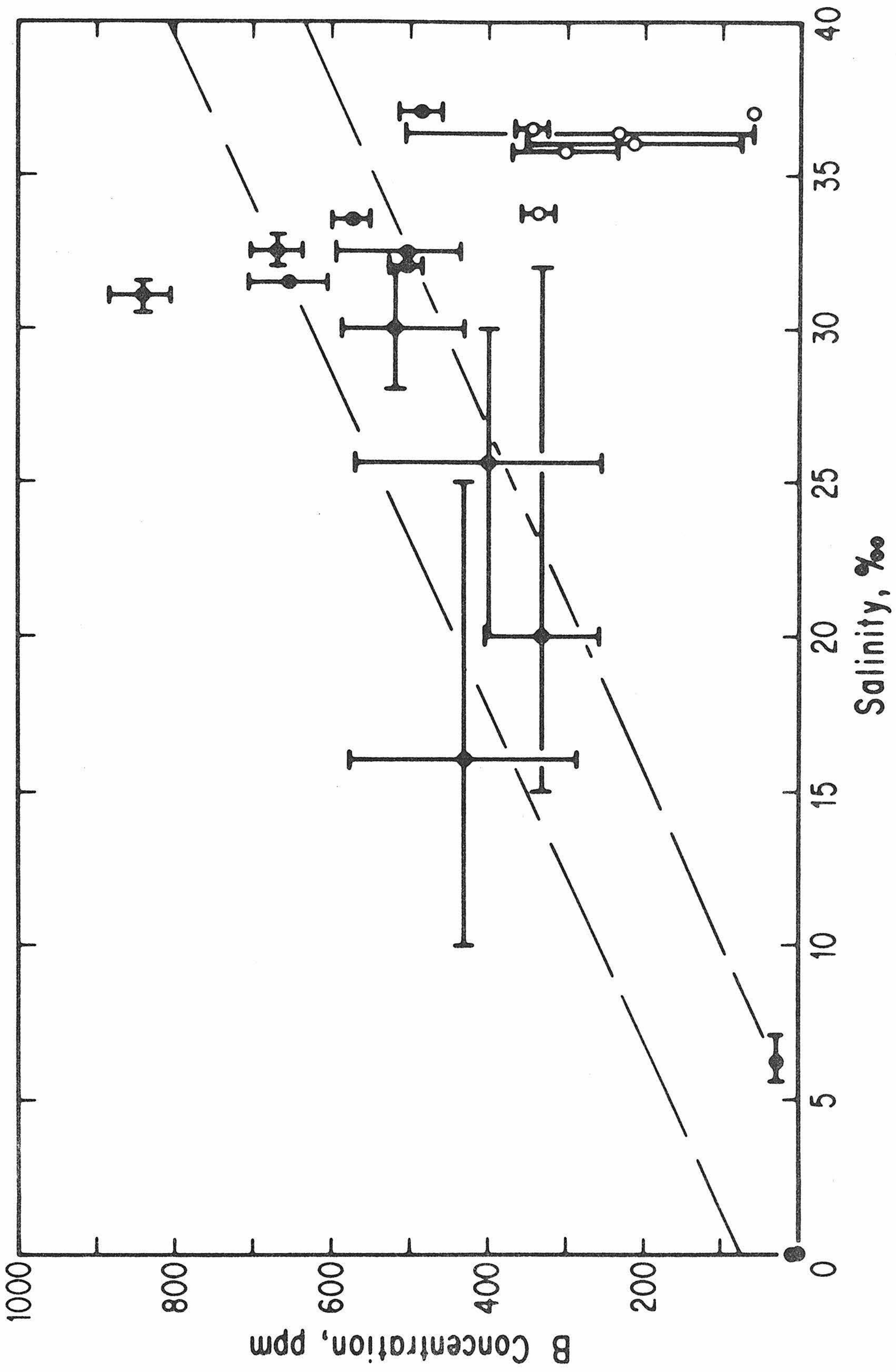

B Concentration, ppm
1000
800
600
400
200
Salinity, ‰
0
5
10
15
20
25
30
35
40

FIGURE 9

Plot of boron concentration versus surface water temperature for live-collected sponge spicules from normal marine localities. Each point represents analyses of spicules from a single sponge. Representative error bars indicate standard deviations in B concentrations based on counting statistics and the ranges in surface water temperatures, except the San Nicholas Island specimens, for which the actual temperature at the collecting site was measured. The temperature data for all locations except San Nicholas Island are from U. S. Department of Commerce, NOS Publications 31-1 and 31-3. The symbols represent the following locations:

● - Arthur Harbor, Antarctica

◈ - Block Island, Rhode Island

◬ - Massachussetts Bay, Massachussetts

⊙ - San Nicholas Island, California

◆ - Eastport, Maine

⊡ - San Juan Islands, Washington

○ - Jamaica

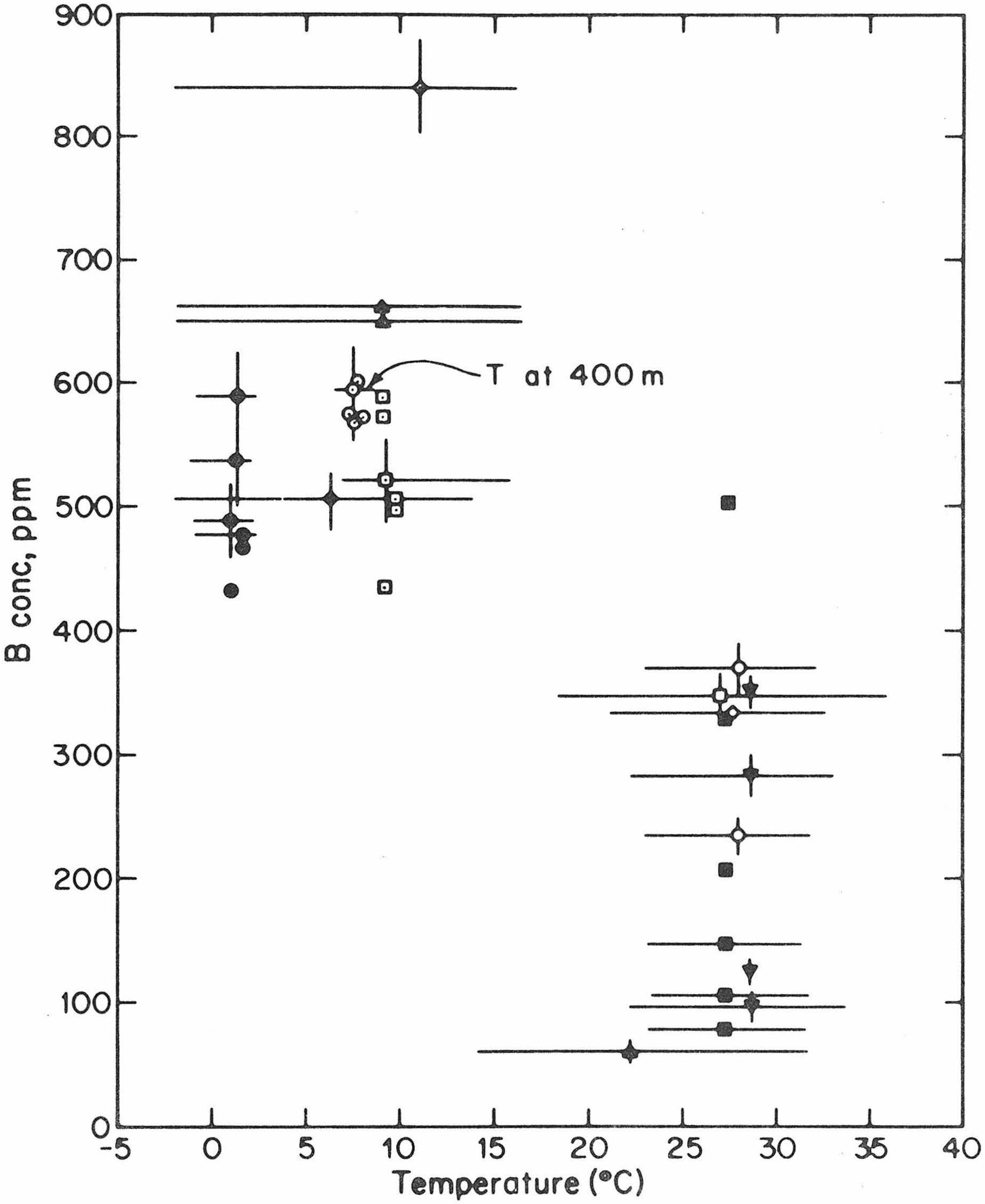
▽ - British Honduras

■ - Barbados

▲ - Bermuda

□ - Bahamas

◇ - Puerto Rico


T at 400m
B conc, ppm
Temperature (°C)
0
100
200
300
400
500
600
700
800
900
-5
0
5
10
15
20
25
30
35
40

There does not appear to be a simple correlation between temperature and boron concentration; for temperatures less than 15° C the boron concentrations are uniformly high, and for temperatures greater than 20° the boron concentrations are lower and more variable. The Block Island, Rhode Island sample, with 840 ppm B, is anomalously high, possibly reflecting polluted water. Water samples collected near population centers may have markedly increased boron concentrations due to the presence of industrial wastes and household detergents (Ahl and Jonsson, 1972; Matthews, 1974). Long Island Sound is surrounded by a region of high population density. It has also been suggested that the wide variation in B concentrations found in the Barbados sponges may be due to localized mixing of sea water and fresh water which travelled downward from the surface of the island through the porous reef carbonate (Senn, 1940; Fischer, 1979).

However, water temperature is not the only environmental factor which differs in the temperate and tropical locations from which these specimens were obtained. All of the tropical specimens are from water of low productivity and all of the temperate specimens are from areas of high productivity (Lisitzin, 1977). By productivity is meant the number or mass of planktonic organisms found per unit volume of water; the number of organisms is dependent on the available supply of nutrients, particularly nitrogen and phosphorus. Further, it is not known how the sponges obtain the boron which is incorporated into their spicules. It could come directly from sea water or indirectly through particulate food.

The possibility that the boron concentration in the spicules is a reflection of the boron/silicon ratio in sea water where the sponge grew was also considered. The sponges from the areas with the largest silicon concentrations (Antarctica, Southern California, and Washington) have high boron concentrations in their spicules. Recall from Chapter I (Table I) that the boron concentration in sea water is uniform within 10%, independent of ocean, latitude, or water depth. If the sponges were unable to discriminate between the two elements, one would expect that specimens from high-Si water would have lower spicule B contents than those from low-Si water, contrary to the data presented here. Moreover, since the silicon concentration in water increases markedly with depth for the first several hundred meters (Calvert, 1974), one would expect that sponges from deeper water (California) might have a lower B/Si ratio in their spicules, also contrary to observation. It can be concluded that boron and silicon can be discriminated by sponges.

If sponges obtain boron from their food, a more detailed consideration of their food supply is in order.Sponges are all filter-feeders, and all digestion is intracellular. They are indiscriminate, taking in any particles which are small enough. Thus their diet is believed to consist of bits of organic detritus, bacteria and other cells, and dissolved organic compounds (de Laubenfels, 1955; Reiswig, 1971a; Bergquist, 1978). The bulk of this food originates in the surface layers of the water, where the primary producers reside, and rains down to the bottom, possibly being cycled through one or more additional organisms (e.g., zooplankton and bacteria). It is believed that the only differences in food consumption between different sponges are due to possible differences in maximum particle size tolerated (taxonomy-related) and differences in the nature of the food available (dependent mainly on surface conditions). Thus, the food supply is a link between the surface water and the sponge.

In three cases, BB3, BB4, and YH10, analysis of two types of spicules from distinctly separate parts of the sponges yielded different B concentrations (see above discussion of <u>Geodia</u> and <u>Polymastia robusta</u>). In BB3 and BB4 the spicules were differentiated into mega- and microscleres with higher B concentrations in the megascleres, while in YH10 the spicules from the arm-like supports had greater boron concentrations than those from the main part of the sponge. Thus, it appears that B can be handled somewhat differently by different parts of a sponge, despite the relative independence of function in sponge cells.

These two lines of evidence, that boron metabolism in sponges can depend on the location within the sponge(e.g., ease of access to food and nutrients) and that the boron content of the spicules may correlate better with the environment in which the food originates than with the environment of the sponge itself, suggest that sponges may indeed be obtaining the B from their food.

It would be of great interest to determine which part of the food supply provides the most boron to the sponges. It is known that diatoms and other algae require boron and can not reproduce in its absence, and that some types of algae concentrate B in the organic parts of their cells (McIlrath and Skok, 1958; Lewin, 1965, 1966a, 1966b; Yamamoto, <u>et al</u>., 1971; Lewin and Chen, 1976). From this work, it is apparent that diatoms also concentrate B in their frustrules (see section "Diatoms"). Most other types of plankton for which analyses have been found appear to be low in B contents (Nicholls, et al., 1959; Bowen and Gauch, 1966; Yamamoto, et al., 1973).

Boron analyses were conducted on several dried mixed zooplankton samples. Two samples which had been collected near the California coast between Los Angeles and San Diego (high productivity) contained 55 ± 6 ppm B and two samples from the central Pacific, about 1600 km north of Hawaii (low productivity) contained 23 ± 3 ppm. These boron concentrations are very low relative to those found in sponge spicules or diatom frustrules, but the trend of increased boron with increased productivity is in agreement with the observations made with sponges. However, the high-productivity samples were collected near the shore and may contain more B-rich clay than the low-productivity samples.

Little is known about the boron content of the very small particles which the sponges ingest--the bacteria and detritus. Indeed, little is known about exactly what the particles are. The differences between the food supplies for high- and low-latitude sponges could be due to (1) different kinds of planktonic populations which include different abundances of boron-concentrating organisms; or (2) boron-rich and boron-poor organisms of the same type which accumulate boron in response to water temperature, nutrient supply, or some other variable. It may or may not be primary producers which gather B for sponges; if it is, it might be worthwhile to investigate more fully the temperature, salinity, and nutrient-related responses of different types of algae in accumulating boron. Also, it is clear that primary producers are a reasonable place to look for a boron-salinity correlation with fewer complications than have been encountered with sponge spicules. However, there are additional problems encountered in separating and analyzing such small organisms.

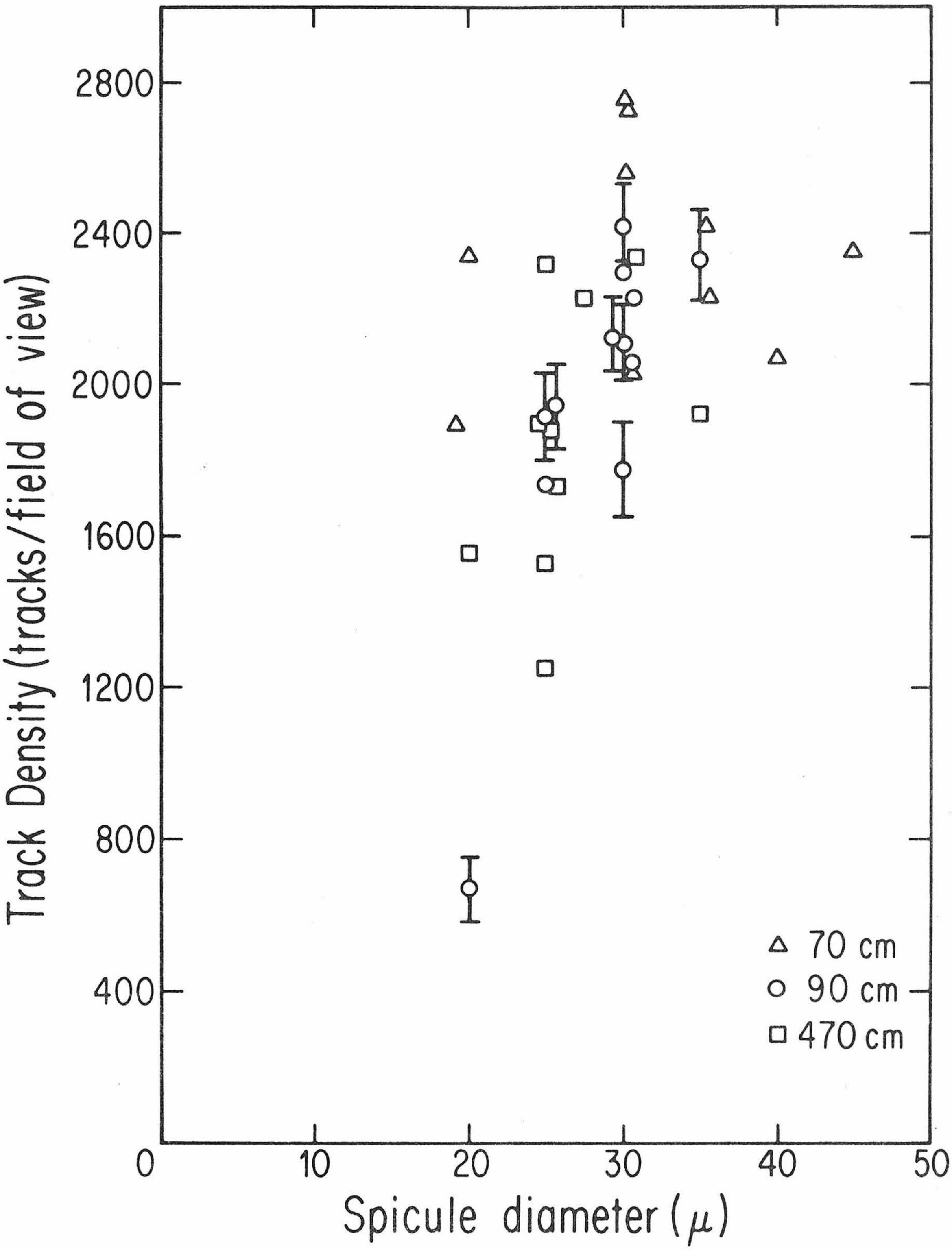
G. Boron analyses of fossil spicules

The spicules selected for boron analyses from core samples were subjected to more stringent selection criteria than the live-collected specimens. The track densities found in a number of spicules from a single core and irradiated at the same time are plotted against spicule diameter in Figure 10. For spicules wider than 25 microns, the B concentration is independent of spicule diameter, but several spicules in the 20-25 micron range gave low B results (less than 1600 tracks/field of view). It was concluded that slightly wider spicules were required for reliable B determinations. The greater spicule diameter required for fossil samples is probably due to the partial dissolution of the spicules along the central canals. After polishing, which removes material from the exterior of the spicule, the remaining wall may be thin relative to the alpha range.

In order to identify spicules which had undergone chemical alteration, electron microprobe analyses were obtained for all fossil spicules whose B analyses are included in this work and for several live-collected spicules also. Spicules from live-collected sponges

FIGURE 10

Plot of track density versus spicule diameter for spicules from the 70-, 90-, and 470-cm. depths of core V23-42. All data were obtained from samples irradiated together and track densities are directly comparable to each other. Representative one sigma errors are based on counting statistics. A track density of 2000/field of view is equivalent to about 450 ppm B.


Track Density (tracks/field of view)
2800
2400
2000
1600
1200
800
400
0
10
20
30
40
50
Spicule diameter (μ)
△ 70 cm
○ 90 cm
□ 470 cm

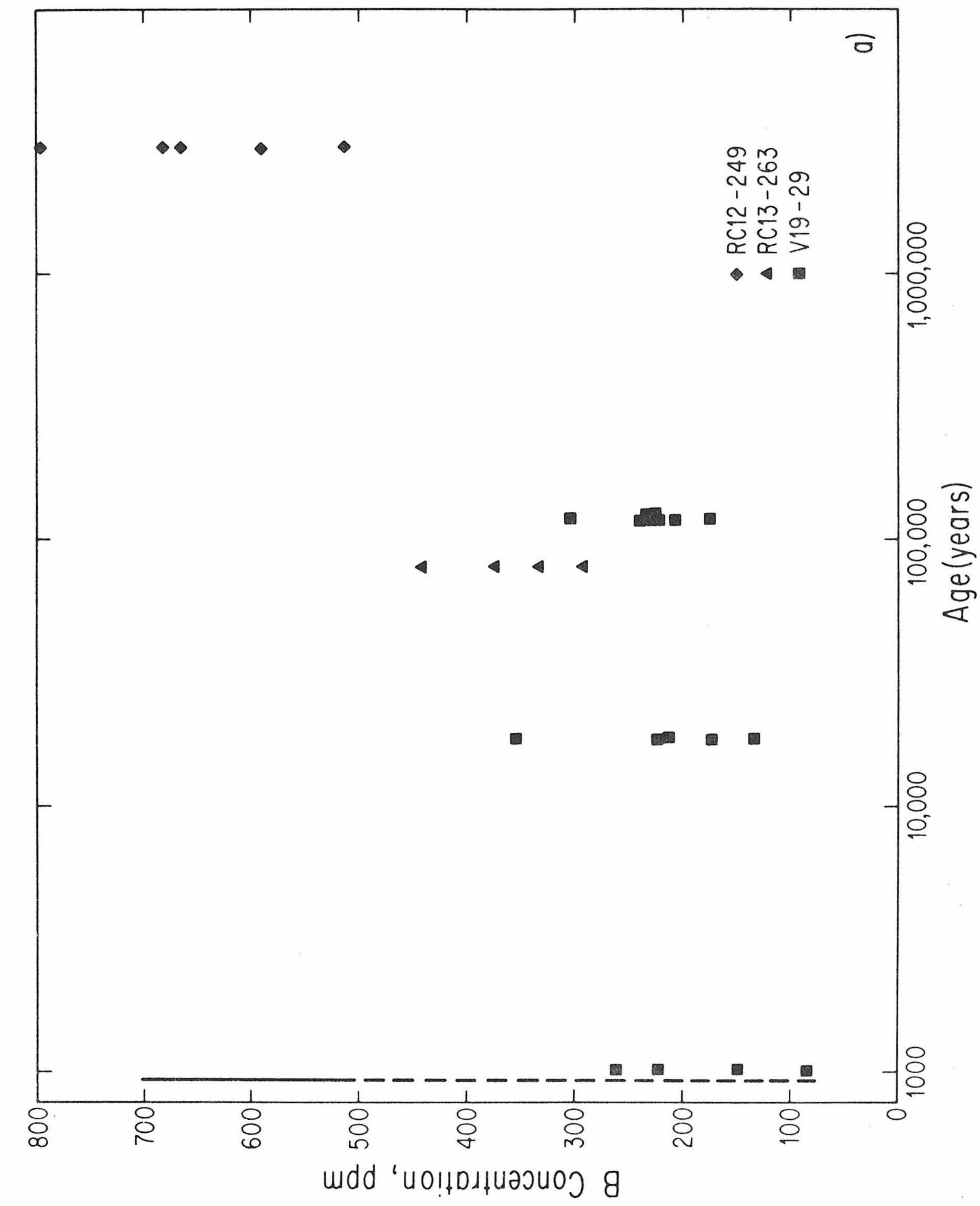
contain up to 20% water and are composed of otherwise very pure SiO_2; no other cations or anions were detected in significant quantities (>0.1%) by the microprobe. Spicules with non-hydrous portions greater than 80% of the total oxide sum, with SiO_2 comprising 99.6 ± 0.4% of the non-hydrous fraction, and which met the optical criteria discussed above (see section "Selection criteria for boron data from sponge spicules") were selected for B analysis. No correlation was found between boron concentration and oxide sum. Only about 5% of the fossil spicules analyzed had to be rejected because of low SiO_2 contents. The oxides present other than SiO_2 in measurable quantities were Al_2O_3, MgO, TiO_2, FeO, and BaO, never in excess of 1% of the total. High Al_2O_3 concentrations may be due to the presence of grains of Al_2O_3 on the surface from polishing. When first probe analyses of a spicule had oxide totals less than 80%, the analysis was repeated on a different spot. Usually the second analysis had a total greater than 80%, and it was assumed that the first analysis included some epoxy due to the difficulty of locating the beam on the narrow spicules. About 2% of the spicules had low second analyses and were rejected. The selection criteria used were stringent and may have resulted in the exclusion of good data, but presumably they were successful in eliminating bad data.

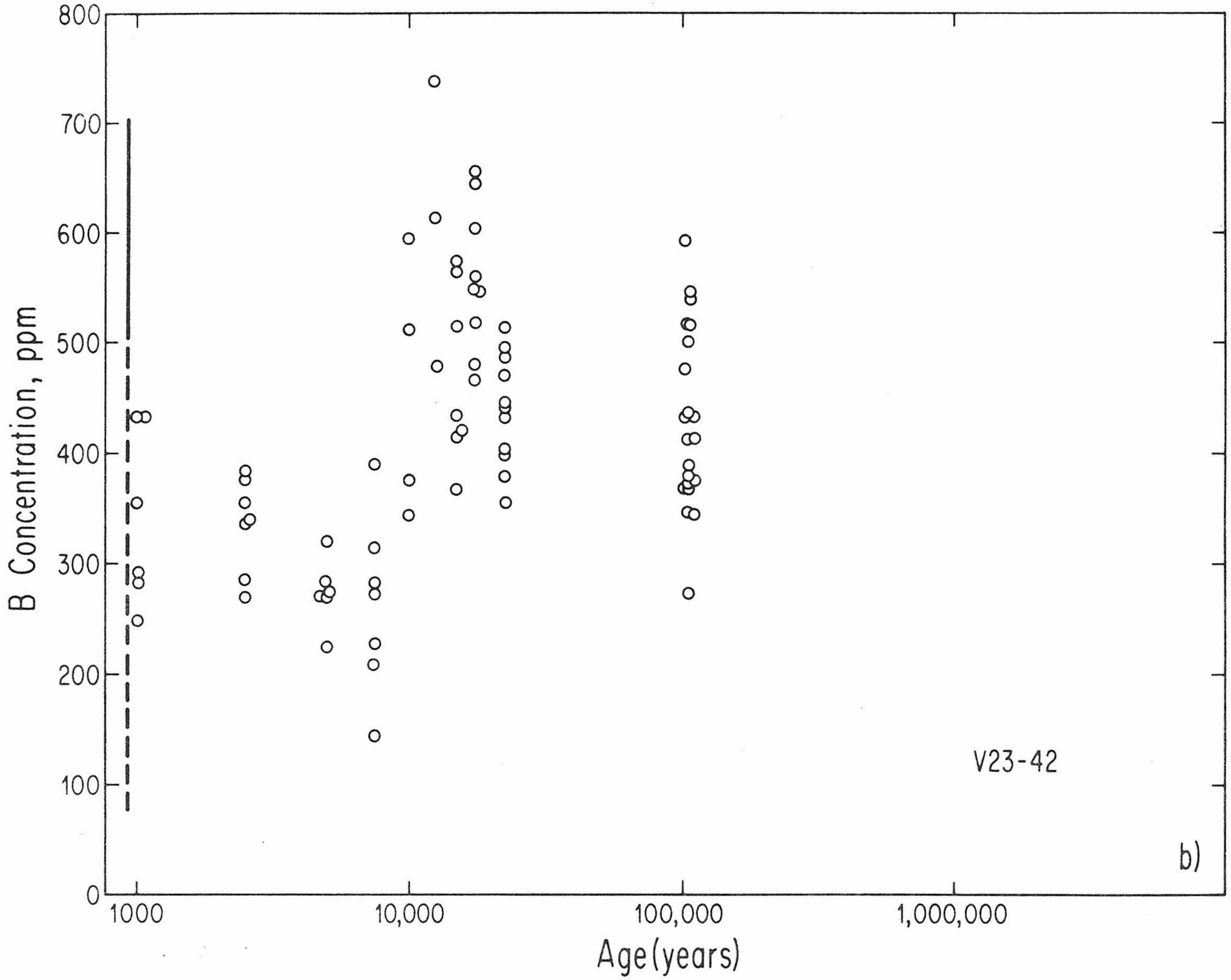
The primary purpose in studying the core samples, which are all from normal marine environments, was to test for diagenetic effects on spicules in sediment samples. Ages were determined on the basis of uniform sedimentation rates inferred from radiometric ages of several tuff layers in nearby cores (V23-42) (Ruddiman, 1978), or by oxygen isotopic composition in relationship to microfauna (Cooke, 1978). Visual examination with a microscope revealed a trend toward increased solution pitting on exterior surfaces and enlargement of the central canal with depth in cores (age). Infrared spectra were obtained for spicules from core V23-42 positions corresponding to approximately 0, 10,000, and about 100,000 year ages. There was no evidence for any alteration of opal to cristobalite or quartz. Similarly, electron microprobe data did not indicate any significant alteration or dehydration except in a few spicules; there were no core positions with abundant large spicules (greater than 25 microns in diameter) from which a significant proportion of the spicules had to be excluded on the basis of chemical alteration. Boron contents of individual fossil spicules are plotted against age in Figure 11. For two cores, V23-42 and V19-29, data were obtained from several positions in each core. V23-42 samples were selected to cover a time interval extending backward through the last major glaciation, demonstrating the changes in boron concentrations in spicules with changes in climate (Figure 11b). There is significantly more boron in the spicules from the glacial interval (9,000-13,000 years) and in the older spicules than in the more recently deposited material. The close of the Wisconsin glacial period was about 11,500 years ago. For the first 7500 years there is no significant change in boron contents of spicules, and there is no significant change in spicules from 10,000 to 100,000 years old. V19-29 spicules exhibit no significant differences in boron concentration over the last 120,000 years, probably reflecting the equatorial location of this core.

FIGURE 11

a) Plot of boron concentration versus age for spicules from cores V19-29, RC12-249, and RC13-263. Each point represents one spicule, selected according to the criteria described in the text. The heavy line along the left edge of the figure indicates the range of boron concentrations observed in live-collected marine spicules. Temperate, high-productivity values are shown with a solid line; tropical, low-productivity values are shown with a dashed line. The core locations were V19-29--west coast of Ecuador; RC12-249--North Central Atlantic; RC13-263--South Atlantic.

b) Plot of boron concentration versus age for spicules from core V23-42, from the Atlantic Ocean between Iceland and Greenland. Each point represents a single spicule; all spicules were selected according to the criteria discussed in the text and also microprobe analyses.


B Concentration, ppm
800
700
600
500
400
300
200
100
0
Age(years)
1000
10,000
100,000
1,000,000
◆ RC12-249
▲ RC13-263
■ V19-29
a)

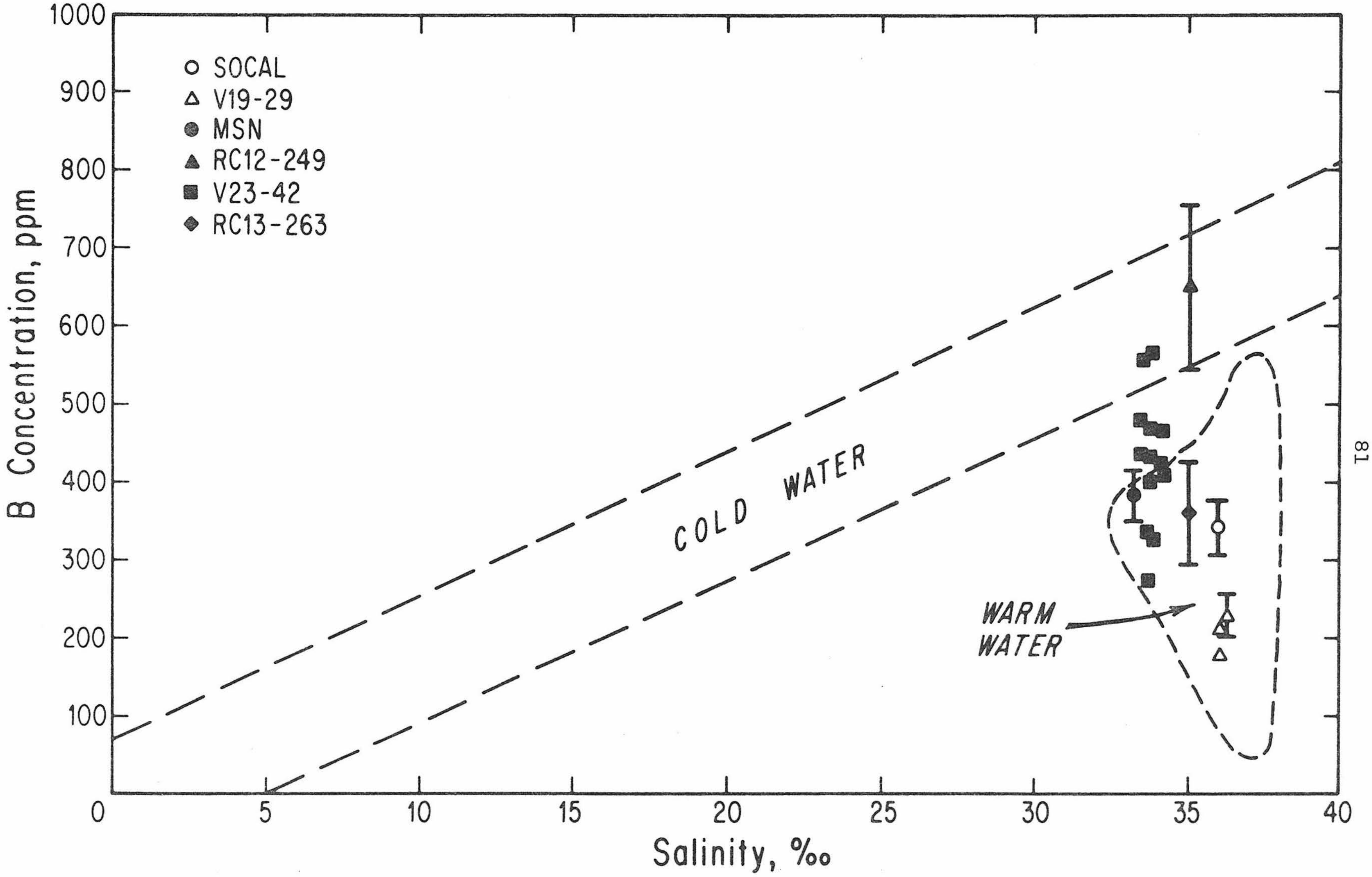

800
700
600
500
400
300
200
100
0
B Concentration, ppm
1000
10,000
100,000
1,000,000
Age (years)
V23-42
b)

The fossil spicules tend to have less boron than live-collected spicules with the exception of RC12-249; the fossil data are compared with live-collected data in Figure 12. A possible explanation is that the fossil spicules have undergone rapid diagenetic loss of some of their B in a manner which is not detectable by infrared spectroscopy or microprobe analysis. The lack of systematic changes in B content in the deeper core samples suggests that at least part of the boron is retained. It is also possible that the different boron concentrations do represent real environmental differences between sponges now and sponges in the past. Neither of these explanations seems entirely satisfactory.

If sponges receive boron directly from water, one would not expect to observe any biologic differences over as short a time interval as 1 million years. If sponges obtain boron from their food, however, one might expect that variations in diet may have occurred as a result of climatic fluctuations. Most of the food supply originates in the surface layer of the ocean, which is subject to climatic fluctuations. Both salinity and temperature variations occur in surface water, reflecting global changes in the amount of water incorporated into glacial ice, precipitation rates, and mean atmospheric temperatures. Variations in the distributions of numerous planktonic organisms in relation to climatic variations are well documented. All of these core samples were collected from deep water (1000 meters or more), which is cold and not subject to major fluctuations. Most of the core locations were quite far from land and the spicules were presumably derived from local, deep-water sources.

FIGURE 12

Plot of boron concentration versus salinity for fossil spicules. The areas within the dashed lines represent the regions in which the live-collected data fall (see Figures 7 and 8). Each point indicates the average of all spicules analyzed for a single core position. Representative error bars show one sigma standard deviations of the values for individual spicules about the mean. Solid symbols represent cold, high-productivity surface water and open symbols represent warm, low-productivity surface water for the core locations at present. Data are shown from two locations which were not included in Figure 11 because the sample ages (Holocene or Pleistocene) are not known precisely.


○ SOCAL
△ V19-29
● MSN
▲ RC12-249
■ V23-42
◆ RC13-263
COLD WATER
WARM WATER
B Concentration, ppm
1000
900
800
700
600
500
400
300
200
100
0
5
10
15
20
25
30
35
40
Salinity, ‰

H. Diatoms

The results of boron analyses of a variety of diatomite samples and of diatom fractions from three deep-sea core samples are presented in Figure 13. With the exception of three diatomites from the Mono Lake drainage system in eastern California, a clear difference in B contents was observed for lacustrine relative to marine samples. The error bars indicate standard deviations based on counting statistics. All of the freshwater samples had boron concentrations of 40 ppm or less, while the marine samples all had more than 80. None of these samples consisted of pure diatom tests; various amounts of other sediments, carbonate cement, etc. were also present. Thus, it is difficult to draw any conclusions about the variations in boron content on a finer scale than distinguishing freshwater and marine deposits. All samples contained well over 50% diatoms, and it is doubtful that the marine/freshwater distinction would disappear if purified samples were analyzed. The Lompoc diatomite sample (L) with the high B concentration of about 150 ppm was stored for a long period of time in a cabinet with specimens of colemanite and other borate minerals. This sample is probably also the cleanest diatomite studied. The high B concentration could be due to less dilution of boron-rich diatom tests by other sediments or to contamination from the borates. A third possibility is that the opal in this sample is significantly more dehydrated than in the others and the lower water content results in a higher boron concentration.

The lacustrine samples have been referred to as "freshwater" in the preceding discussion; this is not strictly speaking the case for

FIGURE 13

Plot of B concentrations observed in diatom samples. Representative error bars are 1σ standard deviation based on counting statistics. Each point plotted represents one analysis. The sample locations are:

EP - Eagle-Pitcher Mine, near Lovelock, Pershing Co., Nevada
CL - Copco Lake Deposit, Siskiyou Co., California
KF - Knight's Ferry, Tuolumne Co., California
EL - Eagle Lake, Lassen Co., California
LB - N. end of Lake Britton, Shasta Co., California - Pliocene
RV - Russel Valley, Nevada Co., California
B - Basalt,Mineral Co., Nevada
BF - Burney Falls, Shasta Co., California - Pliocene
CQ - Chilcoot Quadrangle, Plumas Co., California
D - Near Dorris, Siskiyou Co., California
WC - Willow Creek Area, S. of Dome Mt., Siskiyou Co., California
HC - Hat Creek at Highway 299, Shasta Co., California
LV - Long Valley, Mono Co., California
PI - Paoha Island, Mono Lake, Mono Co., California

Figure 13 (cont.)

IW - Indian Wells Valley, Inyo Co., California

SOCAL - 28 20'N, 112 23'W, 896 m. core sample - Gulf of California

MSN - 63 17'S, 166 58'W, 2639 m. core sample - Antarctic Ocean

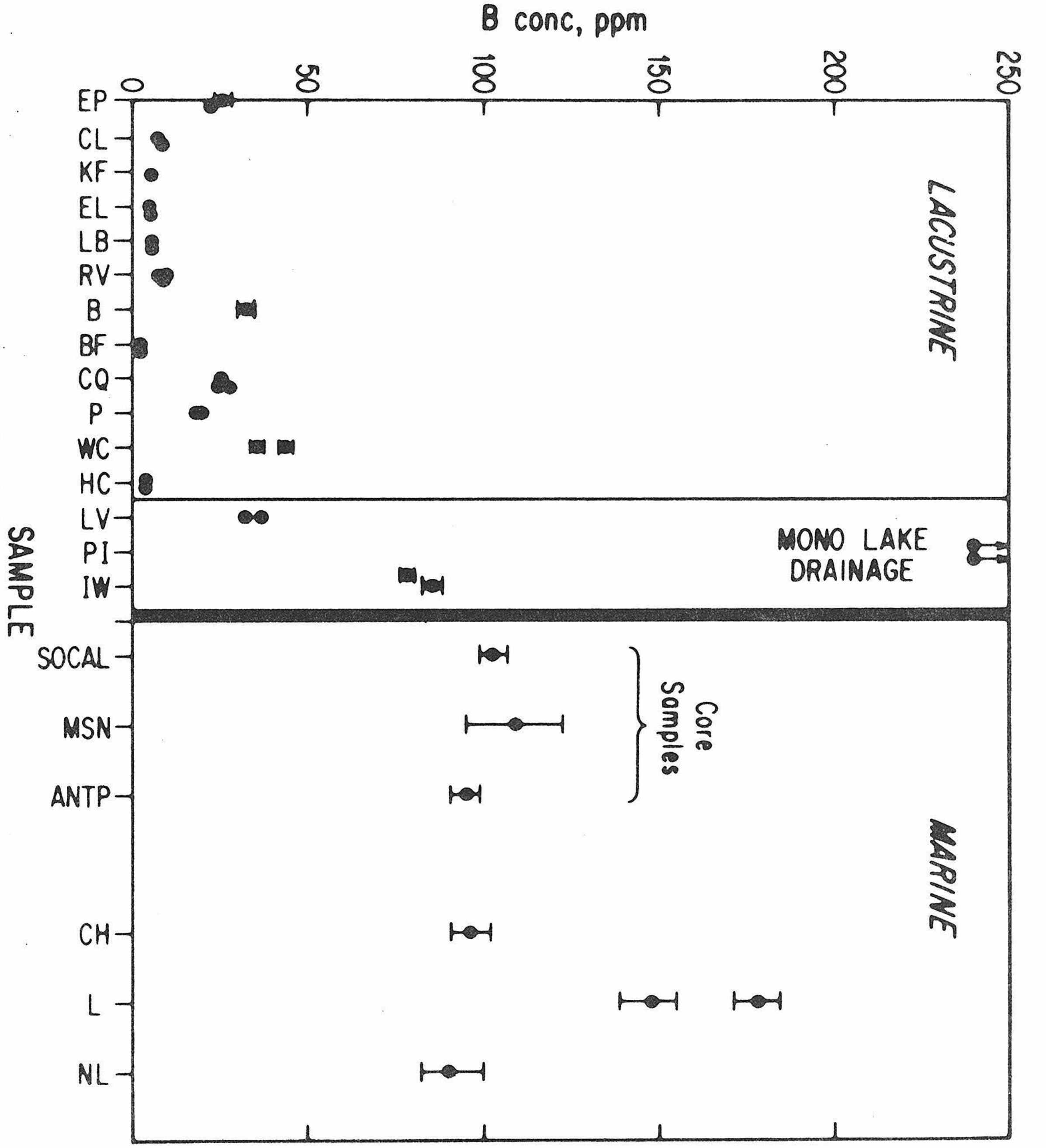
ANTP - 56 23.2'N, 171°4.6'E, 2392 m. core sample - Bering Sea

CH - Chalk Hill, City of Industry, Los Angeles Co., California - Miocene

L - Monterey Formation, Lompoc, Santa Barbara Co., California - upper Miocene

NL - Monterey Formation, Newport Lagoon, Orange Co., California - upper Miocene

Unless specified all samples were of Pleistocene or Recent Age.


B conc, ppm
0
50
100
150
200
250
SAMPLE
EP
CL
KF
EL
LB
RV
B
BF
CQ
P
WC
HC
LV
PI
IW
SOCAL
MSN
ANTP
CH
L
NL
LACUSTRINE
MONO LAKE DRAINAGE
Core Samples
MARINE

all samples. All of them are from Quaternary lake deposits in California and Nevada; the locations are associated with an arid climate and with volcanic activity. There is some evidence that the diatom growth was directly promoted by the addition of nutrients from volcanic gases, hot springs, and rapid weathering of volcanic rocks (Cleveland, 1977). Whether because of the volcanic activity alone or coupled with an arid, warm climate, the mineral contents of these lakes were very likely far different from what is found in a normal freshwater lake. The Mono Lake drainage system is particularly worthy of consideration in this respect; Mono Basin, Long Valley, and the Owens Valley (location of Indian Wells diatomite) have been the scene of extensive Quaternary volcanism, resulting in the addition of large quantities of boron to the water. Whitehead and Feth (1961) found 350 ppm B in Mono Lake, compared to 4.6 ppm in sea water (Mason, 1966) and 0.012 ppm in average river water (Livingstone, 1963). Mono Lake is well-known for its highly unusual chemistry (Reed and Mankiewicz, 1975; Cleveland, 1977). It is significant that these three samples had higher B contents than most of the other lacustrine samples. The Chilcoot Quadrangle (CQ) location is near Mount Lassen, the Basalt, Nevada (B) sample location is associated with evaporite deposits, and the Dorris (D) and Willow Creek (WC) locations are very close to Lava Beds National Monument. All of the other diatomites had less than 10 ppm boron; probably this lower value is representative of a true freshwater situation.

Three sediment samples from the Gulf of California, the Antarctic Ocean, and the Bering Sea were studied. An attempt was made to analyze single large diatoms using the scanning electron microscope to count tracks. It was found that the high-track-densities areas corresponding to diatoms could usually not be located an low power, and that in the few cases when it was possible to find the correct area to count tracks at high power, the observed boron concentrations varied by as much as 400%. The frustrule walls of these specimens are probably too thin and porous to be considered an infinitely thick source for the alphas, and geometry corrections are difficult to make. Navicula pelliculosa (Bréb.) Hilse has walls only about 0.1 micron thick (Riemann, et al., 1966) and Striatella unipunctata walls are 3-4 microns thick (Roth and deFrancisco, 1977); the alpha range in opal is about 6 microns. Thus, it was concluded that only bulk diatom samples can be analyzed properly.

The diatom-rich fractions which had been collected on filter paper and irradiated yielded boron concentrations of about 90-105 ppm; these samples had as much as 30% other mineral material included and also can not be considered pure diatoms. Heavy liquid separations seem to be the most promising means of removing the non-diatomaceous material. However, most of the contaminating grains in the marine specimens (and probably also in the lacustrine samples) are probably quartz, feldspar, and clay minerals, and separation may prove difficult.

Because the true power of this experimental technique lies in its ability to obtain spatial distributions of B within adequately large samples and because of the difficulty in obtaining bulk diatom samples free of other material, further investigation of the boron content of diatom frustrules was not pursued.

Conclusions

A correlation between water salinity and boron concentration has been demonstrated for live-collected siliceous sponge spicules from temperate regions of high productivity. However, boron concentrations also reflect either water temperature or nutrient supply available to the sponge or to organisms at earlier stages in the food chain. At present there are insufficient data available to determine the nature of the relationship between environmental conditions other than salinity and the boron content of spicules.

Fossil spicules tend to contain less boron than is found in live-collected material. More study is required to determine the existence of diagenetic effects; the techniques used to date have provided no evidence for alteration. It would be interesting to determine the chemical form of boron in spicules with nuclear magnetic resonance spectroscopy. A more thorough knowledge of the significance of the boron concentration in spicules may allow additional interpretations of the fossil data; it is possible that the lower boron concentrations reflect different environmental conditions. If the boron content of sponge spicules is sensitive to one or more components of the food supply, it may be more useful to study primary producers such as diatoms and eliminate any questions concerning the possible influence of other organisms in a multistep chain. The data obtained for diatoms suggest that their boron concentrations are sensitive to salinity and continued investigation may provide a useful technique for paleosalinity determinations. However, methods must be developed for obtaining only the diatom fraction of sediments. Normally diatom fragments are combined with other biogenic opal and inorganic material. Neither heavy liquid mineral separation nor hand-picking of diatoms is a satisfactory procedure.

If it can be demonstrated that boron concentrations in diatom frustrules and/or sponge spicules reflect environmental conditions such as nutrient supply or temperature, they may provide information about past and present circulation patterns in the oceans.

IV. BORON IN CARBONATE SHELLS

Mytilus edulis

The bay mussel, or *Mytilus edulis*, was chosen for initial investigation of a possible correlation of boron concentration with salinity because it tolerates a wide range of salinities and because it is abundant in shallow water throughout the temperate regions of the Northern Hemisphere (Wells and Gray, 1960) and in the fossil record. A description of the shells and of the procedures for sample preparation and analysis is contained in Appendix I. The material discussed here considerably extends the work presented in Furst, *et al*. (1976). Figure 14 is a sketch of a *Mytilus edulis* shell.

Sample Preparation and Analysis

The general method of sample preparation is described here. Special cases which required different procedures will be discussed later. Actual sample descriptions are included with the discussions of the results.

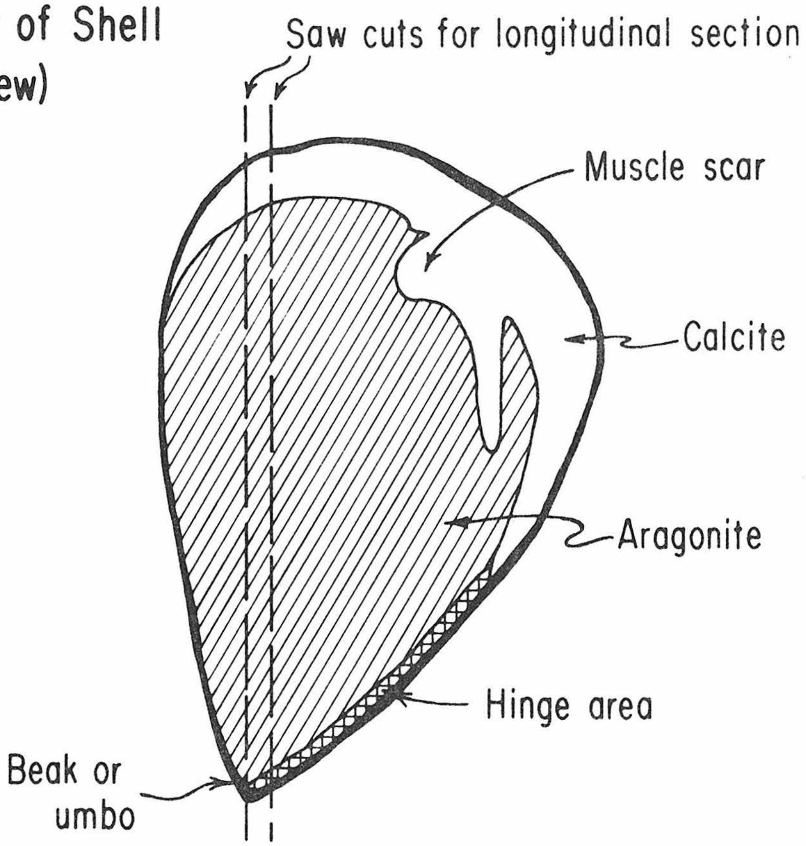
1. Carbonate shells were examined and selected for lack of damage from boring, encrusting organisms, and abrasion. Larger shells were preferred because they provided more sample area for analyses, but smaller shells were generally in better condition because they were younger and had a shorter period of exposure to attack by organisms and abrasion. The two valves were separated with a scalpel and forceps and the soft parts were scraped out with the scalpel. The better-preserved valve was cleaned ultrasonically in distilled water and then in ethanol (95 or 100 %). Large shells were glued to microscope slides with

FIGURE 14

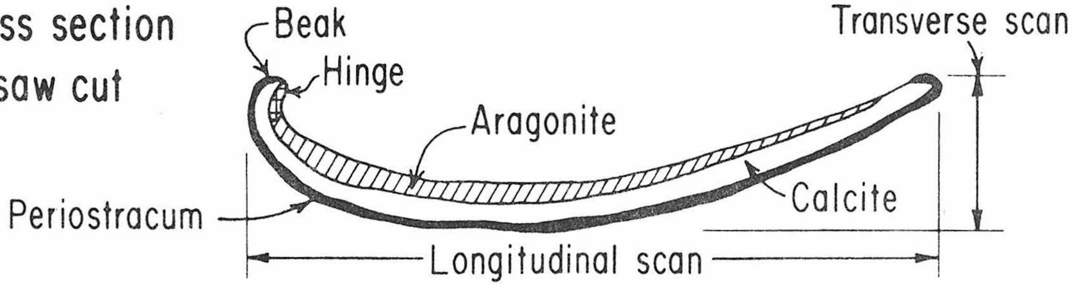
a) Sketch of the interior of one valve (plan view) of a *Mytilus edulis* shell with some of the features labelled. The heavy dashed lines indicate the location of the saw cuts.

b) Cross section of a saw-cut slice of the same shell as mounted in epoxy for analysis. The directions of transverse and longitudinal scans shown in Figure 2 of Appendix I are indicated.

(a)
Interior of Shell
(plan view)



(b)
Cross section
of saw cut



100 %). Large shells were glued to microscope slides with Lakeside resin, anterior margin down. Slices were then made through the umbo or beak and perpendicular to the growth direction of the shell (See Fig. 14), using a diamond blade and a Buehler 11-1180 low speed saw with water as a lubricant/ coolant. Small or delicate samples were not sawed.

2. Samples were cleaned in ethanol and/or methanol, allowed to dry, broken into smaller pieces if necessary, and placed on double stick tape which had been put on a microscope slide or other flat surface. A ring of lucite, generally 1" o.d. x 3/4" i.d., was placed around the specimen. Epoxy resin (Techkits E-7) was poured into the ring, and a needle was used to detach bubbles from the sample, ring, and tape. The epoxy was cured overnight at about 100° C. The mounts were then removed from the slide and marked as to their identity.

3. Samples were polished on a lap wheel using only ethanol as a lubricant. Water was avoided because the carbonates dissolved slightly and became pitted. The alcohol did not introduce significant contamination. An aluminum lap wheel, polishing cloth, and Al_2O_3 powders were reserved only for use with samples for B determinations. The first step in polishing was to use 120 grit Buehler SiC paper to grind the backs of the mounts so that they were flat and there were no remaining bubbles, if possible. 240 grit SiC paper (Buehler) was then used for about a minute on the backs to obtain a smoother surface, and on the fronts of the thicker and less delicate samples. The next step was 600 grit SiC paper, and then 1.0 micron aluminum oxide (all from

Buehler) on a Buehler AB Texmet polishing cloth for a fine polish. Once a flat surface was established and the entire sample cross section exposed, only about one minute of grinding at each successive grit size was required. Samples were cleaned ultrasonically in ethanol between each grit stage to remove all coarse material and allow a finer polish.

4. After the final polishing stage, the samples were cleaned ultrasonically in ethanol and then brought into a laboratory with a filtered air supply. They were cleaned ultrasonically again in ethanol and finally in spectroquality methanol, one at a time. After wiping dry with a clean Kimwipe, each mount was assembled with a cellulose nitrate plastic detector; the plastic was fastened with small pieces of Scotch Magic Tape or with a tiny amount of epoxy resin. Identifying scratches were made on the backs of the detectors. The samples were stacked in holders along with standards and blanks, in alternation with aluminum or silica glass discs, and the entire stack of up to about 35 total mounts was clamped together at the ends to ensure good sample-detector contact. The holder was then placed in a polyethylene vial and sealed with Magic Tape.

5. Irradiations were carried out in the thermal column of the UCLA nuclear reactor. The typical conditions for samples with up to 30 ppm B were thirty minutes at thirty kw power, or a fluence of about 5×10^{12} n cm^{-2}. This resulted in about 8×10^{4} tracks cm^{-2} per ppm B (counted optically). To obtain countable track densities for samples with

higher B contents, the fluence was adjusted appropriately.

6. After irradiation, careful fiducial marks were made on the back of the detector and the detector and sample were photographed when necessary. The detector was then removed and etched for 1-3 hours in 6 N NaOH at 28-30° C. The etching bath was placed in a larger tank of water for thermal insulation. A stirring motor was used to maintain solution circulation and a Fisher proportional temperature controller and Vycor glass immersion heater were used to maintain the temperature within 0.2° C of the established bath temperature. Variations in the etching time of the cellulose nitrate were observed from slow changes in the concentration of the etching bath due to leaks in the seams of the inner tank and exchange with the water in the outer tank. After the leaks were discovered and repaired, the etch time remained constant.

Track-counting Procedures

Tracks were etched as in Chapter II and counted with transmitted light at about 1000x magnification, either directly with the microscope or by using a vidicon camera and a TV screen. The field of view (and hence the sample area) counted at one time is about 100 x 100 microns, although areas as small as 5-10 microns in diameter can be used. Track densities less than about 10^7 cm^{-2} can be readily handled in this manner.

Results

A. Mytilus edulis

Figure 15 shows the results of boron analyses of live-collected Mytilus edulis shells, corrected for background and plotted as a function of salinity. Shells are composed of calcite and aragonite. Each point of the graph represents one shell; duplicate analyses have been averaged except when second irradiations gave clear indications of sample contamination (Appendices III, IV). Standard deviations in boron concentration are generally about 6%, based on compounding counting statistics for both sample and standard. Table VI and Figure 15 indicate the locations and salinities for all samples obtained to date. Specimens from a given water salinity usually show excellent agreement in boron concentrations, independent of sample location or water temperature. It can be seen that generally two and in some cases three different collection sites yielded shells with comparable boron concentrations, even when areas as geographically distinct as the Baltic Sea and Puget Sound were sampled.

There is some scatter among the data at higher salinities (above 30 ^{o}/oo); however, a distinction between near-fresh, brackish, and normal marine water appears possible if one uses aragonite data only. Calcite boron concentrations are generally lower than aragonite values, and there is essentially no difference between observed values from 5 to 30 ^{o}/oo salinities. Thus, aragonite data provide a better means of determining salinities; nevertheless, no distinctions can be made between about 10 and 30 ^{o}/oo in either case. The Naples Bay sample may be anomalous due to the highly polluted

FIGURE 15

Plot of B concentration versus salinity for live-collected *Mytilus edulis* specimens. Sample locations and salinities are given in Table III-1. Analyses of individual shells are shown here, with representative error bars indicating the ranges of salinity variations and 1σ standard deviations based on counting statistics. The symbols on the graph represent the following locations:

✙ - Helsinki Bay, Finland
▲ - Grundkallen, Sweden
■ - Svinbadan, Sweden
◆ - Vinga, Sweden
□ - Port Susan, Washington
△ - Potlatch State Park, Washington
▼ - San Juan Island, Washington
○ - Sequim Bay, Washington
◇ - Malibu, California
▽ - Naples Bay, Italy
● - Roscoff, France

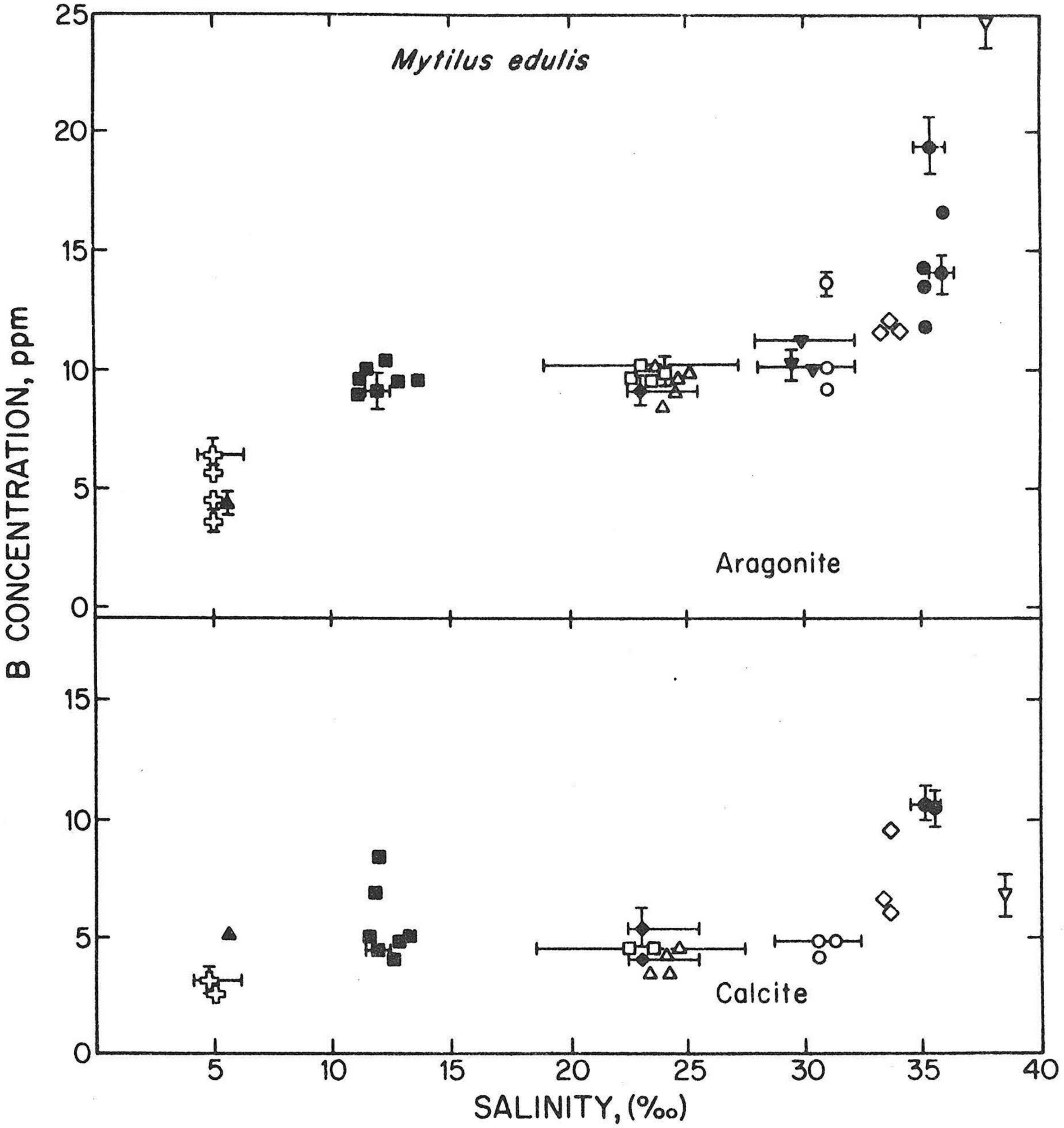

Mytilus edulis
B CONCENTRATION, ppm
25
20
15
10
5
0
Aragonite
15
10
5
0
Calcite
5
10
15
20
25
30
35
40
SALINITY, (‰)

TABLE VI: Boron Analyses of Carbonate Shells

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation date	Species
Roscoff, France	35±.3				
Roscoff box		9.3±.9	18.9±1.5	7/8/74	M. edulis
		11.7±.6	21.5±1.1	8/75	
		11.2±.7	19.2±1.0	2/11/77	
Roscoff box 2			11.5±1.0	1/75	M. edulis
			13.8±1.4	4/75	
		10.6±.5	15.4±.8	8/75	
Roscoff box 3			12.9±1.1	1/75	M. edulis
		13.2±.7	16.1±.8	8/75	
Roscoff alc		8.7±.9	17.1±1.3	7/8/74	M. edulis
			14.2±1.1	4/75	
		13.5±.7	19.4±.9	8/75	
		14.5±.9	17.6±1.0	2/11/77	
Roscoff alc 2			12.2±1.0	1/75	M. edulis
		16.3±.8	14.4±.7	8/75	
Roscoff alc 3			13.7±1.2	1/75	M. edulis
		9.6±.5	18.0±.9	8/75	

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation date	Species
Helsinki Bay, Finland	4.5-6.5				
Finland			3.6±.4	7/8/74	M. edulis
Finland		5.1±.4	6.1±.4	8/75	
Fin 4		2.7±.3	5.2±.4	8/75	M. edulis
Fin 5			4.7±.3	8/75	M. edulis
Fin 6		3.1±.3	6.7±.4	8/75	M. edulis
Grundkallen, Sweden	5.5±0.2				
III			4.1±.4	7/8/74	M. edulis
Svinbadan, Sweden	11.9±0.5				
II		4.5±.4	8.9±.8	7/8/74	M. edulis
II-2		5.6±.5	10.0±.7	10/27/76	M. edulis
II-3		4.7±.4	8.7±.7	10/27/76	M. edulis
II-4		5.0±.5	9.6±.7	10/27/76	M. edulis
II-5		8.5±.7	10.3±.7	10/27/76	M. edulis
II-6		4.1±.4	9.6±.7	10/27/76	M. edulis

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation date	Species
II-7		6.8±.6	9.6±.7	10/27/76	M. edulis
Snail			3	10/27/76	gastropod
Vinga, Sweden	22.5-25.4				
I		4.4±.4 7.8±.4	9.0±.7 14.2±.8	7/8/74 8/75	M. edulis
IB		5.5±.8 6.2±.3	9.0±.8 9.0±.5	7/8/84 8/75	M. edulis
Naples, Italy	37	7.1±.7	26.2±2.1	7/8/74	M. edulis
Port Susan, Wash.	23±4.5				
PS 1		4.4±.2	9.8±.4	3/30/76	M. edulis
PS 2			9.8±.4	3/30/76	M. edulis
PS 3			10.5±.4	3/30/76	M. edulis
PS 4		4.3±.2	9.9±.4	3/30/76	M. edulis
PS 6		1.6±.1		3/30/76	Balanus sp. (barnacle)

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation Date	Species
Potlatch State Park, Washington	24±4.5				
PP 1		4.2±.2	9.8±.4	3/30/76	M. edulis
PP 2		4.5±.2	9.2±.4	3/3/0/76	M. edulis
PP 3		3.6±.2	8.7±.3	3/30/76	M. edulis
PP 4		3.5±.2	8.0±.3	3/30/76	M. edulis
PP 5			9.6±.4	3/30/76	M. edulis
PP 6		1.5±.1		3/30/76	Balanus sp. (barnacle)
Sequim Bay, Wash.	31.0				
SB 1		4.4±.2 5.8±.5	13.4±.4 14.3±.7	3/30/76 2/11/77	M. edulis
SB 2		3.5±.2	9.0±.3	3/30/76	M. edulis
SB 3		4.6±.2	10.2±.4	3/30/76	M. edulis
SB 2B		1.7±.1		3/30/76	Balanus sp. (Barnacle)

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation Date	Species
San Juan Island, Washington	28-32				
JL 1			11.0±1.0	11/21/77	M. edulis
JL 2			9.9±0.8	11/21/77	M. edulis
JL 3			10.3±0.9	11/21/77	M. edulis
AC 1	32		8.9±.8	11/21/77	M. californianus
AC 2	32		6.1±.6	12/21/77	M. californianus
FHL 2			11.1±.9	11/21/77	Modiolus modiolus
FHL 3			13.0±1.1	11/21/77	Modiolus modiolus
Rodeo, California	?				
SFR 1		5.7±.4	13.0±.5	10/27/76	M. edulis
SFR 2		10.7±.4	11.0±.5	10/27/76	M. edulis
SFR 3		6.5±.4		10/27/76	M. edulis

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation Date	Species
Morro Bay, Calif.	33.5				
MB 1		21.7±.4		11/76	Crassostrea virginica
MB 2		18.4±1.1		11/76	Crassostrea virginica
MB 3		18.1±.3		11/76	Crassostrea virginica
Malibu, California	33.5				
Mal 1		9.3±.7	12.3±.9	10/27/76	M. edulis
Mal 2		6.5±.5	12.2±.9	10/27/76	M. edulis
Mal 3		7.2±.7	12.1±.9	10/27/76	M. edulis
Mal 4			13.4±.9	10/27/76	M. californianus
Mal 5		11.1±1.0	19.1±1.3	10/27/76	M. californianus
		19.5±1.1	20.1±1.1	2/11/76	
Mal 6		8.1±.6	14.8±1.1	10/27/76	M. californianus

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation Date	Species
Corona del Mar, California	33.5				
MC 1		2.0±.5	20±2	9/6/73	M. californianus
MC 2		2.5±.5	19±2	9/6/73	M. californianus
San Pedro, Calif.	marine				
226-2b		6.0±.5	9.3±.8	10/27/76	fossil M. edulis
226-4a			9.5±.7	10/27/76	fossil M. edulis
300-1a			7.1±.6	10/27/76	fossil M. edulis
b		5.2±.4	8.2±.6		
300-2b		9.0±.8		10/27/76	fossil M. edulis

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation Date	Species
Punta Cabra, Mexico	35				
PC 1		21.5±.4		11/76	Crassostrea irridescens
PC 2		18.7±.4	5.3±.2 (myostracum)	11/76	Crassostrea irridescens
PC 3		19.6±.7		11/76	Crassostrea irridescens
Atur, Israel	40				
A 1			14.0±1.2	11/21/77	Brachidontes variabilis
A 2			9.9±.8	11/21/77	Brachidontes variabilis
A 3			19.3±1.5	11/21/77	Modiolus auriculatus
Sharm el Sheikh, Israel	40				
SS 1			14.0±1.1	11/21/77	Modiolus auriculatus

TABLE VI (cont.)

Sample & Location	Salinity (0/00)	(B) Calcite (ppm)	(B) Aragonite (ppm)	Irradiation Date	Species
SS 2			14.5 ± 2.5	11/21/77	Modiolus auriculatus
Mediterranean Sea, Israel	37-38				
SW 12B-1		8.4		3/30/76	Orbulina (foraminifera)
SW 19C-2		8.2		3/30/76	Orbulina (foraminifera)
Atlantic Ocean	35				
V13 g#5-1		≤ 25		3/30/76	planktonic foraminifera
V15 z#3-2		≤ 15		3/30/76	planktonic foraminifera
Long Reef, Syndey, Australia					
4562-B	marine		39.6 (vaterite)	3/30/76	Herdmania momus (tunicate)

collection site.

B. Growth of *Mytilus edulis* specimens in the laboratory

In order to determine the influence of temperature and water salinity on the boron contents of shells, it was decided to grow specimens under controlled conditions in the laboratory. In October of 1976 live *Mytilus edulis* specimens were collected at Rodeo, in San Francisco Bay. Thirteen or fourteen small (7-16 mm) specimens were placed in each of four aquaria and maintained under the following conditions in order to further establish the correlation for precisely known salinities and to see whether temperature changes influence the relationship.

Aquarium	Temperature	Salinity
A	15-16°C	10°/oo
B	15-16	20
C	15-16	33.5
D	8-9	33.5

The animals were fed five times weekly with a culture of the dinoflagellate *Dunaliela*. Both salinity and boron content of the water in each tank were monitored periodically, and the growth was checked several times by measuring shell lengths with a mm scale. Little or no growth occurred, so free amino acids were added to the water. After about eight months, no significant growth had occurred, and the animals gradually began to die. No analyses were made of any of these shells.

C. Fossil *Mytilus edulis*

Pleistocene shells were obtained from two locations in San Pedro, California. The presence of unaltered aragonite was confirmed by staining with Leitmeyer-Feigl solution (Feigl and Oesper, 1958), which enables a rapid discrimination between aragonite and calcite on the polished surface of the same section which is irradiated. All shells appeared to be very well-preserved, with pearly luster still apparent in the aragonite. The results of B analyses of the fossil shells are given in Table VI and Figure 16. Two shells from the Palos Verdes Sand, 8th and Palos Verdes St., San Pedro, had 9.3 ± .8 and 9.5 ± .7 ppm B in aragonite, consistent with a salinity below 33 ^{o}/oo based on Figure 15. The calcite values for one of these shells was 6.0 ± .5 ppm, probably indicating a salinity between 31 and 33 ^{o}/oo. Shells from another location in San Pedro had boron concentrations of 7.7 ± .4 in aragonite and 5.2 ± .4 and 9.0 ± .8 in calcite, also consistent with a salinity between 30-33 ^{o}/oo.

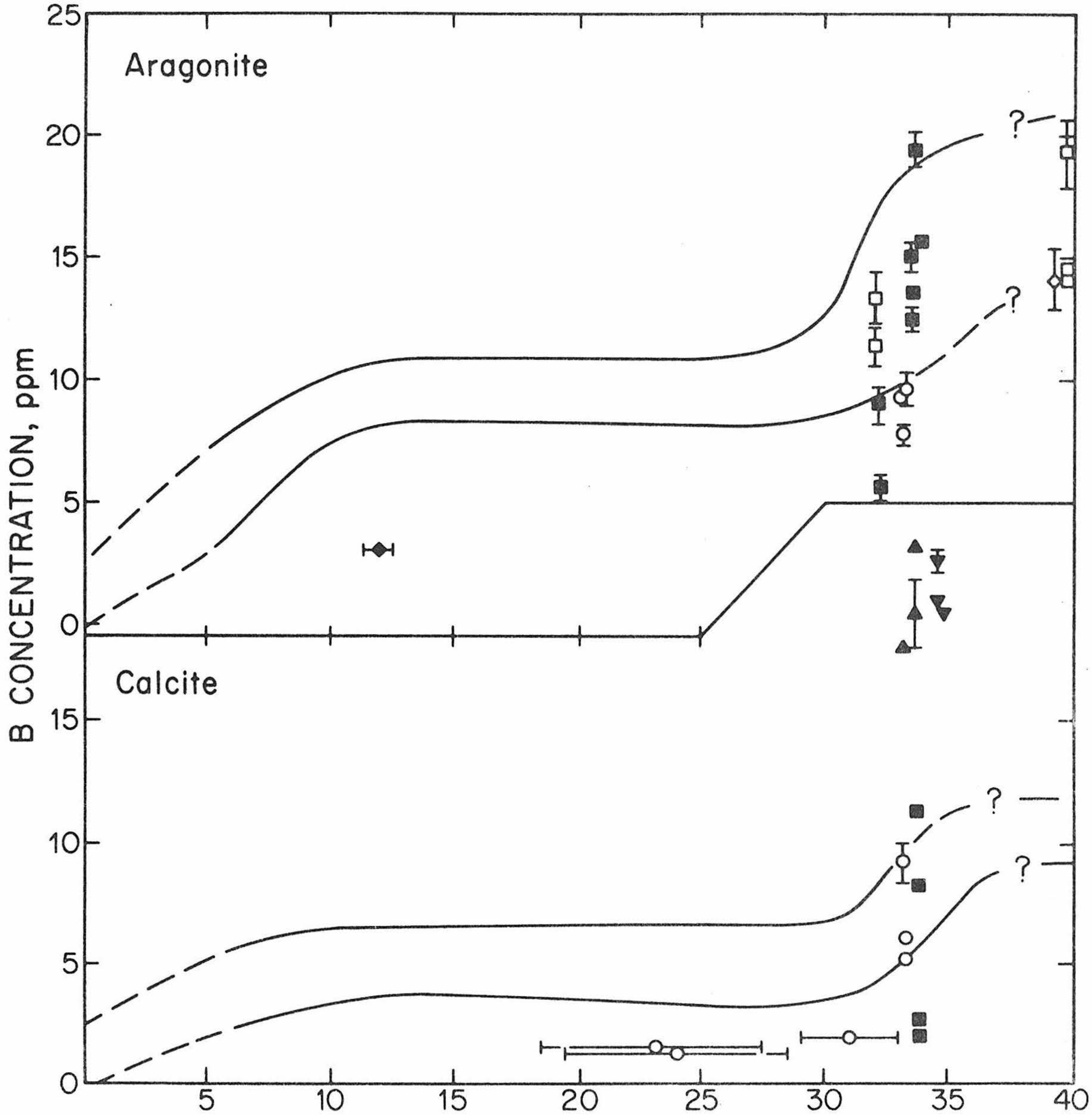
D. Other molluscs

In order to determine how widespread the observed boron/salinity correlation is among molluscs, several other types of shells were analyzed. Specimens of *Mytilus californianus* were obtained from Corona Del Mar, San Diego Co., California, from Malibu, Los Angeles Co., California, and from American Camp, San Juan Island, San Juan Co., Washington. The data are plotted as squares on Figure 16, with error bars as in Figure 15. It can be seen that the boron concentration in the aragonite is approximately the same as in aragonite from *Mytilus*

FIGURE 16

Plot of B concentration versus salinity for fossil *Mytilus edulis* and live-collected shells of other organisms. The designated band indicates the trend of the data for live-collected *Mytilus edulis* shown in Figure 15. Each point represents a single shell. The ranges in salinity are comparable to the widths of the symbols except where shown. The error bars in boron concentration indicate 1σ standard deviations based on counting statistics. The symbols on the graph represent the following species:

● - *Mytilus edulis*, fossil
■ - *Mytilus californianus*
⊡ - *Modiolus auriculatus*
□ - *Modiolus modiolus* (Linne, 1758)
◊ - *Brachidontes variabilis*
▲ - *Crassostrea virginica*
▼ - *Crassostrea irridescens*
◆ - unidentified gastropod
⊙ - *Balanus* sp. (arthropod--barnacle)


Aragonite
Calcite
B CONCENTRATION, ppm
SALINITY, (‰)
25
20
15
10
5
0
15
10
5
0
5
10
15
20
25
30
35
40
?
?
?
?

edulis specimens from the same salinity water. Boron concentrations found in both aragonite and calcite were quite variable. Thus, there is a general similarity between data from the two species, at least for aragonite. Lower salinity specimens of *M. Californianus* are not available, as the species is stenohaline.

Several specimens of *Modiolus* and of *Brachidontes* (all aragonite), representing the same family but different genera from *Mytilus*, were also analyzed. For both hypersaline and hyposaline water, the B contents of shell aragonite are comparable to concentrations found in *M. edulis*. There is apparently no large increase in B content in hypersaline specimens relative to less saline environments.

Two species of oysters, *Crassostrea virginica* from Moro Bay, California and *Crassostrea irridescens* from Punta Cabra, Baja California, Mexico were also studied. The shells are composed entirely of calcite except for the myostracum, or region immediately behind the muscle attachments in the shell. Aragonite from the myostracum of one *C. irridescens* shell had only about 5 ppm B, distinctly below the values found in aragonite of *Mytilus* shells from normal marine salinity; no B concentrations in *Mytilus* myostracum were measured, however. The concentrations found in the calcite were variable on a 1-mm scale in all shells observed, ranging over about a factor of 2. Averages of scans (taking one field of view at each point, with points spaced uniformly at 0.5- or 1.0-mm intervals across a transverse section of the shell) for each shell agreed remarkably well with averages for other shells; both species showed excellent agreement despite the different locations, water temperatures, and growth rates. The *C.*

virginica were from commercial oyster beds and were grown at a maximum rate, while the C. irridescens were from a natural environment.

Two papers have found that oysters do not have good B/salinity correlations. Rucker and Valentine (1961) studied a variety of trace elements in C. virginica and concluded that boron (determined spectrographically) correlates with neither salinity nor temperature. Cook (1977) found somewhat tenuous evidence that boron may be leached out of oyster shells with time, based on a study of Holocene shells with no species identification. The discussion presented in these two papers and the lack of uniformity within individual shells suggest that oysters are not suited for additional investigation of B/salinity correlations.

Leutwein and Waskowiak (1962) found a B/salinity relationship in Cardiidae, which have all-aragonite shells. They observed a range of 1-7 ppm over a salinity range of 0-40 ^{o}/oo, but with considerable scatter in the data.

A single gastropod shell from the Baltic Sea (Station II) was analyzed; the boron concentration was no more than 3 ppm, distinctly less than in aragonite from M. edulis collected at the same location.

E. Foraminifera

Two types of planktonic foraminifera, Orbulina and Globigerina, were briefly studied, with the hope that they may contain sufficient salinity-correlated boron that deep-sea sediments could be studied and oxygen isotope paleotemperature determinations could perhaps be reinterpreted in the light of paleosalinity information. Specimens were obtained from the Mediterranean Sea and from the Atlantic Ocean, representing 37-38 $^{o}/oo$ and 35 $^{o}/oo$ salinities, respectively. Less than 5 ppm B were found in all individual tests analyzed, and no strong correlation with temperature or salinity could be elucidated. The tests are porous and composed of very thin (about 20 microns) calcite, and it was concluded that good measurements probably can be made only if numerous individuals are crushed and homogenized, rather than with individual shells as was attempted here. It is possible that benthic forams, which have thicker walls, may be usable individually; however, in light of the low B concentrations found in the specimens analyzed and the resulting inability to detect possible salinity-related variations in B content, additional study of B in foraminifera does not seem profitable.

Discussion and Conclusions

A study of the boron concentrations in calcite and aragonite which have been inorganically precipitated from aqueous solution has been carried out by Kitano, et al.,(1978). Using a spectrophotometric technique with curcumin for boron determinations, they found that boron was incorporated into both aragonite and calcite in proportion to the concentration of $B(OH)_3$ in the solution. The addition of Na^+ to the solution resulted in a decrease of the boron content in aragonite but apparently had no effect on calcite. The smaller aragonite B concentration may be related to a smaller grain size. With the boron and sodium concentrations approximately the same as in sea water (4 mg B/1 and 10.5 g Na/1) the ratio of the concentrations of boron in aragonite to calcite was about 2, similar to the ratio observed in this study in *Mytilus* shells. For both calcite and aragonite, the boron concentrations measured by Kitano, *et al.* are about one-third to one-half of those measured in marine shells using tracks. It appears that *Mytilus edulis* is able to control the boron concentration in its shells organically, at least in part.

As indicated in Figure 15, a correlation of boron content with water salinity has been observed in live-collected *Mytilus edulis*. The correlation is not a straight-line function and allows discrimination of salinities only into three general categories: nearly fresh-water (less than 10 ^{o}/oo salinity), brackish water (10-30 ^{o}/oo), and marine (greater than 30 ^{o}/oo). The step-function relationship of boron concentration in the shells with salinity is difficult to explain. There may be a temperature-boron correlation, since shells from warmer water tend to contain larger and more variable amounts of boron than shells from cooler water, despite similar salinities. Roscoff, France has a range in water temperature of 9-15^{o} C with an average of 12^{o} (Cabioch, 1975) and Malibu, California has water temperatures ranging from 15-22^{o}, with an average of 17^{o} (U. S. Department of Commerce, 1970). The temperature differences between Puget Sound and the Baltic Sea may not be as great, resulting in better agreement of boron concentrations in samples from the two areas. The flattening of the boron-salinity correlation between 10-20 ^{o}/oo salinity may also be due to the presence of sodium and perhaps other ions which suppress the incorporation of B into aragonite.

The correlation of boron with salinity in shells appears to exist in other molluscs which are related to Mytilus edulis at the family level or closer, but is not a general characteristic of bivalve shells or other organically precipitated carbonates, as indicated in Figure 16 and supported by the work of A. Ng (1978). This technique of determining salinities is therefore limited in applicability to forms for which a B/salinity correlation can be established using live-collected shells.

The data for B concentrations of calcite in fossil M. edulis show reasonable agreement with results for live-collected shells from the probable salinity of the water at the time of the fossil shell growth, 33-35 ^{o}/oo. The aragonite fossil results are not consistent with normal marine live-collected shells and there may have been some loss of boron from the shells. The Palos Verdes Sand is a marine deposit which covers Late Pleistocene marine terraces. It ranges from several inches to about fifteen feet in thickness and consists of sand with some silt, coarse sand, and gravel. The environment had partially protected shallow water (Woodring, et al., 1946; Valentine, 1961; Yerkes, et al., 1965). Additional shells from several locations should be analyzed to determine the stability of boron in aragonite and calcite before drawing conclusions concerning the validity of the technique for paleosalinity determinations.

At best, paleosalinity determinations are restricted to deposits no older than the maximum age of fossil occurrences of extant species, genera, or families for which the correlation has been established. The technique may enable paleosalinity determinations at the level of nearly fresh-water, brackish-water, or marine, and can be readily conducted. Because specimen identification is important, reasonably complete shells are required; small fragments can not be used.

V. A REEXAMINATION OF BORON CYCLING IN THE SEA

During the investigation of the boron contents of various biogenic materials, questions arose concerning the significance of biologic activity in boron cycling in the sea. Harriss (1969) approached this subject and concluded that the dominant mechanism for removal of boron from the ocean is via mineral-water reactions. The following is a reconsideration of his discussion and some additional thoughts.

The sources of boron entering the ocean are volcanic activity and rivers. Harriss assumes without discussion that the contribution of submarine volcanism is negligible. Livingstone (1963) gives the average boron concentration of river water as 0.012 ppm. With an annual freshwater influx of 3.3×10^{16} liters, the input is about 4.0×10^{11} g B/yr (Harriss, 1969).

The sources of removal of boron from sea water are reactions between detrital minerals and dissolved boron, authigenic mineral formation, and biogenic material. Assuming that clays will adsorb an additional 45 ppm B in the marine environment (Harriss, 1969) and that the transport of sediment to the ocean is about 7.4×10^{15} g/yr, the total amount of boron removed from the sea by mineral-water reactions is 3.3×10^{11} g/yr. Assuming that 7% of the sediments is authigenic and contains an average of 110 ppm B, Harriss estimates about 0.6×10^{11} g/yr of boron is incorporated into authigenic minerals.

The process of biological removal of B may be considerably more complicated than in Harriss' model, and his estimate of the contribution of skeletal material to the sediments seems somewhat low. Assuming that the boron concentration in diatom, radiolarian, and silicoflagellate remains is 100 ppm (this work; Gross, 1967) and the rate of accumulation of biogenic opal in the sediments is 3.6×10^{14} g SiO_2/yr (Calvert, 1968), the quantity of boron entering the sediments is 0.4×10^{11} g/yr. Harriss also failed to consider the amount of boron in carbonate sediments. Using data from Menard and Smith (1966), the rate of accumulation of carbonate sediments is 2.9×10^{15} g $CaCO_3$/yr. If the average boron content is about 5 ppm (this work; A. Ng, 1978), 0.15×10^{11} g/yr of boron accumulate in sediments. If it is assumed that detrital organic material does not enter the permanent sedimentary record and is totally redissolved in the sea, tha calculation stops here. The total input of boron is 4×10^{11} g/yr and the total removal is $.15 \times 10^{11} + .36 \times 10^{11} + 3.3 \times 10^{11} + .6 \times 10^{11} = 4.5 \times 10^{11}$ g/yr, the same within errors as the input rate. The biogenic contribution is approximately the same size as the authigenic mineral contribution, and mineral-water reactions still account for 80% or more of the boron removal.

The concentration of boron in sea water is 4.6 ppm (Table I). The volume of the ocean is estimated at 1.35×10^9 km^3. Thus, the boron contained in the oceans has a mass of 6.2×10^{18} g. With an annual input of 4×10^{11} g, a residence time for boron in the ocean can be calculated:

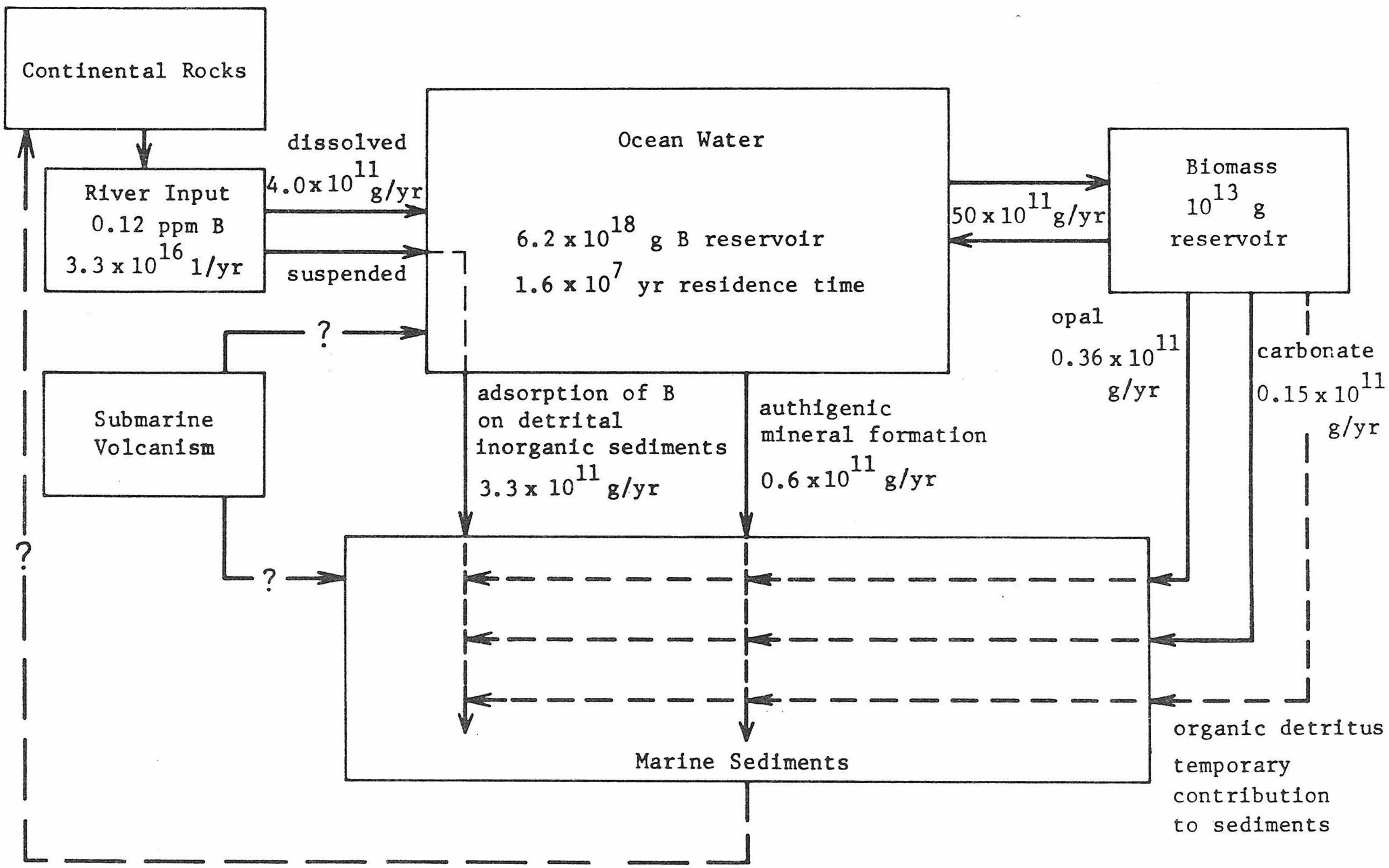
$$\text{residence time} = \frac{\text{amount in ocean}}{\text{annual input}} = \frac{6.2 \times 10^{18}}{4.0 \times 10^{11}} = 1.6 \times 10^7 \text{ yr.}$$

Vallentyne (1966) estimated the total annual organic carbon production as 3.6×10^{16} g (cited in Harriss). The B/C ratio in phytoplankton can be estimated as 2×10^{-3} (Curl, 1962 and Nicholls, _et al_., 1959). Thus the phytoplankton boron uptake is 7.2×10^{13}g/yr. Using the rate of deposition of biogenic boron given above and assuming that 1% of the skeletal material produced eventually accumulates on the sea floor, 5×10^{12} g/yr of additional boron are involved in biologic activity. Allowing for recycling of material several times per year, the biomass contains about 10^{13} g B in the standing crop. This number is significantly larger than the annual oceanic input or outflow of B, but several orders of magnitude smaller than the total amount of B in the sea. Figure 17 summarizes the above discussion of boron cycling in the sea.

It should be pointed out that although mineral-water reactions dominate the picture, the other two sources (organic and skeletal material) may be extremely important in maintaining a uniform concentration in the water. The rapid recycling of organic material could result in fixation of B in organisms and their skeletons on a short time scale relative to the rate of adsorption and fixation of boron in clays. Increased boron input into sea water may stimulate the incorporation of B into the biomass, in turn inhibiting the trend toward increased concentration in the water. Increased biogenic sedimentation of boron would then occur. The importance of biologic activity in B cycling may be primarily kinetic rather than thermodynamic, providing a much more rapid response of the ocean-sediment system to changing concentrations in sea water than would be

FIGURE 17

Box model of boron cycling in the sea. The dashed line through the "ocean water" box represents the process of adsorption of boron on detrital mineral grains and the dashed lines through the "marine sediments" box represents processes of post-depositional incorporation of boron into inorganic sediments.


Continental Rocks
River Input
0.12 ppm B
3.3×10^{16} 1/yr
dissolved
4.0×10^{11} g/yr
suspended
Submarine Volcanism
?
?
?
Ocean Water
6.2×10^{18} g B reservoir
1.6×10^{7} yr residence time
50×10^{11} g/yr
Biomass
10^{13} g
reservoir
opal
0.36×10^{11} g/yr
carbonate
0.15×10^{11} g/yr
adsorption of B
on detrital
inorganic sediments
3.3×10^{11} g/yr
authigenic
mineral formation
0.6×10^{11} g/yr
Marine Sediments
organic detritus
temporary
contribution
to sediments

anticipated with a residence time of more than 10^7 years.

In the event that the fraction of directly biogenic B in sediments is overestimated here, biologic activity may still play a crucial role in regulating boron in the oceans. The biomass may provide a concentrated source of boron near the sediment-water interface, with abundant supplies available for adsorption on clay minerals or authigenic mineral formation. Biogenic opal and organic detritus are rich in boron, with concentrations as much as 200 times greater than sea water. The major means of transport of organic and skeletal material to the sea floor is probably in fecal pellets of copepods and other planktonic organisms (Honjo, 1976). The fecal pellets are larger and have much smaller surface/volume ratios than isolated particles and therefore settle much faster. In addition, there is considerably less opportunity for dissolution of material in pellets while descending through the water column. Several lines of evidence are available to support this hypothesis. Boron concentrations have been measured at many depths and there is usually little or no enrichment of boron in sea water at the oxygen minimum layer (about 1000 m), unlike a variety of other elements such as silicon, nitrogen, and phosphorus (Rakestraw and Mahncke, 1935; Igelsrud, et al., 1938; Ryabinin, 1972; Broecker, 1974; Uppstrom, 1974). The oxygen depletion and element enrichment is due to a high rate of decomposition of organic material at this depth. The boron concentrations of pore water in several JOIDES cores were found to be about 1-2 times that in sea water (Sayles,, et al., 1970; Presley, et al., 1973), indicating that boron-rich material may be dissolving. In addition, in this study it was observed that sponge spicules from a core in the North Atlantic

(V-23-42) tended to have decreased wall thicknesses and increased solution pitting on interior and exterior tube surfaces with increasing core depth, but there was no evidence for leaching of B from the spicules which ranged in age from 0 to about 10^5 years. Additional evidence for loss of boron from biogenic sediments might arise from a study of the boron concentrations of cherts, originating from biogenic opal. Y. Kolodny (1978) has found some indication of decreasing boron concentration with increasing quartz content (relative to opal-CT) of some Eocene cherts.

If biogenic materials are the dominant means of transport of boron to the sediments, a contribution may be made also to the controversy over the time of incorporation of boron into clay minerals. Whether boron fixation occurs during deposition or diagenesis may be dependent on the amount of biogenic B-rich material which is available as a source. If gradual dissolution of opal is occurring, a steady supply of boron is available; if the opal does not dissolve, the boron may not be released until diagenetic changes occur, such as the transition to opal-CT to quartz. Organic detritus may also provide a shorter-lived source of boron.

If diatoms are the most important B concentrators in the biomass, there may be an observable difference in boron concentrations in inorganic pelagic sediments before and after the appearance and sudden abundance of diatoms in the Cretaceous. Reynolds (1965) determined boron concentrations in clay fractions of a number of carbonate rocks ranging in age back to the Precambrian and found no significant differences in boron concentrations with age; however, he presumably was looking at shelf-deposited rather than pelagic sediments. It would be essential to examine pelagic rocks in searching for a difference in B content due to the presence of diatomaceous material.

VI. CONCLUSION: AN ASSESSMENT OF WHERE THE WORK STANDS TODAY AND WHERE IT SHOULD GO IN THE FUTURE

Carbonates

A correlation between boron concentrations and water salinity has been observed for live-collected *Mytilus edulis* and other bivalves related at the family level. However, other groups of molluscs do not have B concentrations comparable to those found in *Mytilus* and there may be no correlation between B and salinity in some cases. Further, temperature may influence the incorporation of boron into shells. For *Mytilus*, observed boron concentrations in aragonite were approximately twice as great as those in calcite from the same shells. Thus, the use of aragonite fossil materials is preferred because of the greater boron contents and because of the greater ease of determining whether diagenetic processes have occurred. Analyses of several Pleistocene shells from two locations indicated that there may have been some loss of boron from shell aragonite.

Future work should include a study of possible temperature effects in the boron concentration in shells, possibly using laboratory-grown material from normal marine salinities. Additional fossil shells should be studied to determine whether material can be found which has boron concentrations expected for the paleoenvironments from which the shells came. Perhaps other groups of bivalves can be found which also incorporate boron into their shells in proportion to the water salinity. However, at present studies of boron concentrations in opal skeletal materials seem more promising and should have higher priority.

Opal

Although there is clearly a species-independent relationship between boron concentrations in siliceous sponge spicules and water salinity, the B content is also related to some environmental parameter such as water temperature or nutrient supply. It is uncertain whether this other environmental effect on boron concentrations involves only sponges or also organisms at earlier levels in the food chain. Thus, it is important to determine what conditions influence the concentrations in spicules. A systematic effort should be undertaken to analyze more specimens which have been collected alive from locations with varying environments; specimens from deep water in high and low productivity regions, both temperate and tropical, and shallow-water tropical high-productivity regions should be obtained. It may be possible to culture sponges in the laboratory under controlled conditions, although it probably would be necessary to conduct such experiments at a site where sea water could be piped directly through the aquariums and not recirculated because sponges require a very large volume of water to collect adequate food.

It would also be useful to determine the chemical form of boron in the spicules. ^{11}B nuclear magnetic resonance spectroscopy may provide such information. Plans have been made to conduct nmr experiments in the near future. Apparently no other method is capable of determining the chemical form of boron at the concentrations found in spicules.

The fossil material examined thus far may indicate some diagenetic loss of boron; however, there is no evidence for dehydration, crystallization, or chemical alteration on the basis of the limited number of analyses carried out. Perhaps O isotopic data would indicate some exchange of material with the environment. Unless the significance of different environmental parameters can be defined for boron incorporation into spicules by living sponges, it will be difficult to interpret the fossil data.

There is a very clear distinction between boron concentrations in marine and freshwater diatomaceous sediments. It is likely that the relationships between nutrient supply, water temperature, salinity, and boron concentration in the water and in the frustrules can be determined more readily than for sponges because diatoms are not dependent on other organisms for their food supply and because they are restricted to shallow water; it should be much more straightforward to study environmental effects on frustrule B contents. Moreover, diatoms can be readily cultured in the laboratory on a short time scale (1-2 weeks), although there is some question whether laboratory conditions are an adequate duplication of the natural environment.

The major problem with the use of diatomaceous sediments for B analyses is the difficulty in obtaining samples free of other material. Diatom fragments are commonly found in association with other opaline biogenic debris, detrital quartz and feldspar, and clay minerals. Separation techniques based on particle size or density will not adequately differentiate the particles. Individual diatoms are too thin-walled to allow good B analyses with the track technique used in this work, and usually they are too small to allow routine hand-picking.

If the sampling difficulties can be overcome, then a detailed study of B concentrations in live-collected diatoms (plankton tows and/or laboratory-grown) should be undertaken. Once the relationship(s) between environment and boron concentration is/are established, then a more systematic investigation of fossil material can be undertaken. In particular, diagenetic effects should be studied--is boron retained while the material is still opal, and what happens during the transition from opal to opal-CT to quartz? Of course, this information is also of value in the investigation of B in sponge spicules.

In the event that all of the above efforts bear fruit, the result may be a two-pronged probe of previous marine environmental conditions. Sponge spicules may provide an indication of conditions at the sea floor and diatoms at the surface. In conjunction they may reveal paleosalinity and/or paleocirculation data, conceivably extending back in time to the Cretaceous for diatoms and to the early Paleozoic for sponges.

One last avenue of investigation is the possible relationship between salinity and boron concentrations in phosphatic shells, particularly of brachiopods.

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APPENDIX I

Radiographic Study of the Distribution of Boron in Recent Mollusc Shells, by Marian Furst, H. A. Lowenstam, and D. S. Burnett. Published in Geochimica et Cosmochimica Acta, 1976, Volume 40, pp. 1381-1386.

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Radiographic study of the distribution of boron in recent mollusc shells*

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Abstract—Studies have been made of the boron content and distribution in recent *Mytilus edulis* shells by mapping the alpha particle distribution produced by the ^{10}B $(n,\alpha)^7Li$ reaction using cellulose nitrate track detectors. Boron is concentrated in the inorganic parts of the shell matrix and is enriched in aragonite relative to calcite by a factor of 1.5–2. The B contents in different parts of individual shells and in different specimens from a given locality are well defined, particularly for the aragonite layer. A correlation was found between the B in the aragonite layer and the salinity of the water in which the shells grew. The method shows promise as a means of using the boron content of fossil shells to determine paleosalinity.

INTRODUCTION

OF PRIMARY interest in interpreting the fossil record is a knowledge of the environments in which the organisms lived. Not only is this information important for the understanding of the ecologic relationships between species, but it also helps to establish how environmental conditions on the surface of the Earth have changed in time. Salinity is a major controlling factor in the distribution of marine organisms.

As early as 1932, GOLDSCHMIDT and PETERS (1932) observed that the boron concentration of sea water is proportional to the total salt concentration. LANDERGREN (1945b; 1949) observed that for certain sediments the boron concentration also was correlated with the total salt concentration and that B in the sediments is concentrated largely in the clay minerals. Although there is general agreement at present that the B content of a sediment is a qualitative measure of the salinity conditions at the time of deposition, quantitative salinity determinations have not been possible (HARDER, 1959; FREDERICKSON and REYNOLDS, 1960; CODY, 1970, 1971; COUCH, 1971; PERRY, 1972). Detailed discussions of the complications are given by COUCH (1971) and PERRY (1972). In essence the problem is that factors other than depositional salinity are also important in determining the B content; for example, (1) the specific clay mineralogy of the sediment (B is concentrated in illite, but is also taken up by other clay minerals); (2) the grain size distribution of the clays (since B may be adsorbed making the B concentration depend on surface area); (3) the presence of detrital B minerals such as tourmaline or illite from pre-existing sediments; (4) changes in the total B concentration of the sediments or even in the B content of illite during diagenesis, etc.

LEUTWEIN and WASKOWIAK (1962) found a positive correlation of salinity with the B contents of the carbonate shells from the euryhaline bivalve species of the genus *Cardium*. This introduced the possibility of obtaining paleosalinity data from fossils without recourse to analyses of their enclosing sediments. Further studies on recent euryhaline species seemed necessary to determine: (1) the reliability of previous B measurements; (2) whether the B content of carbonate shells resides in the carbonate minerals or in their organic matrices; and (3) whether the B contents of skeletal calcites and aragonites both monitor changes in salinities. Hence, we have undertaken a study of the relations between B concentration and salinity of the shells from the bivalve species *Mytilus edulis*, which are mineralized by both aragonite and calcite. This species was chosen because of its wide salinity tolerance and because of the widespread occurrence of samples, both live and fossil. We have employed a nuclear track radiography technique which is relatively specific for boron [see, for example, FLEISCHER *et al.* (1972)]. In this way, we are able not only to determine bulk boron concentrations, but also to observe the spatial distribution of boron in a sample on a scale of 5–10 μm or less.

DESCRIPTION OF *MYTILUS EDULIS* SHELLS

The exterior surface of *Mytilus edulis* shells is a brown organic coating known as the periostracum. This protective sheet is readily detached from the rest of the shell and often is partly eroded during the lifetime of the organism. Underneath the periostracum is a prismatic calcitic layer, with 2–3 μm-long crystallites aligned oblique to the shell surfaces. The inner or nacreous layer consists of aragonite which is deposited in sheets parallel to the shell surface, giving the interior the characteristic mother-of-pearl appearance. The calcite and aragonite crystals are individually enclosed in an intercrystalline organic matrix. The interior surface of the nacreous layer is bounded by the pallial line of the organism and hence is not in direct contact with the external medium.

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* Contribution No. 2666.

Growth occurs radially outward in the calcite part of the shell and in vertically-stacked sheet-like layers in the aragonite. The maximum size attained by the shells depends on the temperature and on the salinity, with lower salinity and lower temperatures tending to retard growth (SEGERSTRÅLE, 1957). The proportion of aragonite to calcite in the shell increases with increasing temperature (LOWENSTAM, 1954; DODD, 1963). A negative correlation between salinity and aragonite content is indicated for populations of some areas (LOWENSTAM, 1954; DODD, 1966), but not for those in other locations (EISMA, 1966). The larger shells investigated measure 10–15 cm in the longer dimension.

EXPERIMENTAL

Boron determinations were made by placing a plastic detector which is sensitive to alpha particles over each sample. Neutron irradiation results in the emission of alphas from the $^{10}B(n,\alpha)^7Li$ reaction. Particles which are produced in the surface layers on the sample enter the plastic detector and cause radiation damage. After irradiation, the detector is chemically etched. The radiation-damaged areas etch faster than the bulk plastic and a series of conical-shaped holes or 'tracks' results. The tracks can be counted with a good optical microscope, typically at about 1000 × magnification. The plastic used was cellulose nitrate with good track registration properties, specially prepared by E. V. Benton of the University of San Francisco.

Other sources of tracks are fast neutron recoil interactions and the $^{17}O(n,\alpha)$ and $^6Li(n,\alpha)$ reactions. The first two account for a background track density in the cellulose nitrate equivalent to about 0.3 ppm B and determine the lower limit of the analytical capabilities of the technique. It is also possible that there is a small contribution to the background by protons from the $^{14}N(n,p)^{14}C$ reaction. Lithium in the sample to be analyzed is a source of interference; however, per gram of target element the Li track production rate is only 18% of that for boron. Since these shells have very little lithium (~1 ppm determined by emission spectroscopy), corrections to the boron concentration for Li interference are never greater than about 5%. The track density observed after correction for cellulose nitrate background and sample Li is proportional to the boron concentration in the sample. Comparison of the sample track densities with those observed for NBS glass SRM 613, which contains a similar B concentration, allows the determination of the sample concentration.

The boron concentrations in the glass standards were in turn determined by comparison with track densities found after irradiation of another NBS glass (SRM 611) which has a B content of 351 ppm as determined by isotope dilution (NBS Certificate of Analysis, revised August 18, 1972). Since the boron concentration does not appear to be completely homogeneous in the low B glasses to which the mollusc results were compared, a specific area on each polished glass section was chosen and its B content determined individually. No evidence for inhomogeneity was found in 5 samples of the high B (SRM 611) glass. Our results ranged from 35 ± 3 ppm to 45 ± 5 ppm in different pieces of the low B glass. These values are somewhat higher than CARPENTER'S (1972) average of 32 ppm for the same glass determined by the same method. More work on the accuracy and uniformity of the B contents of these standard glasses is required; however, our conclusions are primarily based on the relative B concentrations in various shell samples, and absolute concentrations only enter when comparisons are made between our results and those of other workers.

Several live specimens of *Mytilus edulis* were collected at various locations in northern Europe and stored in 70% ethanol or dried and stored in cardboard boxes. The sample locations are indicated in Fig. 1. (The Roscoff samples were collected in 1965. The Baltic Sea samples were collected in 1954.) Two separate collections (I and IB) were made at Station I. From each location, the largest and best-preserved samples were chosen for study. The two valves were carefully opened and separated, and the soft parts were gently scraped off. The shell was then cleaned ultrasonically in distilled water and in ethanol. A thin (~2 mm) cross-sectional slice was cut with a Buehler 11-1180 low speed saw from the hinge to the farthest edge of the shell, through the thickest part. The slices were embedded in epoxy (Techkits E-7) and then polished with alumina (Buehler) in ethanol.

Each mount was assembled with a plastic detector and irradiated with a fluence (i.e. neutron flux × irradiation time) of about 5×10^{12} neutrons/cm^2 in the thermal column of the UCLA reactor. A series of fiducial marks were scratched on the back of the transparent plastic, and the shell sample, together with its detector, was photographed. The plastic was then removed and etched for 70–100 min in 6.25 N NaOH at 30°C, and tracks were counted. By comparison of the location of fiducial marks on the plastic with the overlay photograph, one can locate the point on the shell corresponding to a point on the plastic and thereby restrict attention to areas of interest in the shell.

Control samples of cellulose nitrate, epoxy, and SiO_2 glass were also analyzed. Control epoxy samples were polished and cleaned identically to the mollusc samples. Typical background track densities based on the cellulose nitrate blanks are equivalent to about 0.3 ppm B. Values ranged from 0–1 and 0.5–1 ppm for the epoxy and SiO_2 'blanks', respectively. All observed track densities have been corrected for background and lithium contributions. Boron concentrations in all samples were calculated relative to the low B standard glasses. No correction was made for the different ranges of alpha particles in the glass and in the shells, because such a correction is small (~1%) (NORTHCLIFFE and SCHILLING, 1970).

RESULTS AND DISCUSSION

In addition to the measurements of actual boron concentrations, it was important to ascertain how the

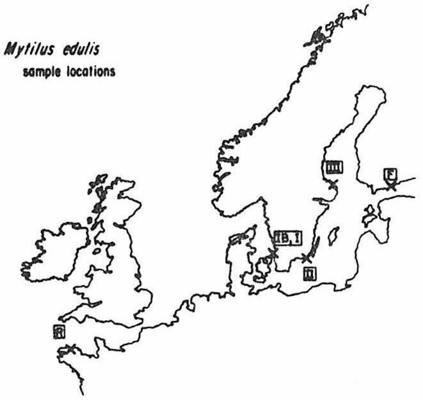

Fig. 1. Map showing sample locations and salinities. Locations are: F—Helsinki Bay, Finland; R—Roscoff, Finistère, France; I, IB—Vinga Lighthouse Styrsö, Bohuslän, Sweden; II—Svinbadan, Lerberget, S. of Höganäs, Skåne, Sweden; III—Grundkallen, N. E. Gräsö, Uppland, Sweden.

boron is distributed in the shell, and particularly whether the boron is associated with the organic or inorganic fractions of the shell. Organic material comprises the periostracum and the intercrystalline matrices in mollusc shells. It has also been reported to form the intracrystalline matrix (WATABE, 1965; TRAVIS, 1970) but this has been denied (TOWE and HAMILTON, 1968). Our technique is not capable of resolving features smaller than 2–5 μm. The following discussion refers to the intercrystalline organic matrix.

Three experiments were carried out. (1) Thin sections were made of several shells and deliberately exposed to higher neutron fluences (~10^{14} neutrons/cm^2). This produced a 'boron radioautograph' of the shell in that different track densities were associated with the growth layers in the shells, and these layers could be readily observed in the plastic detectors at very low magnification. The dark-colored organic-rich layers were associated with lower track densities, showing that the boron is not correlated with the intercrystalline organic material in the shell. The periostracum, however, does have a high B content (values ranging up to 30 ppm).

(2) It was impossible to associate the boron in *Mytilus edulis* specifically with inorganic crystals, since in this species the crystals are smaller than the spatial resolution of the track technique. However, in a shell of *Arca orbicularis*, which has coarser bioinorganic crystals and well-defined (~5 μm width) organic layers interstitial to ~20–50 μm aragonite crystals, the track density in an 'overexposed' section was not concentrated in 5 μm bands, but instead, was uniform. This experiment proves that the B is not highly concentrated in the intercrystalline organic layers and, by inference, that most of the observed B must be associated with the inorganic crystals.

(3) One of the more boron-rich *Mytilus edulis* shells was crushed and passed through a 200-mesh sieve. A portion of this powder was then soaked in commercial bleach to dissolve the organic portions. After a thorough rinsing with distilled water and ethanol, the powder was pressed into a pellet and irradiated along with a pellet made from unbleached material. The mean values of the track densities associated with the two pellets agreed to within 8%, with 6% counting statistics for each pellet. This experiment provides additional evidence that the boron is not associated with the organic matrix.

However, we have not uniquely demonstrated that boron resides in the crystal lattice of the carbonate minerals comprising the shell and not, for example, in trace inclusions within the carbonates. In the remainder of the paper, however, we shall assume that it is in the carbonates.

A critical question for the feasibility of relating shell B content to salinity is the inter- and intra-specimen variability in the B content of shells from a given locality. Figure 2 shows track density profiles for a single shell from Station I. The profiles shown were taken from the interior of the shell through to the outside ('transverse') and along the shell ('longitudinal') within the aragonite and calcite layers. The B content is seen to be uniform within statistical errors in the aragonite; the calcite is somewhat more irregular. The increased B content of the periostracum is clearly seen. Conceivably the B in the periostracum represents entrapped salts; however, no consistent differences were observed between dried and alcohol-preserved specimens. The data shown in Fig. 2 are typical of the shells that have been analyzed, although some cases have been observed with variations somewhat larger than can be accounted for from counting statistics alone.

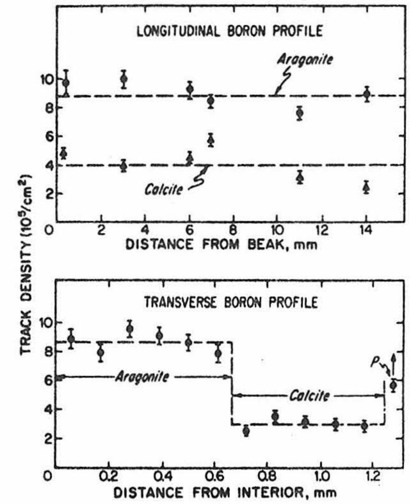

Fig. 2. Boron variations within a single *Mytilus edulis* shell from Baltic Station I (Fig. 1). The upper figure shows longitudinal scans for both aragonite and calcite as a function of distance from the beak. The data represent averages over the transverse thickness in each layer at the indicated longitudinal distance. The aragonite boron content is quite uniform, whereas the calcite is more variable. The lower figure shows a transverse B profile from the interior to the outside of the shell, showing the distinct B contents in the various structural layers. P refers to periostracum. All error bars are one standard deviation based on counting statistics.

The results of the different analyses are plotted as a function of water salinity in Fig. 3. Analyses of different specimens from a given location are plotted separately. B concentrations from all shells from the same location have been averaged, and the averages are listed in Table 1. Some of the differences observed for duplicate analyses of the same shell may be due in part to variability in a given shell. However, re-irradiation of a given shell has tended to give B concentrations slightly higher than the initial irradiation. The origin of this trend is uncertain, although it may reflect airborne surface contamination equivalent to

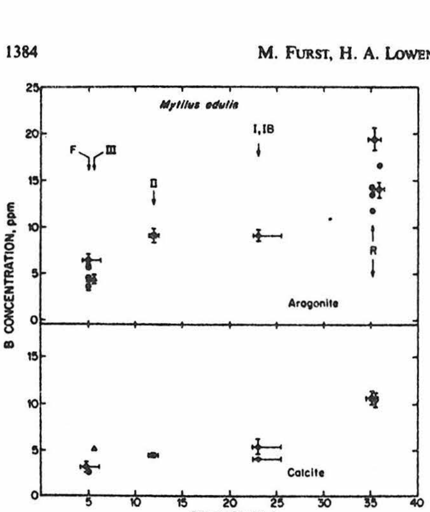

Fig. 3. Boron concentration as a function of water salinity for *Mytilus edulis* shells. Each point represents the analysis of a single shell. Representative error bars indicate 1σ deviations based on counting statistics for all tracks counted for a single shell. Letters refer to localities shown in Fig. 1. Data for aragonite are plotted above; those for calcite below. The seasonal ranges in salinity are about 6‰ for Station F (SEGERSTRÅLE, 1957), 0.4‰ for Station III, and 1‰ for Roscoff (R) (CABIOCH, 1975), and are indicated in the figure; 1.0‰ for Station II, 1.9‰ for Stations I and IB, (ARRHENIUS, 1976). Symbols are ●—Helsinki Bay, Finland, and Roscoff. France; △—Station III; ■—Station II; ◆—Stations I and IB.

as much as 1–2 ppm B. If the epoxy and SiO_2 control samples have negligible B, a blank of 0.5 ± 0.5 ppm is suggested but has not been applied. The blank corrections are probably the dominant source of error for the lower boron specimens (Finland, Station III), but interspecimen variation is a greater source of scatter for the specimens with higher B content. Nevertheless, the total spread for aragonite from one locality does not exceed ±20%, while the observed boron concentrations vary by as much as 400%.

Thus, although there is some scatter, a correlation between boron concentration and water salinity is observed in the salinity range investigated for both the aragonite and calcite. It is not clear at present whether the correlation is linear. These data are reasonably free of influences by water temperature fluctuations, since summer surface temperatures in the Baltic Sea are similar to average annual temperatures at Roscoff. Assuming growth occurs year-round at Roscoff and only in summer for the Baltic samples, any variations in B content due to seasonal growth layers would be averaged in our track-counting technique.

The greater variability of the B content of the calcite could be due in part to the much greater susceptibility of the outer part of the shell to attack by boring and encrusting micro-organisms. Another possible explanation is that variations in the amount of organic material present serve to dilute the boron-containing calcite crystals to varying degrees.

The boron concentrations observed are in fairly good agreement with those found by LEUTWEIN and WASKOWIAK (1962) using emission spectrographic analysis. They found a range of 1–7 ppm B over the same range of salinity in the aragonite-shelled species *cardiidae*. These workers also found boron concentrations between 2 and 8 ppm in total *Mytilus* shells. A correlation between total B and aragonite content was observed, using aragonite contents determined by X-ray diffraction.

LEUTWEIN and WASKOWIAK (1962) determined the concentrations of several other elements in calcitic and aragonitic portions of shells of several species of molluscs. They found that Cu, Mg, Mn, Pb, and Fe were enriched in calcite relative to aragonite, while Sr and B concentration were higher in aragonite. They suggested that ionic size is the factor which determines how an element is distributed between the two polymorphs, with ions larger than 1.26 Å preferentially entering the aragonite crystal lattice. However, B seems to be an exception; it has a very small ionic radius (0.23 Å) (AHRENS, 1952) but is found predominantly in aragonite. It is possible that B is substituting for C rather than for Ca in both crystal structures.

Table 1. Boron concentration of calcite and aragonite layers in *Mytilus edulis* shells

Sample Location	Salinity* (°/oo)	B Concentration** in Aragonite (ppm)	B Concentration in Calcite (ppm)	B Aragonite/B Calcite
Helsinki Bay (F)	5	5.1 ± 1.3 (4)	2.9 ± .3 (2)	1.8
Station III	5.5	4.1 ± .4 (1)	(a)	(a)
Station II	11.9	8.9 ± .8 (1)	4.5 ± .4 (1)	2.0
Station I	23.2	9.0 ± .7 (1)	4.4 ± .4 (1)	2.0
Station IB	23.2	9.0 ± .8 (1)	5.5 ± .5 (1)	1.6
Roscoff	35	15.1 ± 2.5 (6)	9.0 ± .4 (2)	1.7

* See caption of Fig. 3 for sources of salinity data.

** Errors are 1σ deviations from mean for averages of concentrations in all samples analyzed for each location. (See text). Numbers in parentheses indicate number of samples analyzed. (a) No data. (b) Salinity assumed same as for Station I.

Because of its larger and more uniform boron concentration, only aragonite has been emphasized in this study. Since it is hoped that this technique can be used in determining paleosalinites, it is reasonable to restrict analyses to aragonite. Fossil marine invertebrate shells with preserved original aragonite are known from sedimentary rocks as old as the Lower Carboniferous (HALLEM and O'HARA, 1962). The Sr and Mg contents of much material commonly shows little diagenetic alterations (HALLEM and PRICE, 1966; LOWENSTAM, 1964; WEINER *et al.*, in press). Hence an investigation of their boron contents may be meaningful.

Several of the problems which are encountered in using the B contents of sediments as salinity indicators (COUCH, 1971; PERRY, 1972) can be eliminated by using shell material. The use of original aragonite as confirmed by other geochemical tests (1) eliminates the need to consider the effect of *in situ* diagenesis of the material analyzed, and (2) circumvents the frequently encountered problem in clay analyses that the B concentration of the first environment of deposition is preserved, regardless of subsequent transportation and redeposition of clays. However, there are a limited number of organisms which can exist over a wide range of salinities.

CONCLUSIONS

This investigation has shown that (1) there is a correlation between B concentration and salinity in calcite and aragonite layers of *Mytilus edulis* shells, (2) the boron is located in the inorganic constituents of the shells and in the periostracum, and not in the intercrystalline organic matrix, and (3) the boron is more concentrated in the aragonite than in the calcite. The first two results are necessary conditions for meaningful paleosalinity studies in fossils. A similar salinity relationship was observed by LEUTWEIN and WASKOWIAK (1962) for the entirely aragonitic shells of *cardiidae*. It is at present unknown whether temperature also plays a role in determining the boron concentration in mollusc shells, or whether the source of the boron is in the water itself or in the food supply of the organisms. All of these questions could be answered through controlled laboratory experiments. Further, it is not known where the boron substitutes in the carbonate crystal lattices. It is also important to determine whether the correlation between shell B content and salinity is valid for other euryhaline species in the marine biomass.

The advantages of the radiography techniques are:

(1) There is no need to treat the shells chemically to eliminate interfering components, as is the case in clay analyses.

(2) The nuclear reaction used is unique to boron and lithium. Interference from lithium is minimal because of its low concentration in the samples and its lower efficiency of detection.

(3) There is no difficulty in selecting the proper part of the sample for analysis, whereas in clays, illite must be distinguished from montmorillonite and other clays.

(4) Unusual or anomalous concentration effects, e.g. zoning are very readily noticed. It is quite practical to make a radioautograph of each sample.

(5) The same samples can be analyzed as many times as desired; indeed, if one wishes to use the shells for other purposes, epoxy mounting is not necessary.

If the question concerning the effects of temperature and other environmental parameters can be answered, this nuclear track technique looks promising as a means of determining paleosalinities.

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APPENDIX II

IDENTIFICATION AND ORIGIN OF SAMPLES

Taxonomic Group	Species	Designation	Location of Collection	Source	Salinity (°/oo)	Salinity Reference	Sample Type	Identification by
Phylum Protozoa		V13g#5	Atlantic Ocean	17	35		cleaned tow	
Class Sarcodina		V15z#3	Atlantic Ocean	17	35		cleaned tow	
Order Foraminiferida	Orbulina universa	SW19C 4741	Holon, Israel 600-800m	2			cleaned tow	S. Weiner
(planktonic foraminifera)	Orbulina universa	SW12B	Ashdod, Israel 600-800m	2			cleaned tow	S. Weiner
Phylum Porifera	H	4544					single spicules	
Class Hexactinellida=H	H	4545	Magdalena Bay, Mexico	1			single spicules	
Class Demospongia=D	H	4081					single spicules	
	H-Staurocalyptus sp	25765-1					whole sponge	G. Bakus
	H-Aphrocallistes vastus	25765-2	Cortez Ridge, California				whole sponge	G. Bakus
	H	25765-3					whole sponge	G. Bakus
	D-family Craniellidae	25765-4	32°58'30" N.	3	33.5	n	whole sponge	G. Bakus
	D-Lissodendoryx sp.	25765-5					whole sponge	G. Bakus
	D-Axinella sp.	25766-1	119°32'72" W.				whole sponge	G. Bakus
	H	25766-2					whole sponge	G. Bakus
	H	25767-2					whole sponge	G. Bakus
	H	25767-3					whole sponge	G. Bakus
	D	26601	Catalina Island, California	3	33.5	n	whole sponge	
	D-Halichondria bowerbanki	GP 1	Gloucester Point,				whole sponge	K. Webb
	D-Lissodendoryx carolinensis	GP 2	Chesapeake Bay, Virginia	4	10-25 (17)	a	whole sponge	K. Webb
	D-Syringella sp.	FP 1	Flat Point, San Juan Islands,				whole sponge	E. Kozloff
	D-Myxilla, sp.	FP 2	Washington 50 m	3			whole sponge	E. Kozloff
	D	PV 2	Peavine Pass, San Juan				whole sponge	M. Furst
	D-Iophon pattersoni	PV 3	Islands, Washington 50 m	3			whole sponge	M. Furst
	D-Lissodendoryx firma	PV 4			28-32	b	whole sponge	M. Furst
	D	WS 1	West Sound, Orcas Island,					
			Washington 50 m	3			whole sponge	E. Kozloff
	D	MV 1	Mar Vista, San Juan Island,					
			Washington 0-3 m	3			whole sponge	M. Furst

Appendix II (cont.)

Taxonomic Group	Species	Designation	Location of Collection	Source	Salinity (°/oo)	Salinity Reference	Sample Type	Identification by
Porifera (cont.)	D	SH	Snug Harbor, San Juan Island, Washington 0.5 m	3	28-32	b	whole sponge	M. Furst
	D-Spongilla sp.	Egg	San Juan Island, Washington	3	0		whole sponge	M. Furst
	D-Spongilla sp.	CBS	North Carolina Lake	5	0		whole sponge	Carolina Biological Supply
	D-Ephydatia fluviatilis	AI 1,2,3	Asko Island, Sweden 0.5 m	11	5.7-7.1 (6.3)	n	whole sponge	S. Ankar
	D-Microciona sp.	WH 1,2,3	Woods Hole, Massachusetts	12	20-30 (25)	o	whole sponge	J. Valois
	D-Halichondria sp.	WH 13,14,15						
	D-Calliospongia vaginalis	Ber-1	Bermuda 50 m	1	37 ± 1	p	whole sponge	
		BB 1					whole sponge	
		BB 2					whole sponge	
	D-Geodia sp.	BB 3	Barbados 210 m	1	36-36.75	p	whole sponge	M. Furst
	D-Geodia sp.	BB 4					whole sponge	M. Furst
		BB 8					whole sponge	
	D-Thalysias juniperina	C 1					whole sponge	G. Bakus
	D-Iotrochata birotulata	C 2	Caribbean, Honduras 0-20 m	13	36 ± 1	q	whole sponge	G. Bakus
	D-Agelas clathrodes	C 3					whole sponge	G. Bakus
	D-Neotibularia nolitangere	C 4					whole sponge	G. Bakus
	D-Xestospongia muta (Schmidt)	YH 1	Runaway Bay, Jamaica 51 m	14	36 ± 1	q	whole sponge	W. Hartman
	D-Cliona celata (Grant)	YH 2	New Haven, Connecticut 3-4 m	14	15-32	q	whole sponge	W. Hartman
	D-Tethya crypta (deLaubenfels)	YH 3	Discovery Bay, Jamaica 2.5 m	14	36 ± 1	q	whole sponge	W. Hartman
	D-Haliclona oculata (Pallas)	YH 4	Northumberland Straits, Nova Scotia, Canada	14	32 ± 1 ?	q	whole sponge	W. Hartman
	D-Axinella polypoides (Schmidt)	YH 5	Cadaques, Cataluna, Spain20-40m	14			whole sponge	W. Hartman
	D-Microciona prolifera (Ellis and Solander)	YH 6	New Haven, Connecticut 5 m	14	15-32	q	whole sponge	W. Hartman
	D-Haliclona oculata (Pallas)	YH 7	Massachusetts Bay, Mass. 40 m	14	31.6 ± 2	q	whole sponge	W. Hartman
	D-Suberites ficus (Johnston)	YH 8	Sandy Point, Block Island, R.I. Rhode Island 40 m	14	31.1 ± .2	q	whole sponge	W. Hartman
	D-Iotrochata birotulata (Higgin)	YH 9	Nassau, N. P., Bahamas	14	37 ± 1	q	whole sponge	W. Hartman
	D-Polymastia robusta (Bowerbank)	YH 10	Massachusetts Bay, Mass. 40 m	14	31.6 ± .2	q	whole sponge	W. Hartman
	D-Haliclona rubens (Pallas)	YH 11	Cayo de Caballo Blanco, La Parguera, Puerto Rico 3 m	14	34 ± 1	q	whole sponge	W. Hartman
	D-Isodictya palmata (Johnston)	YH 12	Eastport, Maine	14	32 ± 1	q	whole sponge	W. Hartman

Appendix II (cont.)

Taxonomic Group	Species	Designation	Location of Collection	Source	Salinity (°/oo)	Salinity Reference	Sample Type	Identification by
Porifera (cont.)		AA 1	30 m				whole sponge	
		AA 2	25 m				whole sponge	
		AA 3	Arthur Harbor, Antarctica 18 m	20	32.5 ± .5	r	whole sponge	
		AA 4					whole sponge	
		AA 5	30 m				whole sponge	
		AA 6					whole sponge	
		MSN	63°17' s., 166°58' W., 2639 m	10		m	core	
		SOCAL	28°20' N., 112°23' W., 896 m	10	34.5	k	core	
		ANTP	56°23.2'N.,171°4.6'W., 2932 m	10		1	core	
		V-23-42	62°10.8'N., 27°55.6'W.,1514 m	15			core	
		RC13-263	53°48.3'S., 8°13'W., 3389 m	17			core	
		V19-29	3°35' S., 83°56' W., 3157 m	16			core	
		V22-204	15.01° N., 23.14° W.,	15			core	
		23782	Cedros Island, Mexico					
		23783	28° N., 115° W., 1000 m	1			box core	
Phylum Mollusca Class Gastropoda	unidentified	snail	Svinbadan, Sweden	1	11.9 ± .5	d	shell	M. Furst
Class Pelecypoda	*Mytilus edulis*	I, IA	Vinga, Sweden	1	22.5-25.4 (23.2)	d	shell	M. Furst
		II	Svinbadan, Sweden	1	11.9 ± .5	d	shell	M. Furst
		III	Grundkallen, Sweden	1	5.5 ± .2	d	shell	M. Furst
		Fin	Helsinki Bay, Finland	1	5	e	shell	M. Furst
		Rosc	Roscoff, France	1	35.0 ± .3	f	shell	M. Furst
		Naples	Naples Bay, Italy	1	37-38		shell	M. Furst
		Mal 1,2,3	Malibu, California	3	33.5	n	shell	M. Furst
		SFR	Rodeo, San Francisco Bay, Calif.	3			shell	M. Furst
		PS1,2,3,4,5	Port Susan, Washington	3	20-29 (24.4)	b	shell	M. Furst
		PP1-2,3,4,5	Potlatch State Park, Washington	3	24,2	b	shell	M. Furst
		SB 1,2,3	Sequim Bay, Washington	3	31.0	b	shell	M. Furst
		JL	Jakell Lagoon, San Juan Island, Washington	3	28-32	q	shell	M. Furst

Appendix II (cont.)

Taxonomic Group	Species	Designation	Location of Collection	Source	Salinity (^{o}/oo)	Salinity Reference	Sample Type	Identification by
Phylum Mollusca (cont.)	Mytilus californianus	AC	American Camp, San Juan Island Washington	3	32	b	shell	M. Furst
		Mal 4,5,6	Malibu, California	3	33.5	n	shell	M. Furst
		MC	Corona del Mar, California	1	33.5	n	shell	M. Furst
	Modiolus auriculatus	A 3	Atur, Israel	2	40	g	shell	S. Weiner
		SS	Sharm el Sheikh, Israel	2	40	g	shell	S. Weiner
	Modiolus modiolus (Linne) 1757	FHL	near Fish Creek, San Juan Island, Washington	3	28-32	q	shell	M. Furst
	Brachidontes variabilis	A1,2	Atur, Israel	2	40	g	shell	M. Furst
	Crassostrea irridescens	PC	Punta Cabra, Baja California Mexico	2	33.5	n	shell	M. Furst
	Crassostrea virginica	MB	Moro Bay, California	2	33.5	n	shell	M. Furst
	Mytilus edulis, fossil	226	San Pedro, California	6	33-34	i	shell	M. Furst
		300	San Pedro, California	6	33-34	i	shell	M. Furst
Phylum Arthropoda (barnacles)	Balanus sp.	SB 2b	Sequim Bay, Washington	3	31.0 ± 1	b	shell	M. Furst
	Balanus sp.	PS 6	Port Susan, Washington	3	20-29 (24.4)	b	shell	M. Furst
	Balanus sp.	PP 6	Potlatch State Park, Washington	3	23-29 (24.2)	b	shell	M. Furst
Phylum Chordata Subphylum Urochordata (tunicate)	Herdmania momus	4562 B	Long Reef, Sydney, Australia	1	marine		spicules	K. Mather
Phylum Chrysophyta Class Bacillariophyceae (Diatoms)		BF	Burney Falls, Shasta Co., CA	8	lacustrine		diatomite	
		IW	Indian Wells Valley, Inyo Co.,CA	7	lacustrine		diatomite	
		D	near Dorris, Siskiyou Co., CA	7	lacustrine		diatomite	

Appendix II (cont.)

Taxonomic Group	Species	Designation	Location of Collection	Source	Salinity (°/oo)	Salinity Reference	Sample Type	Identification by
Chrysophyta (cont.) (Diatoms)		CL	Copco Lake Deposit, Siskiyou Co. California	7	lacustrine		diatomite	
		B	Basalt, Mineral Co., Nevada	7	lacustrine		diatomite	
		CQ	Chilcoot Quadrangle, Plumas Co., California	7	lacustrine		diatomite	
		WC	Willow Creek Area, S. of Dome Mountain, Siskiyou Co., CA	7	lacuatrine		diatomite	
		EL	Eagle Lake, Lassen Co., CA	7	lacustrine		diatomite	
		LB	N. end Lake Britton, Shasta Co., California	7	lacustrine		diatomite	
		PI	Paoha Island, Mono Lake, Mono Co., California	7	lacustrine		diatomite	
		EP	Eagle-Pitcher Mine, near Lovelock, Pershing Co., Nevada	7	lacustrine		diatomite	
		HC	Hat Creek at Highway 299, Shasta Co., California	7	lacustrine		diatomite	
		LV	Long Valley, Mono Co., CA	7	lacustrine		diatomite	
		KF	Knight's Ferry, Tuolomne Co., CA	7	lacustrine		diatomite	
		RV	Russell Valley, Nevada Co., CA	7	lacustrine		diatomite	
		L	Monterey or Wisquoc Fm., Lompoc, Santa Barbara Co., CA	9	marine	h	diatomite	
		NL	Monterey Fm., Newport Lagoon, Orange Co., CA	3	marine	i	diatomite	
		CH	Chalk Hill, City of Industry, Los Angeles Co., CA	1	marine	i	diatomite	
		SOCAL	28°20' N., 117°55.2' W., 896 m	10	34.5	k	core	
		MSN	56°23.2'N., 171°28.0'W., 2392 m	10		l	core	
		ANTP	63°17' S., 166°58' W., 2639 m	10		m	core	
Mixed Zooplankton	mixture	M 12	33°22' N., 117°55.2' W.,0-50 m	22	33.5	n	tow	
	mixture	M 15	33°28.2'N.,118°28.0' W.,0-50 m	22	33.5	n	tow	
	mixture	TS XI	31°27.6'N.,140°12.9'W.,300±15 m	22	marine		tow	
	mixture	DR II	28° N., 155° W.	22	marine		tow	

Appendix II (cont.)

Sample Sources (indicated by numbers)

1. Heinz A. Lowenstam, California Institute of Technology
2. Stephen Weiner, California Institute of Technology
3. Marian Furst, California Institute of Technology
4. Ken Webb, Virginia Institute of Marine Science
5. Carolina Biological Supply, Burlington, N. C.
6. Ed Wilson, Los Angeles County Museum of Natural History
7. George Cleveland, California Division of Mines and Geology
8. Eileen Burnett, California State University, Los Angeles
9. Caltech Mineral Collection
10. Tom Walsh, Scripps Institute of Oceanography
11. Sven Ankar, University of Stockholm
12. John Valois, Woods Hole Oceanographic Institute
13. Gerald Bakus, University of Southern California
14. Willard D. Hartman, Peabody Museum of Natural History, Yale University
15. William F. Ruddiman, Lamont-Doherty Geological Observatory
16. Peter Thompson, Lamont-Doherty Geological Observatory
17. David W. Cooke, Lamont-Doherty Geological Observatory
18. Allan Be, Lamont-Doherty Geological Observatory
19. Don Miser, California Institute of Technology
20. Gary Zumwalt, University of California, Davis
21. K. Mather, Sydney, Australia
22. Mike Mullin, Scripps Institution of Oceanography

Salinity References (indicated by letters)

a. Ken Webb, Private communication
b. Collias and Barnes, 1964, 1966
c. experimental--B determination
d. Gustaf Arrhenius, private communication
e. Segerstrale, 1957
f. L. Cabioche, private communication
g. S. Weiner, private communication
h. Dibblee, 1954
i. Yerkes, et al., 1965
j. Whitehead and Feth, 1961.
k. Roden and Groves, 1959
l. BOREAS Expedition, 1966
m. Decon, 1937
n. Sven Ankar, private communication
o. John Valois, private communication
p. Lewis, et al., 1962
q. U. S. Department of Commerce, NOS, 1971,1973
r. Krebs, 1977

APPENDIX III

The Solar System Boron Abundance, by Martha Riherd Weller, Marian Furst, T. A. Tombrello, and D. S. Burnett. Published in *The Astrophysical Journal*, 1977, Volume 214, pp. L39-L43.

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THE SOLAR SYSTEM BORON ABUNDANCE*

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ABSTRACT

The concentrations of B in seven carbonaceous chondritic meteorites have been determined by the use of two different analytical techniques. The data correspond to a B/H ratio of about 10^{-9} compared to the value of 10^{-8} previously proposed by Cameron, Colgate, and Grossman. However, the meteoritic abundance remains at least a factor of 2–10 higher than various estimates of the solar photosphere abundance. We conclude that both meteoritic and photospheric B and Be abundances must be considered in comparisons with nucleosynthesis calculations. Using our revised B abundances and assuming ^{7}Li was synthesized in the big bang, we find that the residual ^{6}Li/^{10}B, ^{9}Be/^{10}B, and ^{11}B/^{10}B abundance ratios are well matched by the production rates for bombardment of a CNO mixture of solar proportions by protons and α-particles with a kinetic energy per nucleon spectrum of the form $E^{-1.8}$.

Subject headings: abundances — meteors and meteorites — solar system: general

I. INTRODUCTION

The typical good agreement between solar photospheric abundances of nongaseous elements and abundances derived from analyses of carbonaceous chondritic meteorites (Anders 1971; Ross and Aller 1976) is readily understood in terms of contemporary ideas of chondrite formation (see, e.g., Grossman and Larimer 1974). Carbonaceous chondrites resemble the solid material expected when a gas cloud of solar composition cools to temperatures of ~300 K at low pressure (10^{-4} to 10^{-6} atmospheres). Thus, elements which are gases (CNO, rare gases, and perhaps Cl) are depleted in meteorites relative to the Sun. However, cases where elements are enriched in meteorites provide important information. For example, the 200-fold enrichment of Li (Nichiporuk 1971; Grevesse 1968) indicates thermonuclear destruction of solar Li, either in an earlier, totally convective, phase of solar evolution or by burning at the base of the surface convection zone during the main-sequence lifetime. Measurements of boron in the solar photosphere (Hall and Engvöld 1975; Kohl, Parkinson, and Withbroe 1977), the interstellar medium (Morton, Smith, and Stecher 1974), and Vega (Boesgaard *et al.* 1974) imply $B/H \approx 10^{-10}$ while Cameron, Colgate, and Grossman (1973) calculated a meteoritic $B/H = 1.5 \times 10^{-8}$ based on carbonaceous chondrite data from Quijano-Rico and Wänke (1969). Several papers concluded that boron is enhanced in carbonaceous chondrites and thus that these meteorites do not provide a valid solar system abundance for this element (Hall and Engvöld; Morton, Smith, and Stecher; Boesgaard *et al.*). The B concentrations obtained by Quijano-Rico and Wänke for ordinary chondrites suggest that B was in a volatile form in the solar nebula. Since ordinary chondrites are known to be depleted in moderately volatile elements, these chondrites cannot be used for estimating the solar system abundance, although Audouze, Lequeux, and Reeves (1973) proposed their use on a strictly ad hoc basis.

As emphasized by Cameron, Colgate, and Grossman (1973), a B/H value of 10^{-8} is too high to be compatible with otherwise attractive theories of galactic cosmic ray (GCR) nucleosynthesis of Li, Be, and B (Reeves, Fowler, and Hoyle 1970; Meneguzzi, Audouze, and Reeves 1971). The lower value of 10^{-10} has been generally accepted as more compatible with GCR nucleosynthesis; however, as discussed later, the high implied Li/B presents difficulties.

In view of the large difference between the meteoritic and solar B abundances and the implications for the nucleosynthesis of Li, Be, and B, we have made additional measurements of the meteoritic B abundance.

II. EXPERIMENTAL

We have used two different methods: (1) track counting and (2) beta counting. (1) Tracks are produced in cellulose nitrate plastic by α-particles from the $^{10}B(n, \alpha)$ reaction. The plastic is clamped to a homogenized pellet, irradiated with thermal neutrons, and then chemically etched to reveal cone-shaped tracks. The measured track density relative to a standard gives the B concentration. Corrections (ranging up to 30%) are made for background tracks from $^{17}O(n, \alpha)$, $^6Li(n, \alpha)$, and fast neutron recoils. (2) We produce ^{12}B with the reaction $^{11}B(d, p)$. The β-decay energy (13 MeV) and half-life (20 ms) of ^{12}B provide a unique decay signature. The meteorite is irradiated in 30 ms pulses with 2.8 MeV deuterons. After a short delay, betas greater than 6 MeV are counted in four 15 ms counting periods using a plastic scintillator. The ^{11}B concentration is proportional to the difference between the counts in the first two counting periods and those in the second two.

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Absolute concentrations for both track and beta counting measurements are based on National Bureau of Standards glass SRM 610. Some comparative measurements indicate that there are no systematic differences greater than ~10% in B concentration by the two methods, and this is not important for the questions addressed in this paper. A more detailed description of the experimental methods and results will be published elsewhere (Weller *et al.* 1977).

III. RESULTS

Table 1 summarizes the B concentrations obtained for individual meteorites. The track results (tx) for Haripura and Orgueil in Table 1 are given as upper limits because we had no control over sample preparation. These samples were powders prepared by Gopalan and Wetherill (1970). We have not tabulated track results for other meteorites which gave high (5–15 parts per million [ppm]) values and exhibited nonuniform B distributions indicative of contamination. The Haripura and Orgueil limits are given because they are low enough to be interesting.

All meteorites in Table 1 are carbonaceous chondrites. Our results for Lancé and Murray are distinctly lower than the 6.4 and 9.4 ppm, respectively, reported by Quijano-Rico and Wänke.

The final column in Table 1 gives the atomic B/H ratio calculated using Si as an intermediate normalization: $(B/H) = (B/Si)_{met}(Si/H)_{Sun}$. We have used Si contents for individual meteorites when possible; otherwise, average Si contents for the various C subgroups were used (Mason 1971). We adopt $(Si/H)_{Sun} = 4.5 \times 10^{-5}$ (Ross and Aller 1976). The progression between B/H in the C3, the C2, and the C1 meteorites is close to the 0.4/0.55/1 progression normally observed for C3/C2/C1 meteorites (Grossman and Larimer 1974). Our results indicate a B/H ratio which is different from both the 10^{-8} proposed by Cameron, Colgate, and Grossman (1973) and the 10^{-10} upper limit for the solar photosphere obtained by Hall and Engvöld (1975).

TABLE 1

B CONCENTRATIONS IN CARBONACEOUS CHONDRITES

Chondrite	Number of Samples Analyzed	ppm B*	(B/Si) (Si/H) (10^{-9})
C3:			
Allende, tracks (tx).	3	1.0 ±0.1	<0.75
Allende, betas (β)..	4	1.28±0.31	
Lancé (β).........	2	1.46±0.56	0.84
C2:			
Murray (β)........	5	1.18±0.25	1.1
Murchison (β).....	7	1.41±0.26	1.3
Haripura (tx)......	1	≤1.0	≤0.9
C1:			
Ivuna (β)..........	2	2.7 ±0.3	3.1
Orgueil (tx)........	1	≤1.8	≤2
Orgueil (β)........	2	1.58±0.14	1.8

* ppm = micrograms B per gram meteorite; errors are average deviations of individual sample analyses.

From our data, we propose a meteoritic solar system value of $B/H = 2 \times 10^{-9}$. Our abundance is a factor of 5 above the photospheric abundance given by Kohl, Parkinson, and Withbroe (1977) but is only a factor of 2 above the upper error bound given by Kohl *et al.*

The principal difficulty with B analysis is that there are serious contamination problems. All results are based on analyses of freshly prepared and cleaned surfaces. To minimize contamination, we carefully selected the meteorite samples analyzed and minimized the time between sample preparation and analysis. It is conceivable that our results are simply upper limits, but the following arguments indicate they are actual B concentrations. Recall that the important question is whether B/H is 10^{-8} or 10^{-10}. (1) Low B control samples (graphite, SiO_2 glass, and single crystal calcite) were analyzed in parallel with the meteorites. These samples showed consistently lower B concentrations than the meteorites. (2) The time between sample preparation and analysis and the total exposure time of the sample to the laboratory atmosphere were deliberately varied in the beta counting experiments. For samples prepared within 24 hours of analysis, contamination is not significant. (3) The track data indicate that the B was uniformly distributed on a 0.1 mm scale over the sample as expected for B from the meteorite, whereas the B distribution on a badly contaminated sample was often very nonuniform. Duplicate track analyses of 40 mg aliquots were always in good agreement. (4) After analysis, a Murchison sample was scraped twice with a SiO_2 chisel and the fresh surfaces reanalyzed without atmospheric exposure. All three measurements gave boron concentrations of 1.4 ± 0.2 ppm, indicating no surface contamination.

IV. DISCUSSION

Given our revised meteoritic abundance ($B/H = 2 \times 10^{-9}$) and the photospheric value of Kohl, Parkinson, and Withbroe (1977) of 4×10^{-10}, the factor of 100 discrepancy between the photospheric and meteoritic B abundances which previously existed in the literature has been reduced to a factor of 5. If the upper error limit of the Kohl *et al.* measurement is considered, the difference with the meteoritic abundance can be reduced to a factor of 2. The photospheric upper limit ($B/H < 2 \times 10^{-10}$) cited by Hall and Engvöld (1975) remains distinctly lower than our result or that of Kohl *et al.* However, taking all observations at face value it still appears that the photospheric B abundance is lower than the meteoritic abundance by a factor of 2–10. Independent of specific theoretical considerations about Li Be B nucleosynthesis, there are still several alternative interpretations: (1) If all observational data are correct and if these elements have not been depleted in the Sun by thermonuclear processes, the photospheric abundances must be adopted as the average solar system abundances. It can never be ruled out that a specific element has been anomalously enriched during the formation of carbonaceous chondrites. Such enrichment of boron or any other element would be cosmochemically unique and of great interest since the mechanism for this enrichment is not apparent. There has been considerable discussion of an apparent overabundance of Hg in carbonaceous chondrites (e.g., by Audouze, Lequeux, and Reeves 1973); but, given the amount of Hg in man's environment, we think a more detailed evaluation of the quality of the samples used for Hg analysis is required before the Hg overabundance is accepted. The conclusion that B was in a volatile form in the solar nebula must also be reconsidered. In any case, a reexamination of B concentrations in other types of chondrites seems appropriate, as well as a study of the distribution of B within individual meteorites. (2) The validity of the carbonaceous chondrite B abundance as a solar system average should be kept as a viable option. This requires explaining why the astrophysical abundances are lower. The solar B abundance upper limit of Hall and Engvöld is based on infrared B I transitions, whereas the interstellar (Morton, Smith, and Stecher 1974) and Vega (Boesgaard *et al.* 1974) observations used the B II resonance line in the far-ultraviolet (1362 Å) and the Kohl *et al.* photospheric result is based on rocket-UV observations at 2497 Å. It is possible that there are systematic differences (e.g., in *gf*-values) for these different lines. However, except for Kohl *et al.*, none of the above papers discusses the quality of the *f*-values used; in view of the uncertainties which have existed in the past, additional laboratory *f*-value measurements would be desirable. Further, independent of theories of nucleosynthesis and galactic evolution, it cannot be assumed that the B abundance for the interstellar gas or for Vega should be the same as for the Sun. The chief difference of interest is between the meteoritic and solar photospheric abundance. (3) An interesting alternative is that the anomalous abundance measurement is not B, but Be (Cameron, Colgate, and Grossman 1973). Our evaluation of new meteorite Be analyses by Quandt and Herr (1974) would yield $Be/H = 4 \times 10^{-11}$ in contrast to the generally accepted photospheric abundance of 1×10^{-11}. Thus, thermonuclear depletion of Be and B as well as Li in the Sun cannot be totally dismissed. However, if B were depleted by a factor of 5–10, one might expect a depletion of Be much larger than a factor of 4. The photospheric Be abundance is based on Be II lines around 3130 Å which is in a very complex region of the solar spectrum. Perhaps the identification of these lines or the effects of blending of interfering lines should be reexamined. We would also like to see an authoritative discussion of the accuracy of the Be II *f*-values. (4) The data are compatible with the meteoritic abundances of both B and Be being about a factor of 5 higher than the corresponding photospheric values. This suggests the possibility of an inhomogeneous solar photosphere in which a fraction, x, of the photospheric material has been subjected to high temperatures (e.g., by deep convective overturn) and has been totally depleted in Li Be B. The remaining $(1 - x)$ of photospheric material has been depleted in Li (e.g., by only shallow convective mixing) but not in B or Be. For $x \sim 0.8$, the photospheric B/H and Be/H would be a factor of 5 below the true solar system value, but B/Be would be correct. (5) Our own results may be upper limits due to contamination. Although we have already presented arguments against such an interpretation, it would be desirable for our abundances to be confirmed by additional B measurements on chondrites, preferably by a technique which analyzes samples with a smaller surface-to-volume ratio and which is thus less sensitive to surface contamination. Such a method, based on γ-rays from $^{10}B(n, \alpha)^{7}Li^{*}$, has been used by Curtis, Gladney, and Jurney (1976), and their initial results appear compatible with ours.

In summary, we conclude that at present both meteoritic and photospheric Be and B abundances must be considered in assessing theories for the nucleosynthesis of these elements. If subsequent work confirms the accuracy and applicability of the photospheric values, those from meteorites would have to be considered irrelevant.

V. IMPLICATIONS FOR Li Be B NUCLEOSYNTHESIS

Table 2 summarizes our adopted "solar" and meteoritic Li Be B abundances. As is customary, we assume that Li has been depleted in the Sun by thermonuclear processes; consequently the meteoritic Li is used in both sets of abundances. A survey of the present literature indicates that the number of proposed mechanisms for light-element nucleosynthesis exceeds the number of nuclei involved; consequently, it seems profitable only to seek the simplest mechanism which can explain the observed abundances in an astrophysically consistent manner. It is reasonable to assume the validity of the big bang and the accompanying nucleosynthesis of D, ^{3}He, and ^{7}Li (Wagoner, Fowler, and Hoyle 1967). Given the relative abundances of D and B, it is difficult to synthesize them in a single process. Further, calculations using very low-energy particle fluxes have not been able to satisfactorily produce $^{7}Li/^{6}Li$ ratios as high as the solar system value of 12.5 (see, for example, Bodansky, Jacobs, and Oberg 1975; Roche *et al.* 1976). Consequently, we shall focus on the remaining four nuclei: ^{6}Li, ^{9}Be, ^{10}B, and ^{11}B. We consider the simplest synthesis: spallation of CNO nuclei by protons and

TABLE 2

"SOLAR" AND METEORITIC
Li Be B ABUNDANCES
(units of 10^{-11})

Ratio	"Solar"	Meteoritic
Li/H......	200[*]	200[*]
Be/H......	1[†]	4[‡]
B/H.......	$\leq$ 20[§]	200[‖]

[*] Nichiporuk 1971. The meteoritic value is taken for the "solar" nebula because of the presumed depletion of Li in the sun.

[†] Grevesse 1968.

[‡] Quandt and Herr 1974.

[§] Hall and Engvöld 1975.

[‖] This work.

α-particles, e.g., irradiation of the interstellar medium by galactic cosmic rays as first discussed by Reeves, Fowler, and Hoyle (1970).

We first consider the spectral shapes compatible with the two sets of *relative* abundances and later consider the required particle fluences (integrated fluxes), since the fluences depend on spectral shape. The above four nuclei define three abundance ratios: ^{6}Li/^{10}B, ^{9}Be/^{10}B, and ^{11}B/^{10}B. Clearly, with only three numbers to fit, only simple theories can be considered. Further, the three ratios should not be given equal weight in assessing an acceptable fit. The ^{11}B/^{10}B isotopic ratio is precisely known, and *any calculation which fails to reproduce it to within ±0.1 is unacceptable.* In contrast, the ^{6}Li/^{10}B and ^{9}Be/^{10}B are elemental ratios, and to reproduce these to within a factor of 2 is quite acceptable. Table 3 compares the meteoritic and solar abundance ratios with spallation production rate ratios from Roche *et al.* (1976). The following discussion assumes that all relevant spallation cross sections are known with sufficient accuracy. Because the cross sections are constant at high energies, the abundance ratios in this energy range are unaffected by the spectral shape. Observations imply that the GCR spectrum above ~0.5 GeV is represented by a total energy power law. However, due to solar modulation, the GCR spectral shape cannot be determined at energies below 100 MeV per nucleon where it has the greatest effect on the abundance ratios. Results of two low-energy spectra are shown in Table 3: extrapolation of the total energy power law which has been adopted in many recent papers as a representation of the interstellar GCR spectrum, and a power law in kinetic energy per nucleon. For the latter spectrum, the exponent of 1.8 is chosen to fit the ^{11}B/^{10}B isotopic ratio; and, when this is done, excellent agreement is obtained with the revised *meteoritic* ratios. The total energy power law provides an acceptable fit to the meteoritic elemental ratios, but fails to match the boron isotopic ratio. This observation is not new to us, but its importance appears to have been underemphasized previously. Table 3 also shows that it is much more difficult to describe the "solar" abundances, particularly the high ^{6}Li/^{10}B ratio. Consideration of a wider variety of spectral shapes (Roche *et al.* 1976; Meneguzzi, Audouze, and Reeves 1971) does not alleviate this difficulty. Thus, we conclude that the meteoritic relative abundances are more compatible with simple spallation synthesis than are the "solar" abundances. This point has not been considered in most recent astrophysical papers which have tended to focus on the B/H ratio; however, it has been noted in papers written by nuclear physicists (Roche *et al.*; Bodansky, Jacobs, and Oberg).

TABLE 3

COMPARISON OF RELATIVE ABUNDANCES AND SPALLATION PRODUCTION RATES*

Parameter	^{6}Li/^{10}B	^{9}Be/^{10}B	^{11}B/^{10}B
Spectral shape:†			
$(1+E)^{-2.6}$	1.0	0.16	2.0
$E^{-1.8}$‡	0.46	0.09	4.0
Abundances:§			
"Solar"	≥ 5	≥ 0.3	4.0
Meteoritic	0.4	0.1	4.0

* Taken from Roche *et al.* 1976; includes both proton and alpha spallation for a CNO mixture of relative abundances = 3/1/5 by number.

† E refers to kinetic energy per nucleon.

‡ Exponent chosen to fit ^{11}B/^{10}B value.

§ See Table 2.

Because of the low threshold for ^{11}B production by ^{14}N(p, α), particle fluxes down to 5 MeV per nucleon must be considered in estimating the required particle fluences. For the $E^{-1.8}$ spectrum, we estimate that a total fluence of 3×10^{19} particles per cm^{2} greater than 5 MeV per nucleon is required to produce the abundances shown in Table 2.

The basic question which remains is whether our proposed $E^{-1.8}$ spectrum can be ruled out on astrophysical grounds. Again we invoke our, perhaps Neanderthal, point of view that this problem is scientifically useful (and interesting) only if it is relatively simple. Specifically, if synthesis of these four nuclei is *not* possible with an *interstellar* GCR spectrum approximately like that of the present-day GCR (both in intensity and in spectral shape) interacting with an interstellar medium of approximately the same density and composition as observed today, then the problem appears open-ended. Previous studies beginning with Reeves, Fowler, and Hoyle (1970) show that there is no basis for ignoring the GCR contributions if the properties of the GCR and the interstellar medium were the same in the period prior to the formation of the solar system as they are today. Thus, if GCR nucleosynthesis fails, there are two alternatives: (1) the GCR and/or the local interstellar medium were very different before 4.5×10^{9} yr ago or (2) a variety of sources and mechanisms (supernova shock waves, solar system synthesis, selective thermonuclear destruction, etc.) are contributing to the abundances of these four nuclei in addition to GCR nucleosynthesis. Case 2 is mundane and uninteresting; requiring two sources to explain the abundances of four nuclei is basically an admission of defeat. But, because case 2 is possible, case 1 or any other interesting variation can *never* be established. Returning to the question of the plausibility of an $E^{-1.8}$ spectrum, the crucial question is then: Could the present-day GCR spectrum be of this form? The demodulated GCR spectrum of Goldstein, Fisk, and Ramaty (1970) considered by Meneguzzi, Audouze, and Reeves (1971) has the form of the total energy power law in Table 3 and does not fit the solar system B isotopic ratio. Therefore, if this form of demodulated spectrum is correct, we have reached the logical stalemate discussed above. If it is not, and something similar to an $E^{-1.8}$ spectrum could be valid, it would be appropriate to face additional problems such as the heating of the interstellar medium.

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APPENDIX IV

Boron Concentrations in Carbonaceous Chondrites, by Martha Riherd Weller, Marian Furst, T. A. Tombrello, and D. S. Burnett. Published in *Geochimica et Cosmochimica Acta*, 1978, Volume 42, pp. 999-1009.

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Boron concentrations in carbonaceous chondrites*

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Abstract—We have analyzed B in carbonaceous chondrites in order to clarify a factor of 100 difference between the solar system B abundance derived from the solar photosphere and that inferred from previous meteorite data. Consistent results were obtained from two instrumental methods for B analysis: (a) counting of the high energy betas from ^{12}B produced by the $^{11}B(d,p)$ reaction, and (b) measurement of particle track densities from $^{10}B(n,\alpha)^7Li$ in a plastic track detector affixed to a homogenized meteorite sample. Contamination is a major problem in B analyses, but extensive testing showed that our results were not seriously affected. Our B concentrations are typically 1–2 ppm and are a factor of 2–6 lower than previous carbonaceous chondrite measurements. Our data for the C1 chondrites Ivuna and Orgueil would indicate a solar system B/Si atomic abundance ratio of 58×10^{-6}, but this is still a factor of 2–10 higher than the photospheric estimates. It may be that B is depleted in the sun by thermonuclear processes; however, the similarity of photospheric and meteoritic Be abundances is a problem for this point of view. Alternatively, B may be enhanced in carbonaceous chondrites, but this would make B a cosmochemically unique element. A mm-sized $(Fe,Mn,Mg)CO_3$ crystal from Orgueil shows no B enrichment. We find $^{10}B \leq 10^{16}$ atoms/g in two Allende fine-grained inclusions suggesting that B is not a refractory element under solar nebula conditions. This ^{10}B limit, when taken as a limit on ^{10}Be when the inclusion formed, puts constraints on the possibility of a solar system synthesis of ^{26}Al. For a proton spectrum of E^{-a}, a must be ≥ 3 if a solar gas is irradiated or a ≥ 1.5 if dust of solar composition is irradiated.

INTRODUCTION

CONSIDERABLE controversy has arisen over the large discrepancy between solar system B abundances derived from meteorites and those from the solar photosphere. A variety of astrophysical measurements give low abundances: (a) the solar photospheric upper limit ($B/Si \leq 0.4 \times 10^{-5}$) of HALL and ENGVÖLD (1975), (b) the more recent photospheric value ($B/Si = 0.9 \times 10^{-5}$) of KOHL *et al.* (1977), (c) measurements for other stars (BOESGAARD *et al.*, 1974), and (d) measurements of B in the interstellar medium (MORTON *et al.*, 1974). These astrophysical abundances are also consistent with the B abundance previously adopted for calculations of light element nucleosynthesis by galactic cosmic rays (see e.g. REEVES *et al.*, 1970; MENEGUZZI *et al.*, 1971). However, the B abundance of $B/Si = 30 \times 10^{-5}$ proposed by CAMERON *et al.* (1973), based on B concentrations in carbonaceous chondrites measured by QUIJANO-RICO and WÄNKE (1969), is considerably higher than any of the above values. Consequently, the above astrophysical papers concluded that boron is enhanced in carbonaceous chondrites and that these meteorites do not provide a valid solar system abundance for this element. With the exception of Li (NICHIPORUK and MOORE, 1970; GREVESSE, 1968) and possibly Hg (REED, 1971), no other cases of element enrichment in carbonaceous chondrites compared to the solar photosphere are known. The solar depletion of Li can be explained by thermonuclear destruction, but a similar explanation for B has not seemed possible because Be should be destroyed at lower temperatures than B, and there appears to be a reasonable correspondence between photospheric and meteoritic Be abundances. This situation prompted us to reinvestigate the abundance of B in carbonaceous chondrites. A summary of our results and their implications for light element nucleosynthesis has already been published (WELLER *et al.*, 1977); this paper provides more complete documentation of our techniques and data and explores the implications of the results for planetary science.

EXPERIMENTAL

Because of the complexity of B chemistry and the relative inertness of B to conventional neutron activation techniques, the development of modern methods of B analysis for geochemical samples has been slower than that for other elements. In this work, we have used the nuclear reactions $^{11}B(d,p)^{12}B$ and $^{10}B(n,\alpha)^7Li$ to determine the boron concentrations in carbonaceous chondrites. Because of the importance of these samples, we have pushed our techniques to the ~1 ppm level. At these concentrations, contamination of the samples became a major concern. However, for samples having more than ~10 ppm B, our techniques allow convenient, routine B analysis without the elaborate precautions and testing for contamination which were necessary for this work.

^{12}B *Activation analysis*

Most of our measurements were made using the reaction $^{11}B(d,p)^{12}B$. This reaction is particularly suitable for low-level boron analyses for several reasons. The cross section is large, ranging between 0.2 and 0.6 barns for deuteron energies between 1 and 2.8 MeV (KAVANAGH and BARNES, 1958). Also, the beta-decay of ^{12}B is almost exclusively to the ground state of ^{12}C with a maximum decay energy of 13.4 MeV and a half-life of 20.4 msec. This unique decay signature enabled us to determine the yield of betas from

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* Caltech Contribution No. 2983.

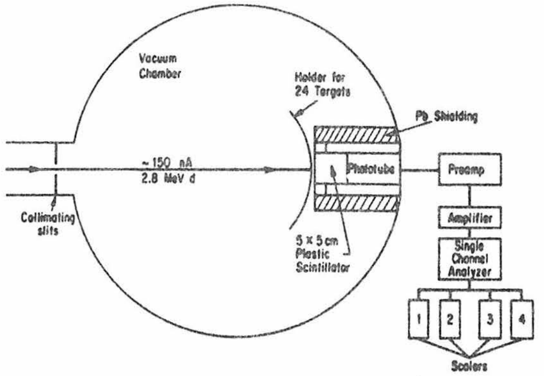

Fig. 1. Schematic experimental arrangement for ^{12}B activation measurement. To maximize counting efficiency the target holder is mounted off-center and the plastics scintillator is mounted on a re-entrant, Pb-shielded tube in the scattering chamber. To minimize background only the higher energy portion of the beta spectrum is allowed to pass the single channel analyzer. The beam is pulsed and counts measured sequentially in each of the four scalers according to the counting cycle shown in Fig. 2.

^{12}B despite significant background from other reactions.

Our experimental arrangement is shown schematically in Fig. 1. One of the 24 targets in the holder was bombarded with about 150 nA of 2.8 MeV deuterons, confined within a beam spot size of about 3 × 3 mm. The maximum beam current was limited by the outgassing of the targets. The bombarding energy of 2.8 MeV was chosen to minimize the effects of background reactions. Deuterons with this energy penetrate about 50 μm into our samples. However, the coulomb barrier between ^{11}B and the deuteron produces a low energy cut-off for the (d,p) reaction at ~0.5 MeV; thus, the actual sample thickness analyzed was about 35 μm, out of a total sample thickness of 0.5–1 mm. A 5 × 5 cm Pilot B plastics scintillator, located 6 mm behind the target, detected the betas, which had already lost an average of 2.5 MeV in energy in the sample and in the material between the target and the detector. The single channel analyzer (SCA) had an energy window corresponding to an energy loss in the detector of 3.5–9.5 MeV. This means that most of the betas accepted by the SCA had initial energies between 6 and 12 MeV. Pulses from the SCA were then fed into four scalers which were gated to count in consecutive time intervals.

The counting sequence is shown in Fig. 2a. The beam was on the target for 30 msec. Because there was a delay of several msec between the signal for the beam to be chopped and the actual chopping of the beam, a 15 msec delay was introduced into the counting cycle to insure that the beam was not on the target during the first counting period. After this delay, four scalers were gated, in turn, for 15 msec counting periods. This cycle was repeated between 20,000 and 100,000 times, depending on the target and the beam current. Assuming constant background, the difference between any two scaler readings was proportional to the concentration of ^{11}B.

There were two important background reactions in this experiment which caused a rather small signal to background ratio (roughly 1/20). (1) Although the Li content of chondrites is small (1–2 ppm), the $^{7}Li(d,p)^{8}Li$ reaction is similar to the $^{11}B(d,p)^{12}B$ reaction. The cross section is large and the 13.1 MeV beta-decay energy of ^{8}Li made it impossible to discriminate between the ^{8}Li and ^{12}B spectra on the basis of energy. The yield of betas from ^{8}Li was approx. equal to that from ^{12}B for a target containing Li/B = 1.5 by weight; however, the large difference in half-life (850 msec for ^{8}Li vs 20 msec for ^{12}B) enabled counts from ^{12}B to be distinguished from those due to ^{8}Li; (2) analysis of the decay rate of the induced radioactivity showed that most of the background for a meteorite sample was due to the beta decay of ^{16}N, produced in the reaction $^{18}O(d,\alpha)^{16}N$. This reaction does not have a large cross section, but oxygen is a major target constituent. ^{16}N decays primarily to excited states in ^{16}O, emitting

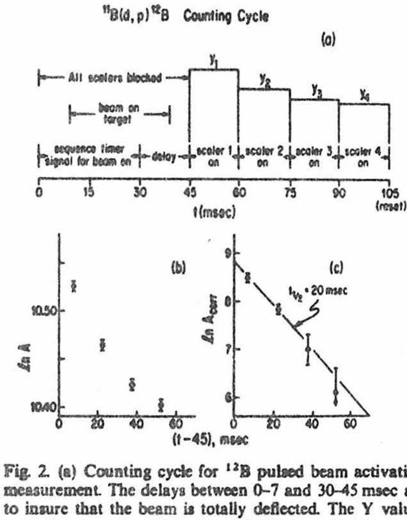

Fig. 2. (a) Counting cycle for ^{12}B pulsed beam activation measurement. The delays between 0–7 and 30–45 msec are to insure that the beam is totally deflected. The Y values indicate the number of counts in the four successive counting intervals after beam deflection. The decrease from Y_1 to Y_4 schematically indicates the ^{12}B decay. (b) Example of an uncorrected decay curve for a meteorite (Ivuna) sample. Decay time is measured after the start of interval Y_1 (Fig. 2a). (c) Background corrected decay curve of data from Fig. 2b. The corrected activity follows the 20 msec decay of ^{12}B.

low energy betas which were not counted. The high energy gammas from the subsequent decay to the ground state did not contribute significantly to the observed background since plastic scintillators are inefficient detectors for gamma rays. However, betas with a maximum energy of 10.4 MeV are emitted in 26% of the ^{16}N decays. Although the low energy cut-off on the SCA was chosen to minimize the effect of this decay on our final error, these high energy betas accounted for 95% of the meteorite background counts.

Although the half-lives of both ^{8}Li (0.85 sec) and ^{16}N (7.2 sec) are much longer than that of ^{12}B, the background could not be considered constant. Such an assumption would have resulted in an overestimate of the boron concentration by about 20%. With four counting periods, one could, in principle, obtain a ^{12}B yield which properly takes into account the decays of ^{8}Li and ^{16}N. However, for the meteorite samples, only a small error was made by assuming that the background was entirely due to ^{16}N, and that it therefore decayed with a 7.2 sec half-life. The estimated error from this assumption was approximately 2%, compared with 10% from counting statistics alone. For our standard samples, which contained 100–200 times more Li than the meteorites, the background was assumed to decay with an 0.85 sec half-life. Again, this introduced only a small error into our results.

Statistically, the most precise ^{12}B yields were obtained by subtracting the sum of the counts (corrected for background) in the third and fourth counting periods from the sum of the first and second. All of our tabulated B concentrations were based on this procedure. Other differences in the number of counts (e.g. between the first and second periods) were routinely checked and found to be consistent, indicating that the ^{16}N and ^{8}Li background corrections were effective. Figures 2a and 2b are examples of actual meteorite decay curves, both uncorrected and corrected for background.

To obtain the boron concentrations, a comparison was made between the ^{12}B yield from the meteorite and that from the National Bureau of Standards glass SRM 610 which contains 351 ppm B. We have confirmed the SRM 610 concentration by comparing it with Pyrex glass which has a well-controlled and well-known boron concentration. In comparing meteorite yields with those for the NBS glass, a correction was made which took into account the differences in deuteron energy loss between the sample and the standard. (The range of the deuterons, and thus the thickness of material analyzed, is dependent on sample composition.) Corrections for these differences were small ($\lesssim 10\%$). A correction was also necessary for differences in the beta yield due to varying sample thicknesses. Compared to a thin sample, a thick sample degraded more betas below the SCA lower limit and, thus, a smaller fraction of the total spectrum was counted. This correction was typically 30%, but was as large as 100% in some cases. Fortunately, this correction could be determined experimentally from 'absorption' curves using various thicknesses of Pyrex glass. Even though high energy betas were being counted, ionization losses dominated brehmstrahllung as the principal mechanism for energy loss since the absorbing materials were composed primarily of light elements. Thus, negligible error was introduced by assuming that the measured beta absorption curve for Pyrex applied to the meteorite samples as well. The uncertainty in the thickness corrections did not contribute significantly to the total error in B concentration. Finally, to get the total boron content, it was assumed that the ^{11}B/^{10}B ratio in meteorites is the same as the terrestrial ratio.

The estimated error for a single measurement on a sample containing 1 ppm B is ±15%. For samples with a higher boron concentration, the percentage error is smaller since most of the error arose from the counting statistics.

Particle track B Analysis

Boron analyses with the ^{10}B(n,α) reaction were made using the techniques described in Furst *et al.* (1976). A sheet of cellulose nitrate was placed in flush contact with an homogenized meteorite pellet and exposed to a fluence of about 5×10^{12} neutrons/cm^2 in the thermal column of the UCLA reactor. Alpha particles and recoil ^{7}Li produced in the sample entered the cellulose nitrate, producing tracks which were revealed by etching for 1–2 hr in approx. 6N NaOH at 35°C. Background corrections for ^{17}O(n,α) and, possibly, ^{14}N(n,p) were made from exposures of back-to-back pieces of cellulose nitrate and were equivalent to about 0.2 ppm B. Boron contents were obtained using the NBS SRM 612 glass as a working standard (Furst et al., 1976). In turn, the SRM 612 glass standards were individually standardized relative to the SRM 610 glass. Individual standardization was necessary because the B concentrations in SRM 612 were somewhat variable, as was also observed by Carpenter (1972). The total range for about 15 pieces of this glass was 35–45 ppm. In contrast, the B contents of different pieces of the SRM 610 glass were uniform to within ±3%. Corrections for alpha tracks from ^{6}Li(n,α) were made using experimental B/Li relative track production rates from Furst *et al.* (1976) and meteoritic Li concentrations from Nichiporuk and Moore (1970). The corrections were typically 10–20%. Given the apparent homogeneity of Li in meteorites (Nichiporuk and Moore, 1970) and the fact that homogenized samples were used, errors from this correction should be unimportant.

A cross-comparison of B concentrations obtained from beta-counting and track counting was made using pieces of a glass containing about 90 ppm B which was prepared for us by the Corning Glass Company. Agreement to within about 5% was obtained.

Sample preparation

Because of the serious contamination problems encountered in this experiment, meteorite samples for analysis were selected and prepared with great care. All operations were carried out with pre-cleaned tools in a restricted use laboratory which has a charcoal filtered air supply system. Totally interior samples were obtained by chipping, sawing, or, in the case of C1 meteorites, by carefully removing the external portions of the samples with tweezers. Chipped or sawed surfaces were scraped with coarse-grit silicon–carbide paper to remove any smeared metal, and the scraped surfaces were then rinsed with high-purity methanol. Surfaces cleaned in this way could be directly analyzed by beta-counting. However, the self-absorption corrections were large and very uncertain for irregularly shaped chips; consequently, we report data only for slices with plane parallel faces. Glass standards for beta-counting were similarly prepared, using different equipment to avoid cross-contamination. For track-counting analyses and for the C1 meteorite samples (because of their friability), meteorite specimens (0.2–0.5 g) were powdered in a ball mill using a ball and container made from either hardened steel or plastic. The powders were then pressed into 5 mm diameter pellets (20–50 mg) using a stainless steel die. Based on tests with Allende, grinding times of about 90 sec with the steel ball produced powders that would pass through a 37 μm sieve. Much shorter (5–10 sec) grinding times with the plastic ball were sufficient for the C1 chondrites and for graphite control samples. No binder was necessary to obtain coherent pellets, although those from Allende were fragile. Glass standards for track counting were mounted in epoxy and polished. These standards were recleaned before each use by light polish with 0.3 μm Al$_2$O$_3$. For general reference, Table 1 shows the B concentrations obtained by track analysis of typical laboratory materials, including those used in sample preparation.

Table 1. Boron contents of laboratory materials, ppm

Stainless steel labware	
pellet press cylinder	14
pellet press ring (440 C)	6
mortar (440 C)	4
ball mill container	1.5
Tantalum	≤0.3*
Tungsten carbide ball mill container	10,000
Hardened steel ball mill container	45
Sandpaper (Busheler, 600 grit)	3-5
Agate	
mortar (Fisher)	36
mortar (VanWaters-Rogers)	24
ball mill container (Spex)	48
Sapphire ball mill container	84
Al_2O_3 0.3 micron powder (Bueheler)	1
Epoxy (Techkits E7)	≤0.3
Powder paper (Glassine, Lilly)	2-7
Transparent plastics	≤0.3
Filter paper (Whatman HP2)	3
Adhesive tape (Scotch Magic) (adhesive side)	~30

* Analysis by ^{12}B activation; all other analyses by tracks.

Contamination effects

An important point to establish was that our data were not seriously affected by contamination. Since both of our techniques were instrumental, it was possible to re-analyze a given sample. However, when this was done, the measured B concentration always increased with each re-irradiation, sometimes by as much as a factor of two to three. Even elaborate precautions in storage of the samples between irradiations failed to prevent this increase. Consequently, all our results are based on first analyses of freshly prepared samples.

It was also necessary to establish that the results from first irradiations were not compromised by contamination. In this regard, the ^{12}B activation technique had an advantage in that the amount of handling of the sample prior to analysis was minimal and the time between preparation of a clean sample surface and analysis could be made relatively short. Furthermore, the ^{12}B activation analyses were less sensitive to surface contamination since the thickness of sample analyzed (35 μm) with this technique was larger than for the track analyses (5 μm). Most of the data presented are, therefore, based on ^{12}B activation.

The following tests indicate that our B concentrations are not merely upper limits because of contamination. Recall that the important question is whether B/Si = 30×10^{-5} or B/Si = 0.4×10^{-5}. (1) Low B control samples were prepared and analyzed in parallel with each batch of meteorites, and these samples consistently yielded much lower B concentrations than the meteorites. If contamination was introduced in any way during sample preparation or analysis, it would affect both meteorite and control samples. (2) The time between sample preparation and analysis as well as the total exposure time of the sample to the laboratory atmosphere were deliberately varied. These tests showed that contamination was not significant for our standard procedures. (3) A fresh surface of a Murchison slice was prepared under vacuum and then analyzed without atmospheric exposure. This sample gave results which were consistent with those obtained from Murchison samples prepared in the standard way. (4) For most 'first irradiation' analyses, track counting showed that the B was uniformly distributed on a 0.2 mm scale as expected for a homogenized meteorite sample, whereas badly contaminated samples usually showed a highly non-uniform B distribution.

We now give a detailed presentation of these test results.

(1) A sample of reactor-grade graphite (nominally 0.4 ppm B, according to the manufacturer's specifications) was prepared and analyzed along with meteorite samples during each ^{12}B activation irradiation. The mechanical and surface properties of graphite made it a reasonable choice for a control sample, particularly for comparison with sawed meteorite surfaces. Individual analyses ranged from 0.1 to 0.4 ppm with the standard deviation of a typical analysis being about 0.15 ppm. Thus, within errors we obtained 0.25 ppm on all the graphite control samples. This sets an upper limit for the amount of contamination which is, at most, 25% of the uncorrected data. Since a sample of the Murchison meteorite was present in most ^{12}B activation irradiations, it was also possible to check for any correlation between the graphite and Murchison data which would have suggested a variable amount of contamination. No such correlation was observed. No differences between sawed slices and pellets were seen. Thus, no correction for a 'crushing blank' was applied to the meteorite results obtained from pellet samples.

For the particle track B analyses, SiO_2 glass and single crystal calcite (Hilton Deposit, San Diego County, CA) were chosen as the control samples because they appeared to have lower B contents than the graphite. This made it possible to check the amount of contamination introduced in the pellet-making process. Uncrushed calcite samples (i.e. fresh cleavage faces) produced track densities which were indistinguishable from the background track density for the cellulose nitrate, indicating a B content ≤0.2 ppm. A crushed calcite pellet gave 0.6 ± 0.1 ppm B and this 'crushing blank' correction was applied to the track data. This is higher than the blank indicated by comparison of results from crushed and uncrushed samples in the ^{12}B activation technique, and probably reflects the necessity to use a hardened steel ball mill container (rather than plastics) and to use longer grinding times for the samples (particularly Allende) used for track analysis. Some batches of SiO_2 glass had high (up to ~3 ppm) B contents and meteorite analyses which relied on this glass as a control sample have not been accepted due to the absence of an adequate control sample.

(2) We found that we could not normally store samples for periods of a few weeks between irradiations without observing an increase in B content. Consequently, it was necessary to demonstrate that our samples did not become contaminated in the time between preparation and the first analysis, i.e. to have some estimate of the rate of growth of surface contamination. These experiments, which were done using ^{12}B activation, also demonstrated that the actual meteorite samples did not 'adsorb' B contamination more rapidly than our control samples. Two times required investigation: (a) the storage time between sample preparation and pump-down of the irradiation vacuum chamber, and (b) the exposure time of a fresh sample surface to the laboratory atmosphere. Typical times for (a) and (b) were 10–20 hr and 15–20 min, respectively. A series of slices of Murchison, Murray, Allende and graphite was prepared in which the times involved for (a) and (b) were deliberately varied. Figures 3 and 4 give the results of these tests for times (a) and (b) respectively. Only the graphite sample which was stored for 64 hr showed any indication of a significant increase in B concentration. There was a general scatter in our analyses of meteorite slices between 1 and 2 ppm which is marginally significant and which we ascribe to sampling. Considering this scatter, there was no significant increase in B concentration with increased laboratory exposure time, except possibly for the Murray sample in Fig. 4 which had an extended exposure.

For track analysis, the time between sample preparation and irradiation ranged from 2 to 13 days. Allende pellets stored for 12–13 days showed an increase in B content of ~0.8 ppm compared with aliquots of the same powdered sample irradiated within 5 days of preparation. However, for times less than 5 days, there was no correlation of the B content of Allende samples with the time

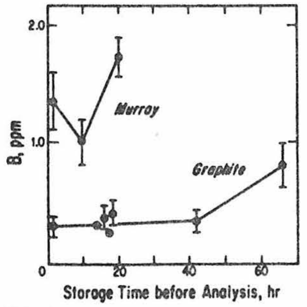

Fig. 3. This figure shows the results of tests to see if B concentrations were dependent on sample storage time (i.e. the time between sample preparation and analysis) due to the influence of airborne contamination. Typical storage histories for ^{12}B measurements were 10–20 hr in a desiccator. No significant increases are observed except for the graphite control sample at 64 hr. Additional data suggest that even this may be atypical.

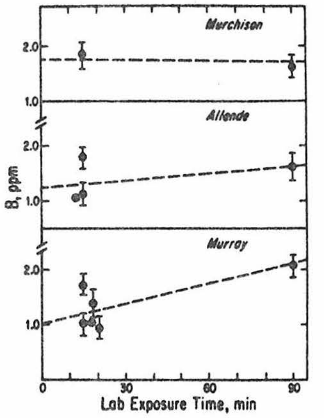

Fig. 4. This figure shows the results of tests to see if B concentrations depended on the exposure time of the sample to laboratory air due to airborne contamination. Typical exposure times for ^{12}B measurements were 20 min. No significant increases were observed except possibly for the Murray point at 90 min.

between sample preparation and irradiation. Specifically, two pairs of aliquots which were analyzed 2 and 5 days after preparation agreed within errors (±0.2 ppm). A contamination rate of 0.1 ppm/day is consistent with the track results and is also compatible with the ^{12}B activation data for graphite (Fig. 3), although a lower rate of contamination is expected for ^{12}B activation since it is less sensitive to surface contamination. It is likely that the apparent contamination of the graphite sample after 64 hr of storage was atypical or possibly reflected a greater 'adsorbtivity' of B contamination on graphite surfaces than on meteorites.

We interpret these tests as showing that negligible B contamination was acquired during the normal exposure and storage of freshly prepared samples prior to analysis.

(3) A slice of Murchison was analyzed in the normal manner by ^{12}B activation. Following the initial analysis, a fresh surface was scraped on the meteorite without breaking the vacuum and the analysis was repeated. This procedure was then repeated a second time. In both cases, enough sample was removed to ensure that a fresh surface was being analyzed. The results of these three analyses were 1.36, 1.41 and 1.38 ppm, respectively, i.e. the fresh surfaces prepared under vacuum gave the same results as the initial surface prepared in the standard way. This test is further confirmation that our sample preparation and handling techniques did not introduce appreciable contamination. It also shows that pump-down of the vacuum system for the ^{12}B analysis was not a source of contamination. This could not be established from our other tests.

(4) The particle track densities for a homogenized meteorite pellet were typically 2–3 × 10^5/cm^2. Thus, it was possible to check for variability at the 10% counting statistics level on areas of roughly 200 × 200 μm. Preliminary experiments with 14 polished meteorite sections showed that B was not highly localized. The absence of track clusters sets a limit of about 5 × 10^3 ppm·μm for the product of the B concentration and the dimensions of the grain in which it is concentrated. Therefore, a uniform track density was expected for a homogenized sample. However, it is likely that a contaminated sample would have a non-uniform distribution of contamination B and samples showing high B concentrations exhibited highly variable track densities. On the other hand, many of the samples yielding low B concentrations had track densities which agreed within 10% counting statistics over mm-sized areas. We have, therefore, rejected as contaminated all powdered, homogenized samples which showed heterogeneous B distributions. It should be emphasized that the samples rejected did not show 'localized' inhomogeneities (i.e. clustering of tracks into stars) such as could be expected if B were concentrated in small particles which escaped our homogenization process. Instead, the rejected samples tended to show large (mm-sized) areas of both high and low track density. For reasons that are not understood, the high track densities occurred preferentially around the circumference of the pellet in many cases.

Based on the above tests we conclude that contamination is not a serious source of error in our results. The following discussion summarizes what is known (and conjectured) about the origin of the contamination.

There was an apparent difference in the contamination rate of samples before and after irradiation which we believe is significant, although this cannot be conclusively proved. Preferential surface contamination for radiation-damaged surfaces is moderately well documented for F (GOLDBERG *et al.*, 1975) and H (LEICH *et al.*, 1974). The primary evidence for the 'radiation-induced-contamination' hypothesis came from ^{12}B activation measurements in which a sample was measured, exposed to air and then remeasured under vacuum. This experiment was done on six meteorite and two graphite samples in three different irradiations with atmospheric exposure times between measurements varying from 0.5 to 12 hr. In two of the three irradiations, the B concentrations for all samples increased by amounts ranging from two to ten standard deviations. In the third irradiation, two Murchison samples showed no significant increase. Our interpretation is that radiation damage was an important factor governing the contamination rate, but that other factors (humidity?) existed as well. An alternative explanation for these results is that the bulk of the surface-adsorbed gases were pumped off in the vacuum exposure and then B contamination occurred immediately upon re-exposure to the atmosphere, regardless of whether the sample had been irradiated or not. We do not believe this interpretation because surface-adsorbed gases would not be removed in the 10^{-5}–10^{-6} torr vacuum used in the ^{12}B activation analyses, and rapid contamination also occurred after track analyses which involved no vacuum. Nevertheless, experiments were performed to test this interpretation. Homogenized meteorite pellets were analyzed by ^{12}B activation, but analysis of one pellet was done only after the vacuum chamber had been vented and re-evacuated. In two experiments, the pellets analyzed after venting showed B concentrations which were one and three standard deviations higher than those obtained from pellets analyzed before venting. However, for the samples which had been irradiated before venting, the B concentrations after venting were even higher. These results support the radiation-damage hypothesis, but still permit some contamination (up to ~0.5 ppm) of the samples which were pumped on and then exposed to air before analysis. However, only a few of our samples had this pressure history and they did not show systematically higher B contents than samples which were pumped on only once prior to analysis.

The source of the contamination B is not known. It is clearly airborne; however, limits on the size of the contaminating particles can be set by the absence of clusters of tracks (stars) which would be expected for contamination by B-rich particles. This observation sets an upper limit of $\lesssim 10^9$ atoms of B per contaminant particle. The most likely form of such small contaminant particles is aerosol droplets, e.g. sub-micron H_3BO_3 solutions. Using a typical measured Na content for Pasadena air (interpreted as originating from sea spray) and assuming no Na/B fractionation in the aerosol relative to sea-water, an airborne B concentration of $\sim 3 \times 10^{13}$ atoms B/m^3 of air is estimated. This estimate may be low because B is probably enriched relative to Na in the aerosol. To account for our contamination rate, the amount of B in 0.04 m^3 of air would have to be deposited on each cm^2 of our samples daily. This is a high rate, but it cannot be ruled out.

In summary, our criteria for accepting a given B analysis as contamination-free were (1) it was the first analysis of that surface, (2) we obtained low results for control samples during the same irradiation (i.e. apparent blanks, 30% or less), (3) the time between preparation of the fresh sample surface and irradiation was less than 5 days, (4) for track analyses, the track density was uniform within counting statistics, (5) for ^{12}B activation analyses, the sample had plane parallel faces, and (6) powdered samples were prepared in our laboratory.

General comments on instrumental B *analysis*

In this work two techniques for B analysis were utilized which are 'instrumental' in the sense that the sample is not chemically destroyed by the analysis. The method of GLADNEY *et al.* (1976), based on prompt gamma rays from the reaction $^{10}B(n,\alpha)^7Li^*$, is also of this type. For our techniques, the samples must be physically destroyed. For many ^{12}B activation measurements, the sample can simply be sawed into plane parallel slices. However, for coarse-grained rocks or samples in which B is very heterogeneously distributed and for track-counting analyses, samples should be powdered and pressed into pellets. Sample requirements are about 500 mg in order to cut a 150 mg slice or 50 mg for a pellet.

For track analysis, the analysis time required per sample is essentially independent of concentration. At 10 ppm B levels, the counting time using the ^{12}B activation technique would be about 30 min for ±5% counting statistics, given our experimental conditions. The accelerator and instrumentation required for ^{12}B activation can be found in essentially all nuclear physics laboratories. Access to a nuclear reactor is required for track analysis. Also, if exposures are not carried out in a thermal column, background levels will be much higher due to recoil tracks produced by fast neutrons.

The method of Gladney *et al.* has the advantage in that, unlike ours, a bulk sample is analyzed rather than a surface. Therefore, it should be much less sensitive to surface contamination. However, a rather specialized reactor facility is required for counting prompt gammas from neutron-induced reactions. Also, it is conceivable that contamination problems would be less severe in another location, since our laboratory is located between the ocean and deserts containing extensive borate deposits.

RESULTS

Our detailed results, on a sample-by-sample basis, are presented in Fig. 5. Typical errors for both techniques are ±0.2 ppm.

Duplicate bombardments of the same sample using the ^{12}B activation technique routinely gave results that agreed within statistical errors, provided that the vacuum chamber was not vented between irradiations (see above discussion). This reproducibility shows that our results are not anomalously low due to loss of volatile B compounds by beam heating.

The homogenized pellets provide another test of reproducibility. Analyses of different pellets, prepared

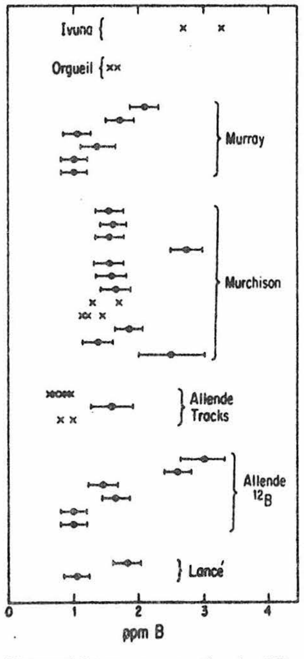

Fig. 5. Measured boron concentration in different pieces of six carbonaceous chondrites. Xs indicate measurements of homogenized aliquots of a single specimen. Errors are not indicated for these samples, but they are approximately the same as the errors for other samples having equivalent B concentration. Reproducibility between aliquots is good. The relatively small spread between different specimens of the same meteorite indicates that our results are not significantly influenced by sampling errors.

from aliquots of a given sample always agreed for both techniques, as indicated by the Xs for a given meteorite sample in Fig. 5. In particular, five track analyses on aliquots of Allende clustered tightly around 0.8 ppm, as indicated in the figure.

Some scatter is expected for different samples of the same meteorite, given the relatively small volume of material analyzed and the petrographic variability of carbonaceous chondrites; however, the results for the C2 meteorites, Murray and Murchison, are remarkably consistent. The Allende results show more scatter with values for individual samples ranging from 0.8 to 3 ppm. The Allende samples showing the largest B concentrations (between 2 and 3 ppm) represent samples with larger absorption corrections but, otherwise, these analyses meet our criteria for acceptability and have not been excluded.

The Allende analyses from track and beta counting measurements agree satisfactorily. Giving each sample equal weight, the Allende track data average to 1.1 ppm, whereas the ^{12}B activation results yield 1.8 ppm. However, this latter average is highly influenced by two samples with 2–3 ppm. The track analyses were carried out in air at room temperature. Thus, the overall consistency of the Allende track and ^{12}B activation results also indicates that our results are not anomalously low because of volatilization of B compounds during the ^{12}B activation measurements.

Table 2 gives the results of all track analyses which met only the criterion that they were the first analysis of a given sample but which were excluded from Fig. 5 because they failed to meet the other criteria given above. Included in this table are results from powders prepared by Kaushal and Wetherill (1970) for Rb–Sr analyses and which had been stored for many years. The results of total rock Rb–Sr analyses of many such powders by Kaushal and Wetherill do not lie on a 4.5×10^9 yr reference meteorite Rb–Sr isochron, suggestive of contamination. No corrections have been applied to the data in Table 2. These results are given only for completeness, and the justifications for their rejection are strong. Nevertheless, the majority of the analyses, particularly for Allende, are in reasonable accord with the accepted analyses in Fig. 5.

Table 2. Rejected B analyses*

Meteorite	B, ppm
Ivuna	5.6
Orgueil	1.8
Essebi	9.1
Haripura	1.0
Mighei	10.4
Murchison	5, 3, 8 5, 4, 2 0.5, 0.9, 4
Allende	5.3, 1.8, 1.5 0.5, 2.5

* Results tabulated meet only the criterion that they are the first analyses of these samples. These analyses fail at least one of the other criteria listed in the text.

Table 3. Average B concentrations in carbonaceous chondrites

Type	Meteorite	No. Samples Analyzed	Average B ppm	Atomic B/Si (10^{-6})
C1	Ivuna	1	3.0	77
	Orgueil	1	1.6	40
C2	Murray	6	1.4	29
	Murchison	12	1.7	35
C3-4	Allende	9	1.8	23
	Lancé	2	1.5	19

All ^{12}B activation results obtained after 26 August 1976 have been accepted. Murchison and Allende analyses prior to this date were made on samples of irregular thickness which resulted in very large uncertainties. These results were not tabulated because of the large errors. They are compatible with our later data, although there is some tendency for the Murchison values to be somewhat higher (2–3 ppm) than those obtained later.

Table 3 gives the average B concentrations for the meteorites studied. Clearly, different ways of averaging the individual analyses would produce somewhat different results. For example, we have included all samples in our averages, although omitting the two highest values for Murchison and Allende (Fig. 5) would have been permitted statistically. If the high results are excluded, the resulting B concentrations for these meteorites become 1.5 and 1.2 ppm, respectively. Alternatively, if each aliquot of a homogenized specimen is regarded as an independent sample (this procedure can be justified given the small amount of material analyzed), no significant change results for Murchison, but the Allende average would be 1.3 ppm. The results in Table 3 differ slightly, but not significantly, from those given in Weller *et al.* (1977).

The final column in Table 3 gives the atomic B abundances, relative to Si = 10^6. We have used Si contents for individual meteorites when possible; when these were unavailable we used Si contents for the various C meteorite subgroups (Moore, 1971). The progression of B/Si between the C3/C2/C1 meteorites in Table 3 is close to the 0.4/0.5/1 progression normally observed (Larimer and Anders, 1967; Anders *et al.*, 1976) between the different types of C meteorites for many other elements.

Based on the B results of Quijano-Rico and Wänke (1969) for 3 C meteorites (Murray, Lancé and Vigarano), we had anticipated B contents of 6–20 ppm for the meteorites analyzed. Our results are much lower. For Murray, we found a B concentration of 1.4 ppm while Quijano-Rico and Wänke obtained 9.4 ppm. For Lancé, our result was 1.5 ppm compared to their value of 6.4 ppm. The analyses of Harder (1961) and Mills (1968) indicated 5–7 ppm for C1 chondrites; we found only 1.6–3 ppm. These differences may represent the use of contaminated samples in the previous studies. It is unlikely that the differences between our results and those of previous workers can be ascribed to sampling. The number of samples of each meteorite analyzed by us is indicated in Table 3. In the cases of Murchison and Allende, the samples were taken from two different specimens, each supplied to us from a different source. It should be emphasized that the chemical separation and analysis procedures used by Quijano-Rico and Wänke produced low blanks and, ironically, have superior sensitivity and precision to those we have used. We have no reason to question the results of these workers for the ordinary and enstatite chondrites where, probably, larger and better quality samples were available for analysis. Nevertheless, it would be desirable to have additional measurements on ordinary chondrites using a technique which is not as sensitive to surface contamination as ours and which has better precision at the sub-ppm level. The neutron-induced prompt gamma ray analysis technique of GLADNEY *et al.* (1976) appears promising, and the initial results of these workers for carbonaceous chondrites appear compatible with ours.

DISCUSSION

Adopting the argument that C1 meteorites provide the best estimate of the average chemical composition of the solar system (ANDERS, 1971; HOLWEGER, 1977), we propose a solar system B/Si ratio of 4.5×10^{-5}. This is roughly a factor of six lower than the abundance proposed by CAMERON *et al.* (1973) based on the older carbonaceous chondrite analyses; however, it is a factor of five higher than that which would be inferred from the solar photospheric B/H of KOHL *et al.* (1977) and at least ten times higher than the photospheric upper limit of HALL and ENGVÖLD (1975). Clearly, the photospheric results are not internally consistent. However, if the result of KOHL *et al.* is accepted arbitrarily, the meteoritic and photospheric B abundances can be made to approach each other within about a factor of two when the stated uncertainties are considered. (See WELLER *et al.*, 1977, for additional discussion).

Nevertheless, the possibility of a B overabundance in carbonaceous chondrites by a factor of at least two must be seriously considered. One possibility is that B in the sun has been depleted by thermonuclear processes. However, a large Be depletion in the sun, compared to meteorites, might have been expected. (See WELLER *et al.*, 1977, for additional discussion). Alternatively, B may have been enhanced in C1 chondrites by cosmochemical processes. If so, this would be of considerable importance because it may be a unique property of B, which in turn would be a significant constraint on the enhancement mechanism.

In general, we prefer to await additional studies of photospheric B and Be abundances before speculating about the causes of a possible B overabundance in carbonaceous chondrites. However, a key question in this discussion is the actual distribution of B in the meteorites. This can be investigated by alpha track mapping techniques (i.e. radiography) using polished sections. We have not pursued such investigations in great detail because of interference from alpha particles produced by $^{6}\text{Li}(n,\alpha)^{3}\text{H}$ (i.e. on any given spot, we can't tell *a priori* whether ^{6}Li or ^{10}B alpha particles produced the observed tracks) and because of our sensitivity to surface contamination. Nevertheless, several sections of carbonaceous chondrites were studied and no localizations of the induced alpha tracks were observed. The strongest conclusions are possible from one Lancé and two Allende sections which were particularly well-polished and which, based on random counting, yielded 1–2 ppm B, indicating that they were relatively uncontaminated. Chondrules and large sulfide grains had low B contents, indicating that, as expected from the calculations of CAMERON *et al.* (1973), B is not behaving as a refractory or chalcophile element under meteoritic conditions.

During the sampling of our Orgueil specimen, a long (~1 mm), transparent (but rust-stained) euhedral crystal was discovered. It fractured during handling, but ~300 μm fragments were recovered for study. Microprobe analysis (in wt %: MnO = 7.4; FeO = 18.5; CaO = 0.66; MgO = 27.0; Na_2O = <0.1) indicates an Fe–Mg–Mn carbonate. Recasting the analysis in terms of carbonate components and assuming FeCO_3 results in a total sum of 99%. If $\text{Fe}_2(\text{CO}_3)_3$ is assumed, the analyses sum to 107%, supporting the assumption of Fe^{2+}. This discovery allowed us to check whether B was highly concentrated in carbonates. Because carbonate minerals are an anomalous feature of C1 chondrites, such an enhancement would have perhaps explained a B overabundance. However, the carbonate contained less than 2 ppm B, giving no support to this possible enrichment mechanism.

The Allende sections used for the alpha track radiography contained Ca-Al-rich inclusions which, based on morphology and texture, appeared to be the 'fine-grained' type (GROSSMAN and GANAPATHY, 1976). The measured track density over the inclusions could be accounted for by ~3 ppm Li which is two to three times higher than the Li content of a single inclusion measured by DREIBUS *et al.* (1977). However, given the variability in trace element abundances in Allende white inclusions, it is possible that all tracks could be produced from Li and that B is highly depleted. Alternatively, even if Li were anomalously absent from our inclusions, the resulting B upper limit is only 0.5 ppm. Thus, we also conclude that B is not enhanced in Allende inclusions, even the fine-grained type which show relatively high alkali and halogen contents. Calculations discussed by CAMERON *et al.* (1973) indicate that B should be relatively volatile under solar nebula conditions. Further, if Li were behaving like most other refractory trace elements, an abundance many times its chondritic value should have been measured (GANAPATHY and GROSSMAN,

Table 4. Production ratios of ^{10}B, ^{10}Be and ^{26}Al for a solar system irradiation with proton flux $\sim E^{-a}$*

	Solar gas irradiation		"dust" irradiation	
a	$(^{10}B+^{10}Be)/^{26}Al$	$^{10}Be/^{26}Al$	$(^{10}B+^{10}Be)/^{26}Al$	$^{10}Be/^{26}Al$
1.5	8.8	3.8×10^{-1}	4.4×10^{-1}	1.7×10^{-2}
2	3.8	1.4×10^{-1}	3.2×10^{-1}	6.1×10^{-3}
3	9.1×10^{-1}	2.0×10^{-2}	5.6×10^{-2}	9.7×10^{-4}
4	1.8×10^{-1}	2.6×10^{-3}	1.0×10^{-2}	1.4×10^{-4}
5	2.0×10^{-2}	3.3×10^{-4}	1.5×10^{-3}	1.6×10^{-5}

* Cross sections used in these calculations were obtained from: ROCHE *et al.* (1976), DAVIDS *et al.* (1970), LAUMER *et al.* (1973), EPHERRE (1972), YIOU *et al.* (1969), YIOU *et al.* (1968), MATHEWS (1977), KING *et al.* (1977), BODANSKY *et al.* (1975), JACOBS *et al.* (1974), FONTES *et al.* (1971), LESTRINGUEZ *et al.* (1972), RAISBECK *et al.* (1972), RAISBECK and YIOU (1975), JUNG *et al.* (1970), FURUKAWA *et al.* (1971) and REEVES (1974).

1976). Our results thus confirm the conclusion of DREIBUS *et al.* (1977) that Li was a volatile element for the conditions under which the white inclusions formed.

The above data provide a strong upper limit of $\sim 10^{16}$ atoms/gm for the ^{10}B content of the Allende inclusions studied which sets some constraints on the possible irradiation history of these inclusions by ancient solar particle fluxes. These constraints are important even though they are highly model-dependent in that they depend on the chemical and physical (mixing) history as well as the time interval between exposure and formation (because of the ^{10}Be decay).

The key question is whether the ^{26}Al present in Allende inclusions at the time of their formation (LEE *et al.* 1976, 1977) could have been produced by such an irradiation, as opposed to supernova ^{26}Al synthesis. The ^{26}Al would be formed by nuclear reactions on Al, Si and Mg by protons of $\gtrsim 10$ MeV. Subsequently, the ^{26}Al($t_{1/2} = 0.7 \times 10^6$ yr) would decay to produce the observed ^{26}Mg excesses. To avoid excessively large fluxes we shall assume that the oxygen anomalies (CLAYTON *et al.*, 1973) have a different origin from the ^{26}Al. We also interpret the overall absence of isotopic anomalies in elements other than Mg as indicating that mixing of irradiated and unirradiated material and chemical separation of Allende white inclusion material occurred subsequent to the irradiation. In other words, we consider an *in situ* irradiation of Allende inclusion material to produce ^{26}Al to be implausible.

We have calculated the relative production of ^{10}B, ^{10}Be and ^{26}Al for a model in which the proton flux has a spectral shape of the form E^{-a} where E is proton kinetic energy. It is also necessary to distinguish between irradiations of a gas of solar composition or 'chondritic dust' (i.e. solar composition with most of the H, He, C, N, O and Ne lost). We consider both cases, and Table 4 gives our estimates of the $(^{10}B + ^{10}Be)/^{26}Al$ and $^{10}Be/^{26}Al$ production rates for several values of a. Because C and O are the most important target elements for ^{10}B and ^{10}Be production, the calculated ratios are much less for the dust irradiation case than the gas.

For a Ca-Al-rich inclusion containing about 20% Al (GROSSMAN, 1975) and having $^{26}Al/^{27}Al = 6 \times 10^{-5}$ initially (LEE *et al.*, 1976), our ^{10}B upper limit would correspond to $(^{10}B + ^{10}Be)/^{26}Al \lesssim 3 \times 10^{-2}$ at the time of formation of the inclusion. If condensation occurred shortly after irradiation, and if B and Al were not fractionated, the above limit would require a steep spectrum for the cases of irradiation of either solar gas ($a \geq 5$) or dust ($a \geq 3.5$). However, it is more reasonable to regard B as a volatile element which was depleted in these inclusions; thus, to the extent that the fractionation can be arbitrarily large, our data provide no constraints. However, it is reasonable to assume that Be behaves as a refractory element during nebular condensation processes, and thus that the $^{10}Be/^{26}Al$ ratio would be preserved. In this sense our data do place some limits on the spectral shape if we attribute all of the ^{10}B which we observe to the *in situ* decay of ^{10}Be. As illustrated in Fig. 6, for irradiation of solar gas, we constrain $a \gtrsim 2.5$ and, for dust, $a \gtrsim 1.2$.

We believe that the above constraints are relatively firm. The assumption of no chemical fractionation between Be and Al can be checked by measurements of the $^{9}Be/^{27}Al$ ratio in Allende inclusions. It is noteworthy that useful conclusions could be drawn even when a total ^{10}B measurement was used as an upper limit to the ^{10}Be content. This is very crude, and it is likely that the actual $^{10}Be/^{26}Al$ was one to two orders of magnitude lower than our limit. Clearly, B isotopic measurements on Allende white inclusions are very important. We predict that ^{10}B isotopic anomalies from ^{10}Be decay should be readily discernible and, because of the sensitivity of $^{10}Be/^{26}Al$ to spectral shape, that these can put very significant constraints on a solar system origin for ^{26}Al. Conceivably, the $^{10}Be/^{26}Al$ ratio can also be used to indicate a solar system, as opposed to a supernova, origin for ^{26}Al because it is possible that very contrived supernova models would be required to produce a high $^{10}Be/^{26}Al$ ratio given the high threshold energy (~ 100 MeV) for ^{10}Be production.

The implications of our measurement for light element nucleo-synthesis have been discussed in WELLER

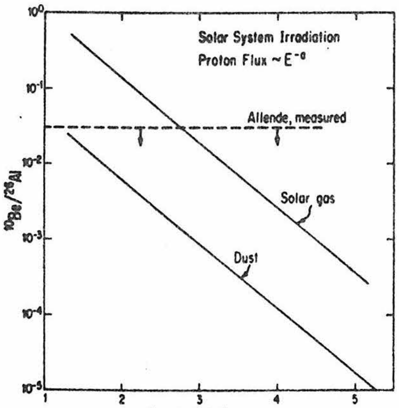

Fig. 6. $^{10}Be/^{26}Al$ production ratio for irradiation of a solar gas or dust of solar composition with a proton spectrum of the form E^{-a}. These ratios may be uncertain by as much as a factor of two due to uncertainties in the production cross sections for both ^{10}Be and ^{26}Al. The $^{10}Be/^{26}Al$ is a steep function of *a* because ^{10}Be is produced only at high energies, whereas ^{26}Al has significant low energy production. The chemical systematics of the Allende Ca-Al-rich inclusions indicate that $^{10}Be/^{26}Al$ should be unfractionated in their formation; thus the calculations can be compared with an experimental upper limit (dotted line) based on taking our measured ^{10}B content as an upper limit to the initial ^{10}Be. Even this crude upper limit puts significant constraints on the production of ^{26}Al through charged-particle bombardment.

et al. (1977). Briefly, we found that the relative meteorite abundances of ^6Li, ^9Be, ^{10}B and ^{11}B could be produced by bombardment of a CNO mixture of solar proportions by protons and alpha particles with a kinetic energy per nucleon spectrum of the form $E^{-1.8}$. New calculations (MATHEWS 1977) using some new cross sections indicate that, while the $^{10}B/^{11}B$ ratio can be reproduced with this spectrum, the calculated $^6Li/^{11}B$ and $^9Be/^{11}B$ ratios are too large by factors of four and two respectively relative to the corresponding meteoritic abundances based on our B data. Steeper spectra are necessary to reproduce these ratios, but these give $^{10}B/^{11}B$ ratios that are too small. Use of the KOHL *et al.* (1977) photospheric B abundance gives a better match to the relative production rates of Mathews than does the meteoritic abundance. It should be noted, however, that experimental cross sections are not available for some important spallation reactions (particularly those involving alphas). With the Mathews production rates it is even more difficult to match the observed ratios with a galactic cosmic ray spectrum of the form $(E + M_0C^2)^{-2.6}$ suggested by MENEGUZZI *et al.* (1971), and we believe that a substantial fraction of these light elements must have been produced by a large flux of low energy particles. However, it also does not appear possible to ignore galactic cosmic ray production; consequently, if at least two mechanisms of nucleosynthesis have contributed, it may be difficult, if not impossible, to define these mechanisms quantitatively since only three abundance ratios ($^{11}B/^{10}B$, $^6Li/^{10}B$, $^9Be/^{10}B$) are available to test against any theoretical model.

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APPENDIX V

Flame Emission Lithium Analyses

Sample	Lithium Concentration
25765-3	7. ± 2.
YH 8	4. ± 2.
AA 4	1.0 ± 2.
25765-4a	2
MC 1(calcite)	.5
MC 1(aragonite)	.6

The first four analyses were performed by Analytical Research Laboratories, Inc., in Monrovia, California. The last two analyses were performed by Elizabeth Bingham at Caltech.